

# FRONTIERS AT THE INTERFACE OF HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

Meeting of the Catalysis Science Program  
Chemical Sciences, Geosciences and Biosciences Division  
Office of Basic Energy Sciences  
U.S. Department of Energy

Westin Annapolis  
Annapolis, Maryland  
June 30 – July 2, 2013



U.S. DEPARTMENT OF  
**ENERGY**

Office of  
Science

This document was produced under contract number DE-AC05-06OR23100 between the U.S. Department of Energy and Oak Ridge Associated Universities.

## FOREWORD

The 2013 Catalysis Science Program Meeting is sponsored by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences (BES), U.S. Department of Energy. It is being held on June 30 through July 2, 2013, at the Westin Annapolis Hotel, Annapolis, Maryland. The purposes of this meeting are to discuss the recent advances in the chemical, physical, and biological bases of catalysis science, to foster exchange of ideas and cooperation among participants, and to discuss the new challenges and opportunities recently emerging in energy technologies.

Catalysis activities within BES emphasize fundamental research aimed at initially understanding and finally controlling the chemical conversion of natural and artificial feedstocks. The long-term goal of this research is to discover fundamental principles and produce ever more insightful approaches to predict structure-reactivity behavior. Such knowledge, integrated with advances in chemical and materials synthesis, *in situ* and *operando* analytical instrumentation, and chemical kinetics and quantum chemistry methods, will allow the control of chemical reactions along desired pathways. Ultimately, this new knowledge should impact the efficiency of conversion of natural resources into fuels, chemicals, materials, or other forms of energy, while minimizing the impact to the environment.

This year's meeting is focused on three topical areas: (i) the interface of homogeneous and heterogeneous catalysis, (ii) catalysis for biomass or solar energy conversion, and (iii) molecular catalysis, with an emphasis on organic synthesis.

Special thanks go to our invited speakers and guest junior scientists, who will expose us to recent advances in their fields; to the program investigators and their students, postdocs, and collaborators, for their dedication to the continuous success and visibility of the BES Catalysis Science Program; and to the session moderators, for their invaluable help. We also thank the Oak Ridge Institute for Science and Education staff for the logistical and web support and the compilation of this volume.

Christopher Jones<sup>1</sup> and Raul Miranda<sup>2</sup>

<sup>1</sup>Georgia Institute of Technology

<sup>2</sup>Office of Basic Energy Sciences - U.S. Department of Energy

This page is intentionally blank.



# AGENDA

## Sunday Afternoon and Evening, June 30, 2013

10:00 - on Registration

12:00 - 1:00 pm Lunch and Welcoming Remarks

### Session I, Moderator: Alex Katz (UC Berkeley)

1:00 – 1:40 pm **Invited Speaker: Christophe Copéret (ETH Zürich)**  
"Controlled Functionalization and Molecular Understanding of Surfaces: Towards Supported Single-Site Catalysts and Beyond"

1:40 – 2:10 pm T. Don Tilley (UC Berkeley, LBNL) "Molecular Routes to Single-Site Catalytic Surface Species for Selective Oxidations"

2:10 – 2:40 pm Steven Tait (Indiana Univ.) "Metal/Organic Surface Catalyst for Low-Temperature Methane Oxidation: Bi-Functional Union of Metal-Organic Complex and Chemically Complementary Surface"

2:40 – 3:10 pm Tobin Marks (Northwestern Univ.) "Supported Organometallic Complexes: Surface Chemistry, Spectroscopy, Catalysis and Homogeneous Models"

### Session II, Moderator: Ted Betley (Harvard University)

3:30 – 4:00 pm Susannah Scott (UC Santa Barbara) "Exploring the Relationship between Homogeneous and Heterogeneous Reaction Kinetics"

4:00 – 4:30 pm Justin Notestein (Northwestern University) "Templating Routes to Supported Oxide Catalysts by Design"

4:30 – 5:00 pm Liviu Mirica (Washington University –St. Louis) "Novel Palladium Catalysts for the Oxidative Oligomerization of Methane & Carbon Dioxide Reduction"

5:00 – 5:30 pm Aaron Appel (PNNL) "An Energy-Based Approach to Bifunctional Molecular Catalysis for CO<sub>2</sub> Reduction and Fuel Utilization"

5:30 - 6:30 pm Dinner

### Session III, Moderator: Brent Gunnoe (University of Virginia)

6:30 – 7:10 pm **Invited Speaker: Huw Davies (Emory University)**  
"Center Approach to C-H Functionalization"

7:10 – 7:40 pm	Dean Toste (UC Berkeley, LBNL) "Selective Reactions of Carbon-Carbon n-Bonds Catalyzed by Cations and Anions"
7:40 – 8:20 pm	<b>Invited Speaker: Scott Miller (Yale University)</b> "Asymmetric Catalysis in Complex Molecular Environments"
8:20 – 10:00 pm	<b>Poster Session I (Odd Numbers)</b>

### Monday Morning, July 1

7:00 - 8:15 am Breakfast

#### Session IV, Moderator: Morris Bullock (PNNL)

8:30 - 9:10 am	<b>Invited Speaker: Wenbin Lin (Univ. of Chicago)</b> "Metal-Organic Frameworks as Single Site Solid Catalysts"
9:10 - 9:40 am	Larry Que (Univ. of Minnesota) "Bio-inspired Nonheme Iron Catalysts for Hydrocarbon Oxidations"
9:40 - 10:10 am	John Hartwig (UC Berkeley-LBNL) "Studies on Homogeneous Catalysis for Efficient Synthesis from Chemical Feedstocks"

#### Session V, Moderator: Mahdi Abu-Omar (Purdue University)

10:30 - 11:10 am	<b>Invited Speaker: Noritaka Mizuno (Univ. of Tokyo)</b> "Design of Polyoxometalate-Based Molecular Catalysts for Bridging the Gap between Homogeneous and Heterogeneous Catalysis"
11:10 - 11:40 am	Harold Kung (Northwestern University) "Nanoconfinement Effects in Heterogeneous Catalysis"
11:40 - 12:10 pm	Geoffrey Coates (Cornell University) "Development and Application of New Carbonylation Catalysts: Improvements in Regioselectivity, Stereoselectivity, Activity and Exploration of New Reactions"
12:10 - 12:40 pm	Robert Crabtree (Yale University) "Moving to Nonprecious Metal Catalysis"
12:40 – 2:30 pm	Lunch - Networking

### Monday Afternoon, July 1

#### Session VI, Moderator: Richard Finke (Colorado State University)

2:30 - 3:10 pm	<b>Invited Speaker: Alan Goldman (Rutgers Univ.)</b> "Addition of O-H Bonds to Olefins Catalyzed by Pincer-Iridium Complexes"
----------------	--

3:10 – 3:40 pm	Malcolm Chisholm (Ohio State Univ.) “Developing s-Block Element Catalysis and New Chemical Transformations”
3:40 - 4:10 pm	Christopher Marshall (ANL) “Fundamental Understanding and Control of Selectivity and Deactivation in Biomass Conversion Catalysts”
4:10 – 4:40 pm	Eugene Chen (Colorado State Univ.) “Catalytic Conversion of Glucose and Cellulose into HMF and Subsequent Upgrading to Value-Added Chemicals and Liquid Fuels”
4:40 – 5:10 pm	Raul Lobo (Univ. of Delaware) “Selective Catalytic Dehydration and Hydrodeoxygenation Reactions for the Production of Fuels and Chemicals from Biomass”
5:10 - 6:20 pm	Dinner

## Monday Evening, July 1

### Session VII, Moderator: Bruce Gates (UC Davis)

6:20 - 7:00 pm	Johannes Lercher (PNNL, T.U. Munich) “Understanding Elementary Steps of Catalytic Conversions in Water to Achieve Complex Transformations”
7:00 - 7:30 pm	Suljo Linic (Univ. of Michigan) “Photo-catalysis on Plasmonic Metal Nanoparticles”
7:30 - 8:00 pm	Andreas Heyden (Univ. of South Carolina) “Theoretical Investigation of Heterogeneous Catalysis at the Solid-Liquid Interface for the Conversion of Lignocellulosic Biomass Model Molecules”
8:20 - 10:00 pm	<b>Poster Session II (Even Numbers)</b>

## Tuesday Morning, July 2

7:00 - 8:15 am                      Breakfast

### Session VIII, Moderator: Robert Waymouth (Stanford University)

8:30 - 9:00 am	Jens Nørskov (SLAC, Stanford Univ.) “Theoretical Description of CO <sub>2</sub> Reduction”
9:00 - 9:30 am	Aditya Bhan (Univ. of Minnesota) “One-Pot Catalytic Conversion of Biomass and Alkanes: Kinetically Coupling Deoxygenation and Dehydrogenation Pathways”
9:30 - 10:00 am	Jose Rodriguez (BNL) “Catalysis: Reactivity and Structure”
10:00 - 10:20 am	Coffee Break

**Session IX, Moderator: Christopher Jones (Georgia Institute of Technology)**

- |                  |   |
|------------------|---|
| 10:50 – 11:20 am | Zili Wu (ORNL) “Revealing the Surface Structure of Ceria Nanocrystals with Well-Defined Facets”                       |
| 11:20 – 11:50 am | Will Medlin (Univ. of Colorado) “Selectivity Control through Modification of Metal Catalysts with Organic Monolayers” |
| 11:50 - 2:00 pm  | Lunch and Discussion – Future Directions  |

## Table of Contents

<b>Foreword</b> .....	i
<b>Agenda</b> .....	iii
 <b>Sunday Afternoon, Session I</b>	
<b>Invited Speaker:</b> Cristophe Copéret – <i>Controlled Functionalization and Molecular Understanding of Surfaces: Towards Supported Single-Site Catalysts and Beyond</i> .....	3
T. Don Tilley – <i>Molecular Routes to Single-Site Catalytic Surface Species for Selective Oxidations</i> .....	4
Steven Tait – <i>Metal/Organic Surface Catalyst for Low-Temperature Methane Oxidation: Bi-Functional Union of Metal-Organic Complex and Chemically Complementary Surface</i> .....	5
Tobin Marks – <i>Supported Organometallic Complexes: Surface Chemistry, Spectroscopy, Catalysis and Homogeneous Models</i> .....	8
 <b>Sunday Afternoon, Session II</b>	
Susannah Scott – <i>Exploring the Relationship between Homogeneous and Heterogeneous Reaction Kinetics</i> .....	13
Justin Notestein – <i>Templating Routes to Supported Oxide Catalysts by Design</i> .....	19
Liviu Mirica – <i>Novel Palladium Catalysts for the Oxidative Oligomerization of Methane &amp; Carbon Dioxide Reduction</i> .....	22
Aaron Appel – <i>An Energy-Based Approach to Bifunctional Molecular Catalysis for CO<sub>2</sub> Reduction and Fuel Utilization</i> .....	25
 <b>Sunday Evening, Session III</b>	
<b>Invited Speaker: Huw Davies</b> – <i>Center Approach to C-H Functionalization</i> .....	29
Dean Toste – <i>Selective Reactions of Carbon-Carbon n-Bonds Catalyzed by Cations and Anions</i> .....	30
<b>Invited Speaker: Scott Miller</b> – <i>Asymmetric Catalysis in Complex Molecular Environments</i> .....	31

## Monday Morning, Session IV

<b>Invited Speaker: Wenbin Lin</b> – <i>Metal-Organic Frameworks as Single Site Solid Catalysts</i> .....	35
Larry Que – <i>Bio-inspired Nonheme Iron Catalysts for Hydrocarbon Oxidations</i> .....	36
John Hartwig – <i>Studies on Homogeneous Catalysis for Efficient Synthesis from Chemical Feedstocks</i> .....	39

## Monday Morning, Session V

<b>Invited Speaker: Noritaka Mizuno</b> – <i>Design of Polyoxometalate-Based Molecular Catalysts for Bridging the Gap between Homogeneous and Heterogeneous Catalysis</i> .....	45
Harold Kung – <i>Nanoconfinement Effects in Heterogeneous Catalysis</i> .....	49
Geoffrey Coates – <i>Development and Application of New Carbonylation Catalysts: Improvements in Regioselectivity, Stereoselectivity, Activity and Exploration of New Reactions</i> .....	51
Robert Crabtree – <i>Moving to Nonprecious Metal Catalysis</i> .....	52

## Monday Afternoon, Session VI

<b>Invited Speaker: Alan Goldman</b> – <i>Addition of O-H Bonds to Olefins Catalyzed by Pincer-Iridium Complexes</i> .....	57
Malcolm Chisholm – <i>Developing s-Block Element Catalysis and New Chemical Transformations</i> .....	58
Christopher Marshall – <i>Fundamental Understanding and Control of Selectivity and Deactivation in Biomass Conversion Catalysts</i> .....	59
Eugene Chen – <i>Catalytic Conversion of Glucose and Cellulose into HMF and Subsequent Upgrading to Value-Added Chemicals and Liquid Fuels</i> .....	61
Raul Lobo – <i>Selective Catalytic Dehydration and Hydrodeoxygenation Reactions for the Production of Fuels and Chemicals from Biomass</i> .....	63

## Monday Evening, Session VII

Johannes Lercher – <i>Understanding Elementary Steps of Catalytic Conversions in Water to Achieve Complex Transformations</i> .....	67
Suljo Linic – <i>Photo-Catalysis on Plasmonic Metal Nanoparticles</i> .....	68

Andreas Heyden – <i>Theoretical Investigation of Heterogeneous Catalysis at the Solid-Liquid Interface for the Conversion of Lignocellulosic Biomass Model Molecules</i> .....	69
--	----

### **Tuesday Morning, Session VIII**

Jens Nørskov – <i>Theoretical Description of CO<sub>2</sub> Reduction</i> .....	75
---	----

Aditya Bhan – <i>One-Pot Catalytic Conversion of Biomass and Alkanes: Kinetically Coupling Deoxygenation and Dehydrogenation Pathways</i> .....	81
---	----

Jose Rodriguez – <i>Catalysis: Reactivity and Structure</i> .....	84
---	----

### **Tuesday Morning, Session IX**

Zili Wu – <i>Revealing the Surface Structure of Ceria Nanocrystals with Well-Defined Facets</i> .....	93
---	----

Will Medlin – <i>Selectivity Control through Modification of Metal Catalysts with Organic Monolayers</i> .....	94
--	----

### **Poster Presentations**

1. Mahdi Abu-Omar (Purdue Univ.) – <i>Oxo Rhenium and Molybdenum Catalysts for C-O Cleavage and Deoxygenation</i> .....	99
---	----

2. Bart Bartlett (Univ. of Michigan) – <i>Bridging Homogeneous and Heterogeneous Catalysis through Ion-Exchangeable Materials</i> .....	102
---	-----

3. Matthias Batzill (Univ. of S. Florida) – <i>Photocatalysis of Modified Transition Metal Oxide Surfaces</i> .....	105
---	-----

4. John Berry (Univ. of Wisconsin) – <i>Metal-Metal Bonded Reaction Intermediates in Catalytic C-H Functionalization</i> .....	108
--	-----

5. Theodore Betley (Harvard Univ.) – <i>Catalyst Design for Small Molecule Activation of Energy Consequence</i> .....	111
---	-----

6. Thomas Bligaard (SLAC) – <i>Bayesian Error Ensemble Functionals for Catalysis Studies</i> .....	112
--	-----

7. Janet Blumel (Texas A&M Univ.) – <i>Homogeneous Catalysts Immobilized on Silica by Optimized Linker Systems for Superior Lifetimes and Activities</i> .....	113
--	-----

8. Suzanne Blum (Univ. of Calif.-Irvine) – <i>Single-Molecule Fluorescence Imaging for Studying Organic, Organometallic, and Inorganic Reaction Mechanisms</i> .....	114
--	-----

9. Morris Bullock (PNNL) – <i>Electrocatalytic Oxidation of Hydrogen by Iron Complexes</i> .....	117
10. Phillip Christopher (Univ. of Calif.-Riverside) – <i>Multifunctional Solid-State Catalysts for Solar Driven Chemical Conversion</i> .....	118
11. Peng Chen (Cornell Univ.) – <i>Chemical Imaging of Single Metal Nanoparticle Catalysis</i> .....	119
12. Tom Cundari (Univ. of North Texas) – <i>Modeling of Late Transition Metal Catalysts for Energy Applications</i> .....	122
13. Paul Dauenhauer (Univ. of Massachusetts) – <i>Natural Catalysts for Molten Cellulose Pyrolysis to Targeted Bio-Oils</i> .....	125
14. Zdenek Dohnálek (PNNL) – <i>Elementary Steps in Dehydration of Diols on TiO<sub>2</sub>(110)</i> .....	127
15. Richard Finke (Colorado State Univ.) – <i>Supported-Nanoparticle Catalyst Formation in Contact with Solution: Kinetic, Mechanistic and Synthetic Fundamental Studies</i> .....	128
16. Annaliese Franz (Univ. of Calif.-Davis) – <i>Hydrogen-Bonding Properties of Organic Silanols for Homogeneous Catalysis and Structural Models for Heterogeneous Catalysis</i> .....	131
17. Michel Gagné (Univ. of North Carolina) – <i>Activation of Carbohydrates for Applications in Biofuels and Biofeedstocks</i> .....	132
18. Bruce Gates (Univ. of Calif.-Davis) – <i>Tuning Catalytic Properties of Molecular Metal Clusters on Supports</i> .....	137
19. Lars Grabow (Univ. of Houston) – <i>From Hydrodesulfurization to Hydrodeoxygenation: What are the Similarities at the Atomic-Scale?</i> .....	142
20. Alex Katz (Univ. of Calif.-Berkeley) – <i>Controlling Heterogeneous Catalyst Selectivity Using Grafted Metallocalixarene Active Sites</i> .....	143
21. Jeffrey Greeley (Purdue Univ.) – <i>Interfacial Electrocatalytic Processes and Heterogeneous Catalysis of Biomass from First Principles</i> .....	146
22. Brent Gunnoe (Univ. of Virginia) – <i>Development of Transition Metal Catalysts for the Functionalization of Carbon-Hydrogen Bonds: Fundamental Studies of Catalytic Hydroarylation of Olefins</i> .....	149
23. Jason Hicks (Notre Dame Univ.) – <i>Highly Selective Bimetallic Hydrodeoxygenation Catalysts</i> .....	152
24. Adam Hock (ANL) – <i>New Single-Atom Catalysts for Activation and Selective Reaction of Small Molecules, Including Alkanes</i> .....	153



25. George Huber (Univ. of Wisconsin–Madison) – <i>Catalyst Design for Hydrodeoxygenation of Biomass: Towards a Molecular Level Understanding</i> .....	158
26. Rongchao Jin (Carnegie-Mellon Univ.) – <i>Atomically Precise Metal Nanoclusters for Catalytic Application</i> .....	159
27. Robert Knowles (Princeton Univ.) – <i>Proton-Coupled Electron Transfer Activation in Organic Synthesis</i> .....	162
28. Johannes Lercher (PNNL- T.U. Munich) – <i>Multifunctional Catalysts to Synthesize and Utilize Energy Carriers</i> .....	163
29. Jared Lewis (Univ. of Chicago) – <i>New Approaches to Selective Carbon-Hydrogen Bond Activation Using Dual Catalysis and Artificial Metalloenzymes</i> .....	177
30. Daniel Lutterman (ORNL) – <i>Reactivity of Phenyl Ethyl Alcohols Over Cerium Oxide</i> .....	178
31. Randall Meyer (Univ. of Illinois–Chicago) – <i>Selective Hydrogenation of Acrolein: Particle Size, Supports, Alloys and Single Sites</i> .....	179
32. Jamal Musaev (Emory Univ.) – <i>Knowledge-Based Catalyst Design: Computational Method Development, Water Oxidation, Stereoselective C-H Functionalization and Nitrogen Fixation</i> .....	180
33. Kenneth Nicholas (Univ. of Oklahoma) – <i>Catalytic Deoxydehydration of Carbohydrates and Polyols to Chemicals and Fuels</i> .....	182
34. Eranda Nikolla (Wayne State Univ.) – <i>Molecular Approaches toward the Development of Efficient Heterogeneous Catalysts and Electrocatalysts for Chemical Energy Conversion and Storage</i> .....	185
35. Gerard Parkin (Columbia Univ.) – <i>Zinc Catalysts for On Demand Hydrogen Generation and Carbon Dioxide Functionalization</i> .....	186
36. Charles Peden (PNNL) – <i>New Insights into the Synthesis of Methanol on Copper Catalysts</i> .....	189
37. Marek Pruski (Ames National Lab) – <i>Homogeneous and Interfacial Catalysis in 3D Controlled Environment</i> .....	190
38. Jeffrey Rimer (Univ. of Houston) – <i>Rational Approaches to Design and Optimize Zeolite Catalysts</i> .....	197
39. Robert Rioux (Pennsylvania State Univ.) – <i>Influence of Multi-Valency, Electrostatics and Molecular Recognition on the Adsorption of Transition Metal Complexes on Metal Oxides: A Molecular Approach to Supported Catalyst Synthesis</i> .....	198
40. Yuriy Román (MIT) – <i>Catalytic Pairs for the Activation of Biomass-Derived Oxygenates</i> .....	201

41. Roger Rousseau (PNNL) – <i>The Chemistry of CO<sub>2</sub> on Rutile TiO<sub>2</sub>(110): The Role of Charge Transfer and Finite Temperature Dynamics</i> .....	203
42. Joseph Sadighi (Georgia Inst. Tech.) – <i>Two-Electron Redox Activity of Trigold Monocations and Related Complexes</i> .....	204
43. Carsten Sievers (Georgia Inst. Tech.) – <i>Surface Chemistry of Polyols on Metals and Metal Oxides</i> .....	205
44. Darío Stacchiola (BNL) – <i>Fundamental Studies on Well-Defined Oxide Catalysts: From UHV to In-Situ Conditions</i> .....	208
45. Franklin Tao (Univ. of Notre Dame) – <i>In-Situ Studies and Catalysis of Transition Metal Oxides</i> .....	209
46. Dionisios Vlachos (Univ. of Delaware) – <i>Rational Design of Innovative Catalytic Technologies for Biomass Derivative Utilization</i> .....	212
47. Robert Waymouth (Stanford Univ.) – <i>Enabling Catalytic Strategies for Biomass Conversion</i> .....	215
 <b>Additional Abstracts</b>	
Christopher Jones (Georgia Inst. Tech.) – <i>Developing the Science of Immobilized Molecular Catalysts</i> .....	219
Steven Overbury (ORNL) – <i>Fundamentals of Catalysis and Chemical Transformations</i> .....	221
 <b>Participant List</b> .....	229
 SUMMARY BULLETS FROM THE SESSION CHAIRS AND CONTRIBUTORS .....	233

# **Sunday Afternoon**

## **Session I**

This page is intentionally blank.

**Controlled functionalization and Molecular Understanding of surfaces:  
Towards supported single-site catalysts and beyond.**

Christophe Copéret

*Department of Chemistry, ETH Zürich, Wolfgang Pauli Strasse 10 CH-8093 Zürich, Switzerland  
e-mail: coperet@ethz.ch*

Homogeneous and heterogeneous catalysts have, each, specific advantages. While homogeneous catalysts are typically associated with efficient chemical transformations at low temperatures (high selectivity), heterogeneous ones are typically preferred in term of processes (easier regeneration and separation processes).

Here, we will show how it is possible to combine the advantages of homogeneous and heterogeneous catalysts by the controlled functionalization of the surfaces of oxide materials and by the characterization of surface species at the molecular level, thus allowing more predictive approaches.

We will illustrate the power of this approach with the development of well-defined “single-sites”, whose performance and stability can in some cases exceed these of homogeneous and heterogeneous catalysts.

With our current level of understanding of surfaces, we will also discuss new directions in this field: understanding defect sites of surfaces and metal-support interactions at the molecular level, introducing diversity in oxide chemistry, controlling the growth of nanoparticles, the development of NMR techniques for the expeditious characterization of surface species...

**Molecular Routes to Single-Site Catalytic Surface Species for Selective Oxidations**

Lead PI: T. Don Tilley

Postdoc: Pascal Guillo

Student: Paul Cordiero

Contact: Division of Chemical Sciences, Lawrence Berkeley National Laboratory,  
Berkeley, CA 94720; [tdtilley@berkeley.edu](mailto:tdtilley@berkeley.edu)

For heterogeneous catalysts, desirable properties are associated with well-defined active sites containing one or only a few metal centers on the surface of a support. This situation is similar to that observed for enzymes, which provide a tertiary polypeptide structure for stabilization of reactive centers, and a secondary coordination sphere for binding/activation of substrates. In principle, these latter roles may also be fulfilled by the surface of a suitably modified support material. Given increasing interest in the structure and catalytic chemistry of supported metal centers, we have attempted to develop reliable routes to stable, well-defined catalytic centers bound to an oxide support. We have utilized a process for the introduction of isolated metal centers, involving grafting reactions with molecular precursors (the thermolytic molecular precursor method). The resulting catalysts display good activities and selectivities for the oxidation of various hydrocarbons, using a variety of oxidants. This presentation will focus on use of peroxide oxidants, and on manipulation of the catalyst center's environment to optimize performance. With use of catalyst systems based on titanium and tantalum, the influence of various structural factors on catalyst activity and selectivity will be described, including surface modifications,[1-3] the nature of the support material,[3] and introduction of substituents onto the catalytic center [1,4].

**References**

1. P. J. Cordeiro and T. D. Tilley, "Enhancement of the Catalytic Activity of Titanium-Based Terminal Olefin Epoxidation Catalysts via Surface Modification with Functionalized Protic Molecules," *ACS Catal*, **1**, 455 (2011).
2. C. W. Yoon, K. F. Hirsekorn, M. L. Neidig, X. Yang and T. D. Tilley, "Mechanism of the Decomposition of Aqueous Hydrogen Peroxide over Heterogeneous TiSBA15 and TS-1 Selective Oxidation Catalysts: Insights from Spectroscopic and Density Functional Theory Studies," *ACS Catal.*, **1**, 1665 (2011).
3. L. Raboin, J. Yano and T. D. Tilley, "Epoxidation catalysts derived from introduction of titanium centers onto the surface of mesoporous aluminophosphate: Comparisons with analogous catalysts based on mesoporous silica," *J. Catal.*, **285**, 168 (2012).
4. P. J. Cordiero, P. Guillo, J. W. Chnag, C. S. Spanjers, M. E. Fasulo, R. M. Rioux, and T. D. Tilley, "Titanium Germolyl Precursor Route to Germanium-Modified Epoxidation Catalysts with Enhanced Activity," in preparation.

**Metal/Organic Surface Catalyst for Low-Temperature Methane Oxidation:  
Bi-Functional Union of Metal-Organic Complex and Chemically Complementary Surface**

Students: Daniel Skomski, Jennifer Sandahl, Christopher Tempas, Benjamin Draper

Contact: Department of Chemistry, Indiana University; 800 E. Kirkwood Ave.,  
Bloomington, IN 47405; Tel. 812-855-1302, E-mail: tait@indiana.edu

**Goal**

Study the formation and chemical activity of metal-organic complexes on surfaces as bi-functional catalytic systems with sequential catalytic activity at the metal surface and at the well-ordered and precisely designed single-site metal centers.

**DOE Interest**

This project is exploring new possibilities in catalysis by combining features of homogeneous catalysts with those of heterogeneous catalysts to develop new, bi-functional systems. The systems are more complex than traditional heterogeneous catalysts in that they utilize sequential active sites to accomplish the desired overall reaction. The interaction of metal—organic catalysts with surface supports and their interactions with reactants to enable the catalysis of critical reactions at lower temperatures are at the focus of this study.

An initial target of this research program is the methane oxidation reaction. Steady advances in homogeneous catalysis have led to capabilities for this reaction to run at temperatures as low as 200 °C. However, the current catalyst technologies operate in a sulfuric acid solution, which provides an oxygen source for the reaction, but complicates scale-up and handling of the process. We are working to develop a bi-functional catalyst system, consisting of a metal—organic complex stabilized on a silver surface. The surface is capable of activating molecular oxygen, which may subsequently react with methane at a Pt center, stabilized in an organic ligand.

This project will lead to new ideas and insights into complex, multi-functional catalysts. There is a rich field of scientific questions to be explored. Especially of interest is the degree to which the chemical activity of a metal center can be tuned through stabilization in a ligand field when coupled with the catalytic processes of a metal surface. This program provides rich training opportunities to graduate student researchers, the next generation of energy solution innovators.

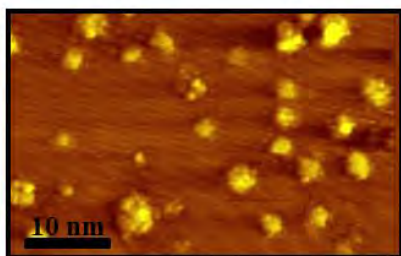
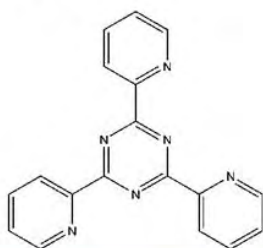
**Recent Progress**

During the first seven months of this research program, we have focused on methodologies to generate stable Pt metal centers in organic ligand complexes on silver surfaces for use as bi-functional surface catalysts. The experiments to date have resulted in three classes of Pt compounds at surfaces involving pyridyl / triazine coordinating ligands, triazole ligands, and porphyrin incorporation. Each of these has been imaged with high resolution at the surface to study metal complexation, ordering, and self-organization (Figure 1). We have also characterized each system using X-ray photoelectron spectroscopy to gauge the effectiveness of the preparation procedures and to observe chemical changes in the metal complexes. XPS also allows us to verify successful deposition without molecular decomposition or chemical change.

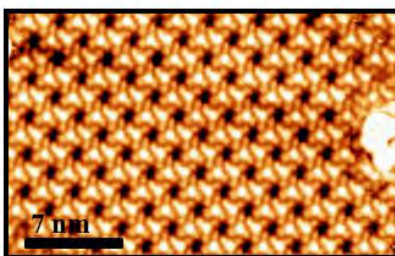
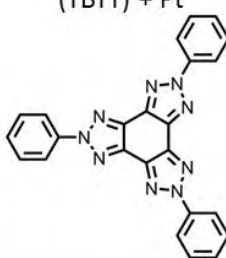
*Metal-organic Pt complexes.* Figure 1 shows three molecules that have been studied recently for Pt complexation and corresponding STM images of those molecules deposited to the Ag(111) surface with Pt. Each is vapor deposited to the surface under ultra-high vacuum conditions and assumes a flat-lying geometry. TPTZ (Fig. 1A) can achieve either two-fold or three-fold coordination, depending upon the conformational state of the pyridyl ring positions. TBTT

presents three triazole ligand sites that are uniform (Fig. 1B). The structure is well-ordered, but leaves nanopore regions, which may allow for dissociative oxygen adsorption during the target reaction process. The use of a metal-porphyrin complex (Fig. 1C) to order transition metal centers on a surface is a logical approach to creating well-defined Pt centers at a surface and provides a point of reference to prior studies by other groups. The Pt porphyrins pack in a (5x5) arrangement with respect to the unit cell basis vectors of the Ag(111) surface.

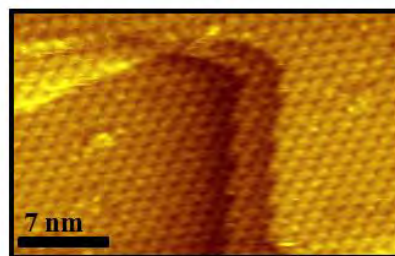
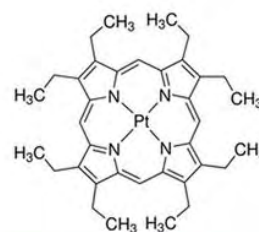
(A) Tri-pyridyl triazine (TPTZ) + Pt



(B) Triphenyl-benzotris(triazole) (TBTT) + Pt



(C) Platinum octaethylporphyrin (Pt-OEP)



**Figure 1.** Organic complexes deposited to the Ag(111) surface with Pt to form metal organic complexes. Bottom row are high resolution STM images of each system at room temperature.

We are still investigating the nature of these structures and how effective they may be as surface catalysis systems. In each case there is some indication of the Pt interaction with the molecule. Experiments are on-going to study the binding of Pt and the stability of the complexes in comparison to the competing formation of Pt nanoparticles.

*Interfacial organic layers.* Recent results in our group have demonstrated the ability to use an interfacial organic layer (IOL) to drive a highly ordered organic structure on a metal surface. This may provide a capability useful in tuning the interaction of Pt single site catalyst complexes. The IOL concept provides some control over the coupling between a functional organic layer and the underlying surface and may be useful in the development of this project.

*Organic multilayer characterization.* We have also developed methodologies for the characterization of organic systems of up to 10 layers above the metal surface, including ligands of interest for Pt complexation (Fig. 1B), using a combination of scanning tunneling microscopy and atomic force microscopy analysis. Analysis of reveals a crystalline packing of the molecules. This illustrates two important points for this work. The first is the ability to correlate STM and AFM results, which may become important in our catalyst studies, especially if our modification of the Ag(111) surface leads to a decrease in surface conductivity that would necessitate AFM analysis. The other important point is the propagation of the two-dimensional molecular structure into multiple layers of the film. For analysis and design of complex surface catalysts this raises the point that it may be possible to achieve well defined organic complexes in multiple layers above the surface.



## Future Plans

1. *Optimize preparation conditions for Pt—organic catalyst units on surface.* The results so far indicate there are several routes available to for Pt complexes at the surface. We will continue to optimize these conditions as well as to explore other functional group families, especially carboxylates and carbonyls, in the binding ligands. This will be accomplished by high resolution STM experiments as well as complementary low energy electron diffraction measurements. *Chemical characterization of Pt—organic catalyst units* will be made using photoelectron spectroscopy measurements. More detailed measurements are needed to be able to assign chemical state information for the Pt centers in the different ligand fields. These measurements will be designed so that in studies of reactions, they can be helpful in identifying modifications in the chemical structure during the reactions at the catalyst sites.

2. *Analyze the dissociative adsorption of dioxygen on Ag(111) and the interaction with the metal—organic units, especially transfer of adsorbed O to the Pt site.* These experiments allow us to probe key questions into the function of a multi-site, bi-functional surface catalyst. A pulsed supersonic molecular beam is being constructed for these experiments so that we can control the flux of reactant molecules to the surface. These experiments will probe the dissociative adsorption of oxygen on Ag, including in the presence of the Pt metal complexes. Auger electron spectroscopy, low-energy electron diffraction, and high-resolution electron energy loss spectroscopy will allow for identification of the adsorption products. *Adsorption of methane at the catalyst surface* will be a next step in understanding the nature of the interactions between the functional surface and the Pt complexes.

3. We have successfully imaged an alkali-organic ionic structure *at elevated surface temperature* with molecular resolution on our STM system. This capability would allow us to analyze the Pt complexes on silver at temperatures comparable to the target reaction temperatures. Second, the development of those surface ionic structures has demonstrated a new method for created highly-ordered and thermally robust (up to 180 °C) organic-based frameworks at a surface. This may be of use in the present project using a ligand that would allow for one functional site to stabilize the Pt catalyst center while other functional groups engage in an ionic bonding interaction to order the surface structure (and potentially open up a nanoporous architecture to allow open sites of oxygen adsorption). These capabilities may allow new opportunities in exploring metal-organic complexes for bi-functional surface catalysts.

## Publications (2012-2013)

1. D. Skomski and S. L. Tait,\* “Interfacial Organic Layers as Templates for Crystalline Organic Films with Carboxyl and Thiophene Functionalization,” *submitted*.
2. H. Lim, Y. Ge, D. Skomski, P. Seidel, A. Theertham, H. Adler, L. L. Kesmodel, and S. L. Tait,\* “Chemisorption, Ordering, and Structural Transitions in the Terephthalic Acid Monolayer and Bilayer on Cu(100),” American Vacuum Soc. Symposium, Tampa, FL (2012).
3. S. L. Tait\* and D. Skomski, “Strategies for Highly-ordered and Thermally Robust Organic Layers at Metal Surfaces,” American Chemical Society Meeting, New Orleans, LA (2013).
4. D. Skomski and S. L. Tait,\* “Chemical Design of Robust Two-dimensional Organic Crystals,” Foundations of Nanoscience Conference, Snowbird, UT (2013).
5. D. Skomski, J. Jo, D. Lee, and S. L. Tait,\* “Offset Pi Stacking in Many-Layered Organic Films on Metal Surfaces,” *manuscript in preparation*.
6. J. E. Sandahl and S. L. Tait,\* “Organic Coordination of Cr Metal Centers at Surfaces,” *manuscript in preparation*.

## Supported Organometallic Complexes: Surface Chemistry, Spectroscopy, Catalysis and Homogeneous Models

DE-FG02-86ER13511

Tobin J. Marks

Postdoc: Maximilliano Delferro, Shaofeng Liu, Weixing Gu  
Graduate students: Michael Weberski  
Collaborators: Mark Ratner (Northwestern U.), Ignazio Fragala, Alessandro Motta (U. Catania, Italy), Alceo Macchioni, Cristiano Zuccaccia (U. Perugia, Italy), Jeffery Miller, Chris Marshall (Argonne Nat. Lab.), Michael Lanagan (Pennsylvania State U.), Peter Nickias (Dow Chemical) Christopher Nicholas, Jeff Bricker (UOP).  
Contacts: Department of Chemistry and the Center for Catalysis and Surface Science, Northwestern University, Evanston IL 60208-3113  
[t-marks@northwestern.edu](mailto:t-marks@northwestern.edu) <http://chemgroups.northwestern.edu/marks/>

### Goal

Model, understand at a fundamental level, expand, and exploit pathways by which organometallic molecules of varying nuclearity undergo chemisorptive activation and catalytic activity enhancement on solid surfaces. Such processes connect to real-world, large-scale industrial hydrocarbon processes and to manufacturing cleaner, greener, more environmentally acceptable products, including those from renewable resources. Research combines catalyst synthesis, surface chemistry and spectroscopy, homogeneous analogue catalysis, structural analysis, and computation, and involves collaboration with national laboratories and industry. Objectives in the past year were: 1) Investigate mononuclear and binuclear organometallic chemisorption on “super Brønsted acid” oxides, 2) Synthesize and characterize mononuclear and polynuclear catalyst precursors for chemisorption and homogeneous catalysis, 3) Use this information to produce new types of efficient energy storage materials, 4) Computationally model both chemisorbed catalysts and their reactivity modes.

### DOE Interest

The present catalyst synthesis and characterization activities connect directly with the efficiency, selectivity, and “greenness” of real-world industrial processes currently practiced on a huge scale, and to the ability of these processes to produce cleaner, more environmentally acceptable products. This includes processes using renewable, bio-feedstocks such as sustainable polyolefin production from sugar cane, and those which produce high-capacity, low-cost energy storage materials.

### Recent Progress

The project consists of three complementary, interconnected efforts: 1) Metal Hydrocarbyl Chemisorption on Brønsted “Super Acid” Surfaces to Produce Single-Site Heterogeneous Catalysts, 2) Heterogeneous Catalytic Synthesis of Energy Storage Materials, and 3) Metal Nuclearity Effects on Homogeneous Catalysis. The catalytic transformations of interest here involve modification of small hydrocarbon molecules, including polymerization and hydrogenation, asking how and why the environment of molecule-based catalysts (e.g., support, presence of other metal centers) can so profoundly alter activity and selectivity, and how these fundamental phenomena can be used to produce unusual functional materials.

*Metal Hydrocarbyl Chemisorption on Sulfated Metal Oxide Surfaces.* Electrophilic Zr surface alkyls are created in high coverages by protonolytic chemisorption of group 4 alkyls, and these species exhibit extreme activity for arene and olefin hydrogenation as well as for olefin polymerization--benzene hydrogenation rates exceed those of Pt metal catalysts. The kinetics and mechanism were characterized, revealing that ~ 97% of the surface Zr species are catalytically significant--unusual for any heterogeneous catalyst. Density functional theory (DFT) was used to study the sulfated  $\gamma$ -

alumina (AIS) surface as well as the pathway for  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  (**2**;  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) chemisorption. Using the most stable configuration of the sulfated surface, it is found that Zr- $\text{CH}_3$  protonolysis yields cationic species which interact with the surface sulfate species to form electrostatically anchored cations. Computed changes in sulfate vibrational spectra on zirconocene chemisorption are in good agreement with experiment. Furthermore, Zr K-edge XAFS and XANES characterization of  $\text{Cp}_2\text{ZrH}_2$  (**1**), **2**,  $\text{Cp}^*\text{ZrH}_2$  (**3**) ( $\text{Cp}^* = \eta^5\text{-(CH}_3)_5\text{C}_5$ ) and  $\text{Cp}'\text{ZrMe}_3$  (**4**) and as well as their AIS-supported product catalysts **1**/AIS, **3**/AIS and **4**/AIS are used to elucidate the metrical nature of the Zr...AIS interaction, complemented by high-resolution solid state NMR. The XAFS data yield key structural information: the supported cationic organozirconium catalysts have electrostatic interactions with the surface sulfate O atoms at average (long) Zr...O distances of 2.25 - 2.36 Å, in good agreement with the DFT results. EXAFS analysis of benzene dosing experiments with **4**/AIS reveals that benzene is captured by essentially all of the Zr centers and is bound in an  $\eta^6$  fashion, with an average Zr-C bond distance of 2.27 Å. These results are in excellent agreement with the computational and catalytic mechanistic results.

*Heterogeneous Catalytic Synthesis of Energy Storage Materials.* Inexpensive materials combining the processability and mechanical properties of inexpensive polymers with the high dielectric constants of ferroelectric oxides are highly desirable for energy storage as in large-scale capacitors. To this end, chemisorption of the activated metallocene propylene polymerization catalyst derived from [*rac*-ethylenebisindenyl]zirconium dichloride ( $\text{EBIZrCl}_2$ ) on the native  $\text{Al}_2\text{O}_3$  surfaces of metallic aluminum nanoparticles, followed by exposure to polypropylene, affords 0–3 metal-isotactic polypropylene nanocomposites. The microstructures of these nanocomposites were characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, and atomic force microscopy. Electrical measurements show that increasing the concentration of the filler nanoparticles increases the effective permittivity of the nanocomposites to  $\epsilon_r$  values as high as 15.4. Because of the high contrast in the complex permittivities and conductivities between the metallic aluminum nanoparticles and the polymeric polypropylene matrix, these composites obey the percolation law for two-phase composites, reaching maximum permittivities just before the percolation threshold volume fraction,  $v_f < 0.16$ . These Al-polypropylene nanocomposites perform well as pulse-power capacitor materials, with leakage current densities of  $\sim 10^{-7} - 10^{-9}$  A/cm<sup>2</sup> at an applied field of  $10^5$  V/cm, low dielectric loss in the 100 Hz – 1 MHz frequency range, and recoverable energy storage as high as 14.4 J/cm<sup>3</sup>.

*Metal Nuclearity Effects on Homogeneous Catalytic Chemistry.* The synthesis and characterization of two neutrally charged bimetallic nickel(II) ethylene polymerization catalysts, {2,7-di-[2,6-(3,5-dimethylphenylimino)methyl]-1,8-naphthalenediolato}-bis-Ni(II)(methyl)(trimethylphosphine) ( $(\text{CH}_3)\text{FI}^2\text{-Ni}_2$ ) and {2,7-di-[2,6-(3,5-di-trifluoromethylphenylimino)methyl]-1,8-naphthalenediolato}-bis-Ni(II)(methyl)-(trimethylphosphine) ( $(\text{CF}_3)\text{FI}^2\text{-Ni}_2$ ) are reported. These catalysts, along with their monometallic analogues [2-*tert*-butyl-6-((2,6-(3,5-dimethylphenyl)phenylimino)methyl)phenolato]-Ni(II)-methyl(trimethyl-phosphine) ( $(\text{CH}_3)\text{FI-Ni}$ ) and [2-*tert*-butyl-6-((2,6-(3,5-ditrifluoromethylphenyl)-phenylimino)methyl)-phenolato]-Ni(II)-methyl(trimethyl-phosphine) ( $(\text{CF}_3)\text{FI-Ni}$ ) produce polyethylenes in the presence of  $\text{Ni}(\text{COD})_2$  ranging from low  $M_w$ , highly branched oligomers, to high  $M_w$  polymers with low branch densities. In the bimetallic catalysts, catalyst center–catalyst center cooperative effects are evidenced by increased product polyethylene branching in ethylene homopolymerizations, as well as by increased norbornene incorporation selectivity in ethylene-*co*-norbornene polymerizations, with bimetallic catalysts  $(\text{CH}_3)\text{FI}^2\text{-Ni}_2$  and  $(\text{CF}_3)\text{FI}^2\text{-Ni}_2$  enchaining  $\sim 3\times$  and  $6\times$ , respectively, more norbornene than the monometallic catalysts  $(\text{CH}_3)\text{FI-Ni}$  and  $(\text{CF}_3)\text{FI-Ni}$ . Additionally, bimetallic catalysts  $(\text{CH}_3)\text{FI}^2\text{-Ni}_2$  and  $(\text{CF}_3)\text{FI}^2\text{-Ni}_2$  exhibit enhanced thermal stability over previously reported dinickel catalysts. The mechanism of

bimetallic catalyst deactivation at 50°C was investigated and is found to involve an unexpected polymerization intermediate, {2,7-di-[2,6-(3,5-di trifluoromethylphenyl-imino)methyl]-1-hydroxy,8-naphthalenediolato-Ni(II)(methyl)-(trimethylphosphine), (CF<sub>3</sub>)FI<sup>2</sup>-Ni(OH)}, that contributes to polyethylene formation at 50°C. The molecular structure of (CF<sub>3</sub>)FI<sup>2</sup>-Ni<sub>2</sub> reveals a Ni···Ni distance of 5.8024(5) Å.

### Future Plans

To activate polynuclear molecule-based catalysts to new levels of activity, we will investigate more Brønsted acidic supports, seeking catalytic effects only possible via the agency of adjacent catalytic centers. We will expand our work to hydrocarbon metathesis and coupling processes. A variety of binuclear catalyst precursors will be chemisorbed and studied. Structural characterization will include solid state NMR and EXAFS/XANES at ANL, with operando studies of catalysts turning over and/or being inhibited. Here, our systems with virtually 100% active sites present a unique opportunity. We also plan investigations of cooperative effects in analogous homogeneous binuclear group 10 catalysts, focusing on transformations that are normally exceeding difficult by virtue of steric congestion and/or unfavorable substrate basicity. The possibility of producing high energy storage capacity materials using in-situ catalytic polymerization processes will be further explored by expanding the scope of the metallic nanoparticles (including shape and size effects) and the polymerization and co-polymerization catalysts under investigation.

### Publications (2011-2013)

1. Delferro, M.; Marks, T.J. Multinuclear Olefin Polymerization Catalysis: Structure, Function, and Cooperativity, *Chem. Rev.* **2011**, *111*, 2450–2485.
2. Williams, L.A.; Marks, T.J. Synthesis, Characterization, and Heterogeneous Catalytic Implementation of Sulfated Alumina Nanoparticles. Arene Hydrogenation and Olefin Polymerization Properties of Supported Organo-Group 4 Complexes, *ACS Catalysis*, **2011**, *1*, 238–245.
3. Weberski, M.P.; Chen, C.; Delferro, M.; Marks, T.J. Catalyst Center-Catalyst Center Cooperativity and Deactivation Mechanisms in Bimetallic Nickel(II) Phenoxyiminato-Based Ethylene Polymerization Catalysts, *Chem. Euro. J.* **2012**, *18*, 10715 - 10732.
4. Weberski, M.P.; Chen, C.; Delferro, M.; Zuccaccia, C.; Macchioni, A.; Marks, T.J. Suppression of β-H Chain Transfer in Ni(II) Catalyzed Ethylene Polymerization via Weak Secondary Ligand Interactions, *Organometallics*, **2012**, *31*, 3773–3789.
5. Fredin, L.A.; Li, Z.; Lanagan, M.T.; Ratner, M.A.; Marks, T.J. Enhancing Energy Storage and Suppressing Dielectric Loss in Oxide Core-Shell-Polyolefin Nanocomposites by Decreasing Internal Surface Area and Increasing Shell Thickness, *Advan. Mater.* **2012**, *24*, 5946–5953.
6. Fredin, L.A.; Li, Z.; Lanagan, M.T.; Ratner, M.A.; Marks, T.J. Substantial Recoverable Energy Storage in Percolative Metallic Aluminum-Polypropylene Nanocomposites, *Advan. Funct. Mater.*, **2013**, in press; <http://dx.doi.org/10.1002/adfm.201202469>.
7. Williams, L.A.; Guo, N.; Motta, A.; Delferro, M.; Fragala, I.L.; Miller, J.T.; Marks, T.J. Surface Structural-Chemical Characterization of a Single-Site d<sup>0</sup> Heterogeneous Arene Hydrogenation Catalyst Having 100% Active Sites, *Proc. Nat. Acad. Sci.*, **2013**, *110*, 413-418.
8. Fredin, L.A.; Li, Z.; Ratner, M.A.; Marks, T.J.; Lanagan, M.T. Metallic Aluminum-Polypropylene Nanocomposites with Sustainable High Capacitance at High Frequencies, *ACS Nano*, **2013**, *7*, 396–407.
9. Liu, S.; Delferro, M.; Marks, T.J. Synthesis, Characterization, and Heterobimetallic Cooperative Effects in a Titanium/Chromium Catalyst for Highly Branched Polyethylenes, **2013**, submitted for publication.
10. Gu, W.; Delferro, M.; Motta, A.; Marks, T.J. Molecule-Based Heterogeneous Catalysts for Selective Arene Hydrogenation. Scope, Ligand Structure Effects, and Mechanism, **2013**, submitted for publication.
11. Fredin, L.A.; Ratner, M.A.; Marks, Lanagan, M.T.; T.J. Using Single-Site Heterogeneous Olefin Polymerization Catalysts for the Synthesis of High-Capacity Energy Storage Materials, **2013**, submitted for publication.

# **Sunday Afternoon**

## **Session II**

This page is intentionally blank.

### Exploring the Relationship between Homogeneous and Heterogeneous Reaction Kinetics

Additional PIs: Baron Peters (UCSB), Al Stiegman (Florida State)  
Postdocs: Alessandro Gallo (UCSB), Haibo Yu (UCSB)  
Graduate Students: Daniel Coller (UCSB), Anthony Ferrari (Florida State), Anthony Fong (UCSB), Taeho Hwang (UCSB), Youhong Wang (UCSB)  
Undergrad Students: Daniel Bean (UCSB), Julia Rieb (UCSB)  
Collaborators: B. Chmelka (UCSB)  
Contact: S. Scott, Chemical Engineering, University of California, Santa Barbara, CA 93016-5080; sscott@engr.ucsb.edu  
B. Peters, Chemical Engineering, University of California, Santa Barbara, CA 93016-5080; baronp@engr.ucsb.edu  
A. Stiegman, Chemistry & Biochemistry, Florida State University, Tallahassee FL 32306; stiegman@chem.fsu.edu

### Goal

An integrated understanding of active site structure, function and mechanism is the key to the rational design of new catalysts, yet it remains to be achieved in many heterogeneous oxide systems. These widely-used catalysts are easy to prepare and handle, can be activated just before use, and can be reactivated by simple calcination. The interactions between the active sites and the support are crucial in determining their activity and selectivity. However, little is known about this aspect of the catalyst, because of the lack of techniques to probe support interactions, and the difficulty in modifying the acidity properties of the support surface in a controlled manner. In this project, we combine catalyst synthesis, molecular-level characterization, detailed kinetic/mechanistic analysis, and theoretical modeling of reaction pathways, to achieve an understanding of structure-activity relationships in these complex systems. Using molecular precursors and/or molecular synthetic strategies to create highly uniform reacting sites, we aim to define the key features that distinguish active from inactive sites.

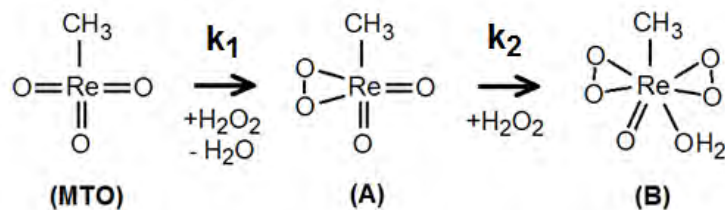
### DOE Interest

A detailed understanding of the factors which lead to active site formation in supported metal catalysts is key to improving their activity and selectivity, with consequent impact on the sustainability (chemical and energy requirements; waste production) of the chemical industry which supplies most of the building blocks for modern manufacturing. Even the catalysts themselves can be scarce commodities, when they involve rare elements. Improving the efficiency of their use is critical at a time when world-wide demand for these non-renewable raw materials is growing rapidly.

### Recent Progress

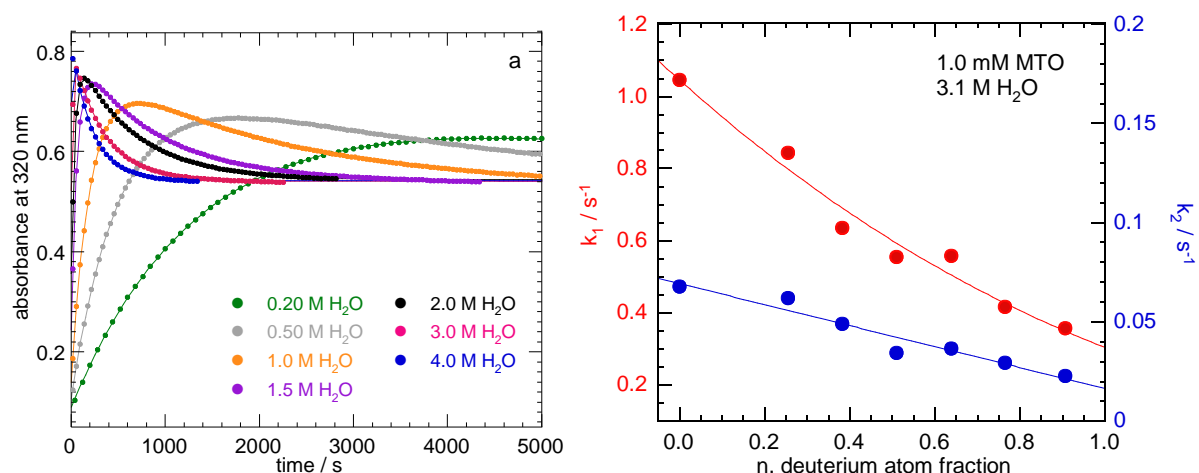
#### *Water-catalyzed ligand exchange of methyltrioxorhenium (MTO) with H<sub>2</sub>O<sub>2</sub>*

The reactions between MTO and H<sub>2</sub>O<sub>2</sub> were chosen to provide a benchmark for computational models involving our supported Re-based catalysts. H<sub>2</sub>O<sub>2</sub> reacts with MTO in two steps, giving first the monoperoxo intermediate **A**, then the diperoxo product **B**, as shown in Scheme 1.



**Scheme 1:** Products of successive reactions of MTO with H<sub>2</sub>O<sub>2</sub>

Previously, we measured all of the forward and reverse rate constants for both reversible reactions and obtained a complete set of thermodynamic and activation parameters for the system in aqueous acetonitrile. Comparison with computationally predicted kinetics revealed very large discrepancies that could be reconciled by postulating a role for water in mediating the ligand exchange reaction via a proton relay. Now we have obtained experimental evidence that the reactions are indeed strongly catalyzed by water, Figure 1 (Left).



**Figure 1.** Time-resolved kinetic profiles at 25.0 °C in CH<sub>3</sub>CN, at two wavelengths: (a) 320 nm; and (b) 360 nm, for the reactions of 1.0 mM MTO with 49.1 mM H<sub>2</sub>O<sub>2</sub>, in the presence of variable amounts of H<sub>2</sub>O (0.20 – 4.0 M), (every 5<sup>th</sup> points for low [H<sub>2</sub>O] and 10<sup>th</sup> points for high [H<sub>2</sub>O] are shown) showing curve-fits obtained using biexponential kinetic equations. Dependence on deuterium atom fraction ( $n$ ) of the rate constants  $k_1$  (red) and  $k_2$  (blue), showing curve-fits obtained using eq 1.

Analysis of the kinetic effect of water is complicated because the activity coefficient in acetonitrile varies non-linearly with concentration. Instead, we applied the proton inventory technique to obtain information about the number of protons transferred in the rate-determining step. The kinetics are measured keeping the total water concentration constant, while varying the H<sub>2</sub>O/D<sub>2</sub>O ratio. The Gross–Butler equation relates the observed rate constant  $k_n^{\text{obs}}$  when the D atom fraction is equal to  $n$  to the rate constant  $k_0^{\text{obs}}$  measured in the absence of D, eq 1:

$$k_n^{\text{obs}} = k_0^{\text{obs}} (1 - n + n\Phi^{\text{T}})^m \quad (1)$$

where  $\Phi$  is the fractionation factor for each proton/deuteron that exchanges with the solvent during the process under study and the superscript T refers to transition state. The exponent  $m$  represents the number of protons/deuterons transferred. The results for the reaction of MTO with

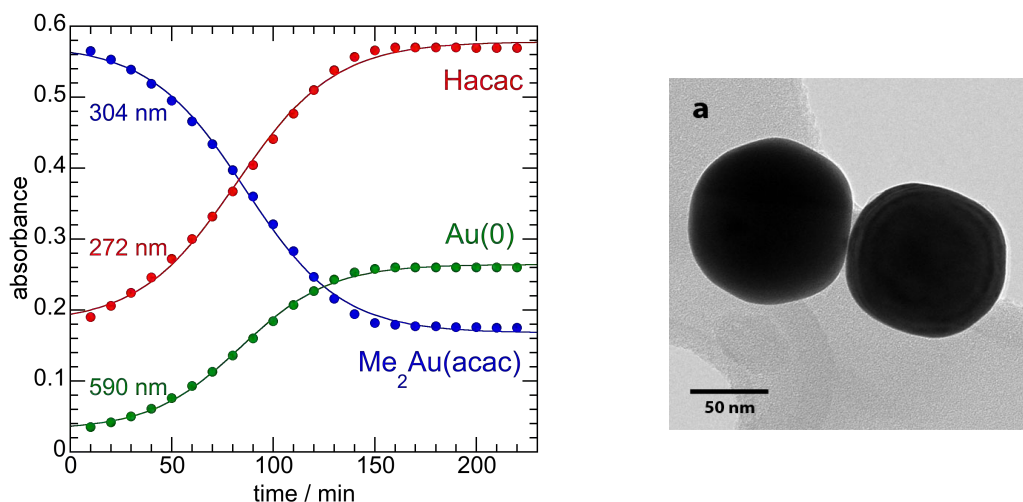


H<sub>2</sub>O<sub>2</sub> are shown in Figure 1 (Right). Clearly the first ligand exchange is more sensitive to the H/D fraction, and therefore involves more proton transfers, than does the second.

### **Reaction kinetics in homogeneous and heterogeneous nanoparticle formation**

We have been studying the kinetics of nanoparticle formation from organometallic precursors both in solution and on surfaces. The autocatalytic nature of Au(0) production from a solution of the organogold precursor Me<sub>2</sub>Au(acac) is evident in Figure 2. Figure 2 (Left) also shows the curvefits to the kinetic expression for a simple, 2-step autocatalytic mechanism, eq 2.

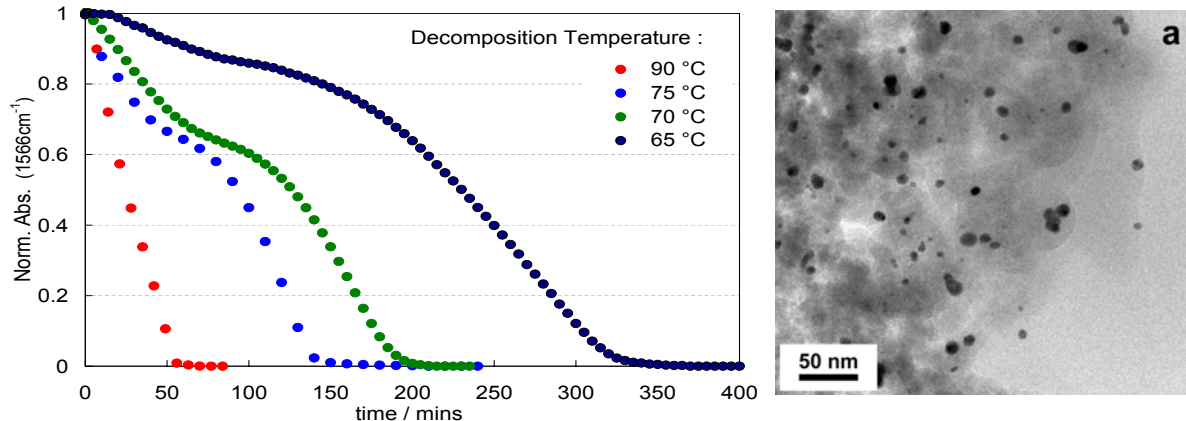
$$C_A = \frac{(k_1 + k_2 C_{A0}) C_{A0} e^{(k_1 + k_2 C_{A0})t}}{k_1 + k_2 C_{A0} - k_2 C_{A0} (1 - e^{(k_1 + k_2 C_{A0})t})} \quad (2)$$



**Figure 2.** Left: UV-vis kinetic profiles for transformation of Me<sub>2</sub>Au(acac) to Au(0) in 2-propanol at 70 °C, showing curvefits to eq 2, and Right: TEM image of the resulting Au(0) nanoparticles.

In 2-propanol with 1 mM Me<sub>2</sub>Au(acac) at 70 °C, the analysis yields rate constants for nucleation ( $k_1 = 2 \times 10^{-5} \text{ s}^{-1}$ ) and particle growth ( $k_2 = 2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ ). According to Finke, particle size depends on the ratio of rates for these two processes. Under these reaction conditions, the rates become similar at just 1 % conversion, leading to the large particle size (ca. 80 nm) shown in Figure 2 (Right).

Kinetic control of nanoparticle size can therefore be achieved by changing the reaction conditions, since nucleation and particle growth have different activation barriers. Another way to control particle size is to deposit the metal precursor on a support, as is commonly done in catalyst preparation. Using *in situ* IR spectroscopy to monitor the reaction of Me<sub>2</sub>Au(acac) supported on silica, we have acquired temperature-dependent kinetic data, Figure 3. The kinetic profiles are more complex and cannot be analyzed simply using eq 3. The supported gold nanoparticles are much smaller than those formed in solution.



**Figure 3.** Left: IR kinetic profiles for transformation of  $\text{Me}_2\text{Au}(\text{acac})/\text{SiO}_2$  to  $\text{Au}(0)$  in the absence of solvent at various temperatures, and Right: TEM image of  $\text{Au}(0)/\text{SiO}_2$  prepared at  $70^\circ\text{C}$ .

### *A new method for modeling isolated catalyst sites on amorphous supports*

Theoretical methods for modeling crystalline metals, oxides, and zeolites have become extremely sophisticated and reliable. By contrast, theoretical methods for modeling isolated catalyst sites on amorphous supports remain primitive. Yet many catalysts, including those central to this project, are prepared as isolated metal centers on amorphous supports like silica and silica-alumina, or crystalline supports whose surface structure is nevertheless poorly defined. Silica and silica-alumina are similar to zeolites in composition and in being insulators. Accordingly, many investigators have modeled isolated metal centers on silica and silica-alumina using cluster models like those commonly used for zeolites. For zeolites, the peripheral atoms of the cluster model are typically fixed at crystallographic positions to mimic approximately rigid connections to the surrounding solid framework. In cluster models for amorphous catalysts, there are no crystallographic positions to guide the placement of peripheral atoms. Typical cluster models for amorphous catalysts use arbitrarily chosen constraints, or else they use no constraints at all. Both strategies are problematic, since: (1) different choices of the constraints change the computed properties, and (2) omitting the constraints entirely leads to unrealistically flexible site models.

In the past year, we made significant progress on a systematic, *ab initio* method to resolve this problem. As is done for zeolites, we partition our active site cluster models into peripheral atoms, which are fixed during the reaction to mimic the solid matrix, and internal atoms which can move within the cage of peripheral atoms during the reaction. For each fixed placement of the peripheral atoms, there are established methods to find the saddle point and the reactant and product minima. Still, the space of possible peripheral atom positions can be enormous. A new systematic algorithm helps us efficiently generate representative cluster models. To see how, we note that each activation energy corresponds to an “ensemble” of peripheral atom positions. We do not know the (non-Boltzmann) distribution that governs the relative populations of different sites, but we do expect sites with lower energies to be more prevalent than high energy sites. Therefore, we systematically generate the lowest energy site for each activation energy. Specifically, we solve the problem

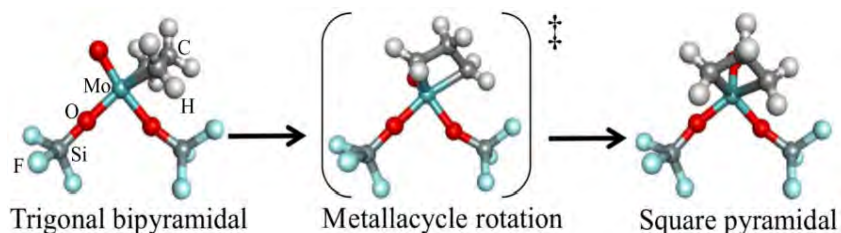
$$\min_{\mathbf{x}_p} E_{red}^A(\mathbf{x}_p) \quad \text{subject to} \quad E_{red}^\ddagger(\mathbf{x}_p) - E_{red}^A(\mathbf{x}_p) = E^\ddagger$$

in the peripheral atom space, while simultaneously solving

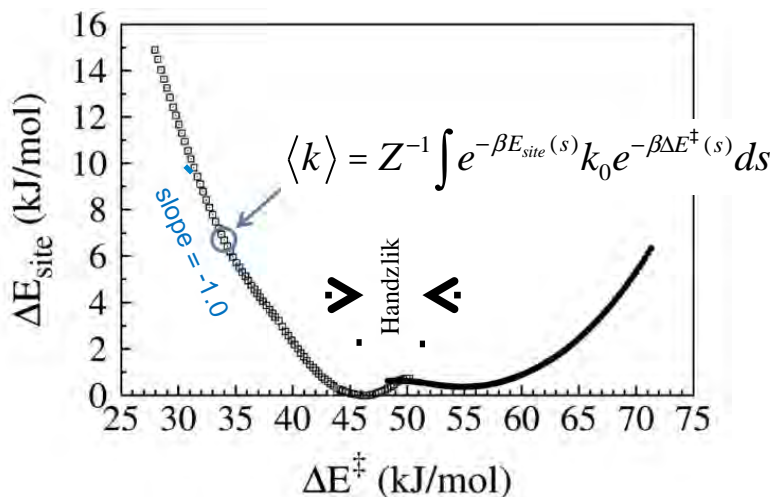
$$E_{red}^A(\mathbf{x}_p) = \min_{\mathbf{x}_i} E(\mathbf{x}_i, \mathbf{x}_p) \quad \text{and} \quad E_{red}^\ddagger(\mathbf{x}_p) = \text{saddle}_{\mathbf{x}_i} E(\mathbf{x}_i, \mathbf{x}_p),$$

and the electronic structure problem at each  $(\mathbf{x}_i, \mathbf{x}_p)$  to obtain the Born-Oppenheimer surface  $E(\mathbf{x}_i, \mathbf{x}_p)$ . In general this is an extremely difficult three-level nested constrained optimization problem. However, if one solution can be found, then a sequential quadratic programming algorithm can be used to efficiently find other conditions.

Figures 4-5 show results for a side-reaction in olefin metathesis by molybdate ions on amorphous silica. A square pyramidal product has been suggested to trap sites in an inactive state. In an attempt to account for the heterogeneity of active sites on the amorphous material, Handzlik used ten discrete models, all carved from different surfaces of  $\beta$ -cristobalite. He performed calculations of the ONIOM type with two regions modeled at two different levels of ab initio description. Each model used approximately 35 silicon atoms to describe the silica environment around the Mo atom. Our model, shown in Figure 4, has only two silicon atoms. The rest of the silica matrix has been replaced by peripheral F-atoms. The F atoms are basis-deficient to mimic the electron-withdrawing ability of the silica matrix. All ten of Handzlik's models give activation energies within the narrow range 46-51 kJ/mol. In contrast, our new SQP algorithm generated sites with activation energies spanning a 40 kJ/mol range, from  $\Delta E^\ddagger = 30$  kJ/mol to  $\Delta E^\ddagger = 70$  kJ/mol, Figure 5. By comparing the structures of these sites, we learned that stretched sites are inactive while sites with nearby anchoring points are active.



**Figure 4.** Off-pathway step leading to a kinetic trap in olefin metathesis by Mo on amorphous silica.



**Figure 5.** Minimum energy of formation for an active site at each activation energy.

## Future Plans

In the coming year, we plan to

- extend our new algorithm for active site generation in amorphous supports to olefin metathesis and polymerization catalysts;
- develop a method for predicting both particle size and particle size distribution in nanoparticle catalysts based on kinetic observables;
- apply isothermal and non-isothermal kinetic analysis to more complex catalysts in more types of reactions, to explore its generality, and extend the analysis to include mass transport effects.

## Publications (2011-2013)

- B. C. Vicente, R. C. Nelson, A. W. Moses, S. Chattopadhyay, and S. L. Scott, "Interactions Involving Lewis Acidic Aluminum Sites in Oxide-Supported Perrhenate Catalysts", *J. Phys. Chem. C* **2011**, *115*, 9012-9024.
- S. D. Fleischman, S.L. Scott, "Evidence for the Pairwise Disposition of Grafting Sites on Highly Dehydroxylated Silicas via Their Reactions with  $\text{Ga}(\text{CH}_3)_3$ ", *J. Am. Chem. Soc.* **2011**, *133*, 4847-4855.
- R.M. Shayib, N. George, R. Seshadri, A.W. Burton, S.I. Zones, B.F. Chmelka, Structure-Directing Roles and Interactions of Fluoride and Organocations with Siliceous Zeolite Frameworks," *J. Am. Chem. Soc.*, **2011**, *133*, 18728-18741.
- J. A. Kurzman, J. Li, T. D. Schladt, C. R. Parra, X. Ouyang, R. C. Davis, J. T. Miller, S. L. Scott, and R. Seshadri, " $\text{Pd}^{2+}/\text{Pd}^0$  Redox Cycling in Hexagonal  $\text{YMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ : Implications for Catalysis by PGM-Substituted Complex Oxides", *Inorg. Chem.* **2011**, *50*, 8073-8084.
- M.-Y. Lee and S. L. Scott, "Quantitative Investigation of a Hybrid Ziegler-Natta Catalyst Support Prepared by Grafting Di(n-butyl)magnesium onto Partially Dehydroxylated Silica", *Chem. Eur. J.* **2011**, *17*, 4632-4639.
- J. Zhu, X. Ouyang, M.-Y. Lee, R. C. Davis, S. L. Scott, A. Fischer, and A. Thomas, "Two-step synthesis of  $\text{Fe}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  nanoparticles: towards a general method for synthesizing nanocrystalline metal oxides with high surface area and thermal stability", *RSC Adv.* **2012**, *2*, 121-124.
- Peters, B. "Headspace diffusion limitations on heterogeneous catalysis in unstirred batch reactors", *Chem. Eng. Sci.*, **2012**, *71*, 367-374.
- Tovar, T. M.; Stewart S. M.; Scott, S. L. "Origin of the  $\text{ZnCl}_2$  Effect on  $\text{CH}_3\text{ReO}_3/\gamma\text{-Al}_2\text{O}_3$  in Olefin Metathesis", *Top. Catal.*, **2012**, *55*, 530-537.
- Crosswhite, M.; Hunt, J.; Southworth, T.; Serniak, K.; Ferrari, A.; Stiegman, A. E., "Development of Magnetic Nanoparticles as Microwave-Specific Catalysts for the Rapid Low-Temperature Synthesis of Formalin Solutions", *ACS Catal.*, **2013**, accepted for publication.
- Goldsmith, B.; Fong, A.; Peters, B. "Understanding reactivity with reduced potential energy landscapes: recent advances and new directions", in Reaction rate constant computations: theories and applications, Han, K. Ed., Royal Society, in review.
- Goldsmith, B.; Sanderson, E.; Bean, D.; Peters, B. "Sequential quadratic programming framework for ab initio structure-activity relationships of catalysts on amorphous supports", *J. Chem. Phys.*, in review.
- Hwang, T.; Goldsmith, B.; Peters, B.; Scott, S.L. "Water-Catalyzed Activation of  $\text{H}_2\text{O}_2$  by Methyltrioxorhenium: A Combined Computational-Experimental Study", *Inorg. Chem.*, in review.

**Templating Routes to Supported Oxide Catalysts by Design**

Graduate students: Andrew Korinda, Todd Eaton, Zhenyu Bo

Collaborators: Dario Prieto-Centurion (NU), Mark Bachrach (NU), Christian Canlas (NU, ANL), Jeff Elam (ANL), Tobin Marks (NU), Jeff Miller (ANL), Peter Stair (NU), Randy Winans (ANL)

Contact: Justin Notestein, Assistant Professor, Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Rd., Technological Institute E136, Evanston IL 60208, 847.491.5357 (ph), 847.491.3728 (fax), j-notestein@northwestern.edu, <http://notestein.northwestern.edu>

**Goals**

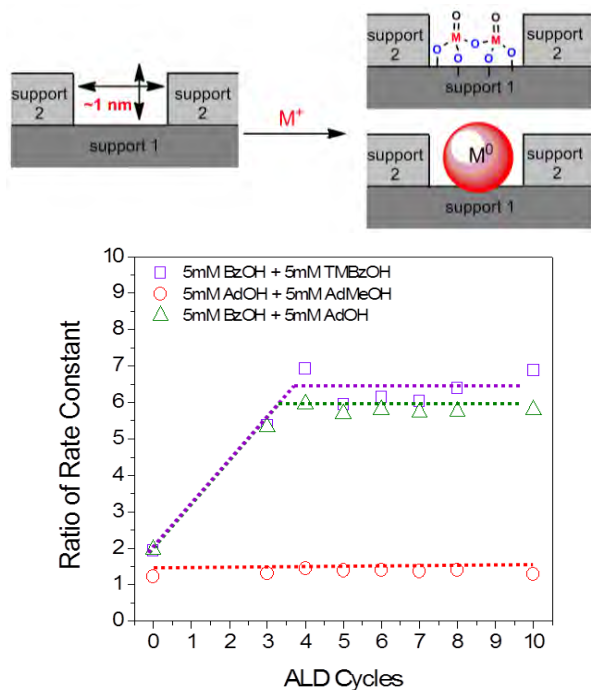
To complement the powerful tools that exist for determining catalyst structures and mechanisms, we seek to advance the design and synthesis of supported oxide domains, which remains a standing DOE grand challenge. This project specifically seeks to develop and apply new synthetic methods to controlling supported oxide catalysts from one atom to a few nm.

**DOE Interest**

Supported oxide catalysts are used extensively in chemicals, fuels, and emissions catalysis, and new atom-precise design methodologies will enable new, more selective or sustainable reactions and the testing of proposed structure-reactivity correlations for existing catalysts. The foci of this project are on selective oxidation, but we also generally seek to demonstrate that controlling nanostructure *around* oxide active sites could allow enzyme-like selectivity on robust oxide catalysts, potentially reducing the need for separations.

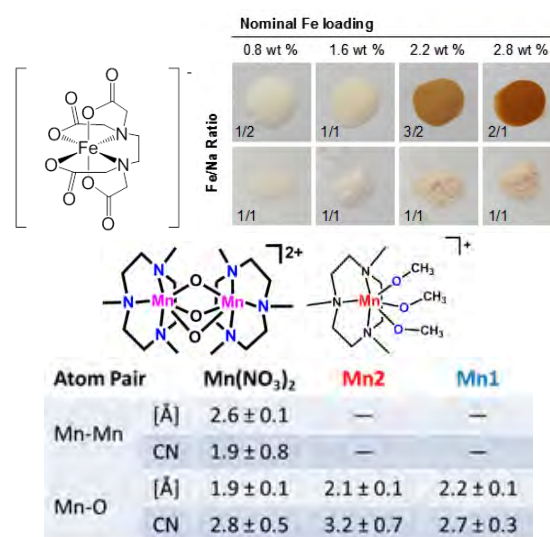
**Recent Progress**

*Templating via Support Design.* We and collaborators have developed a new class of materials by partially overcoating a carrier (oxide) particle with <2nm of a second oxide by repetitive growth methods such as ALD (**Fig 1**). Molecular templates are used to generate nanocavities (nc) 1-2 nm in diameter whose walls and floor can be different oxide compositions. We have first shown that Al<sub>2</sub>O<sub>3</sub>-nc-TiO<sub>2</sub> imparts reactant selectivity to oxidations and reductions catalyzed by the underlying TiO<sub>2</sub>. For example, in the oxidation of equimolar benzyl alcohol and more bulky alcohols to their respective aldehydes, relative rates increased from ~1.5:1 for TiO<sub>2</sub> to nearly 10:1 for the overcoated materials. Such selectivity had not, to our knowledge, been previously demonstrated in a formally non-porous oxide catalyst. In subsequent work, we have shown that such selectivity is retained with more typical catalyst handling, including calcination to 550°C, and we have determined formal reaction orders suggesting that reaction selectivity is controlled by reactant adsorption. These nanostructured supports are also proposed to control domain sizes and structures of catalysts subsequently deposited into the cavities. We are developing a library of supports, templates, and oxide deposition techniques, and we are undertaking basic investigations required before backfilling metal nanoparticles or small oxide domains by adsorption, exchange, or other methods.



**Fig 1.** Cartoon proposing use of 'nanocavity' oxides to template formation of supported oxide or metal domains using strong electrostatic adsorption or exchange. For support 1 =  $\text{TiO}_2$ , and 2 =  $\text{SiO}_2$ , the  $\text{SiO}_2$  regions are expected to be more negatively charged than the  $\text{TiO}_2$ , giving preferential deposition of anionic precursors (ie chloroplatinate or permanganate) at the nanocavities. Alternately, the nanostructured support itself can be used as a selective catalyst, as shown for competitive alcohol oxidation, where relative rates stabilize out at  $\sim 6:1$  favoring the less hindered alcohol over  $\text{Al}_2\text{O}_3\text{-nc-TiO}_2$ .

*Templating via Well-Defined Oxide Precursors.* Here, we seek to control supported oxide catalyst structure via precursor design (**Fig 2**). Current activity focuses on completing a series of investigations with Mn triazacyclononane (TACN) complexes of different nuclearity as precursors to supported  $\text{MnOx-SiO}_2$  catalysts that are more dispersed than typical precursors. We have also extended the use of EDTA ligands to synthesize dispersed Fe or Cu sites on  $\text{SiO}_2$  for alkane oxidation with  $\text{H}_2\text{O}_2$ . The relative amount of counteraction ( $\geq 1$  alkali:metal) controls the oxide structure, while the nature of the counteraction (Li, Na, K, Cs) of these unusual anionic Fe precursors was shown to control oxidation rates over these atomically-dispersed sites. Finally, we are addressing the significant challenge of quantifying catalytic rates per *accessible* surface atom in supported oxide catalysis with light oxides. Among other techniques like DRUV-vis, XRD, and XAS, we are applying phosphonic acid titrations and benzyl alcohol oxidation to a range of supported  $\text{TiO}_2\text{-SiO}_2$  materials made by different grafting methods and the templating route described above (**Fig 3**). From this, we are able to develop improved synthesis-structure-activity correlations that include quantitative estimates for the number of surface active sites



**Fig 2.** Well-defined supported metal oxides are derived from precursor complexes protected by bulky ligands. Counterions are especially useful in maintaining site isolation or tuning subsequent reactivity in a controlled way, such as for supported  $\text{FeOx-SiO}_2$  derived from an EDTA ligand (top) which requires a 1:1 alkali:Fe stoichiometry, regardless of surface density, for high dispersion. At high Fe loadings, these materials can be 10-30x as active as  $\text{FeOx-SiO}_2$  via a nitrate precursor. Likewise, monomeric and dimeric, cationic Mn tmtacn complexes (bottom) give after calcination, more dispersed Mn(III) structures, than do  $\text{Mn}(\text{NO}_3)_2$  precursors.



and the role of the precursor. We find, for example, that crystallinity and UV-visible edge energy are relatively poor predictors of reactivity, and that a lack of crystallinity does not necessarily give accessible sites even for grafted materials. It is believed that this titration method will find utility in many other SiO<sub>2</sub>-supported catalysts.

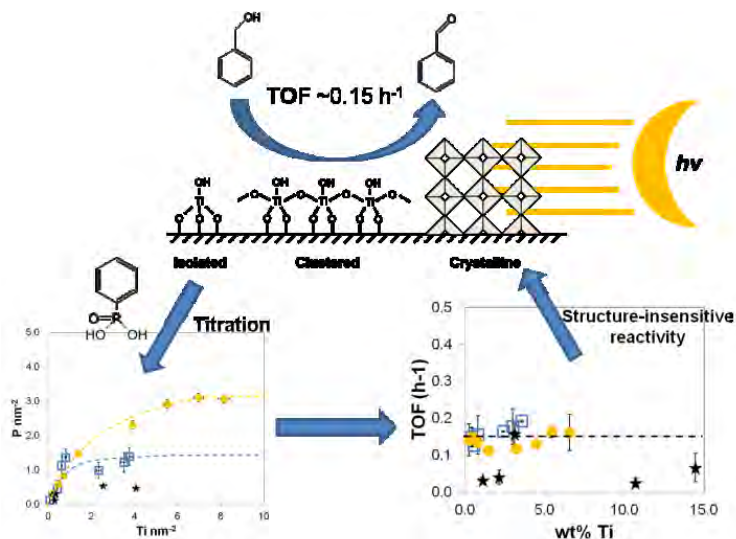
### Future Plans

**Templating via Support Design.** We seek to increase the diversity of nanocavity supports by looking at deeper templates while still focusing on SiO<sub>2</sub>-nc-TiO<sub>2</sub> and TiO<sub>2</sub>-nc-SiO<sub>2</sub>. The new surface titration technique will be essential for properly normalizing available surface areas. We will optimize methods for deposition of metal nanoparticles in nanocavities by photoreduction (for e.g. Ag on TiO<sub>2</sub>) and by strong electrostatic adsorption or impregnation, followed by calcination and reduction, particularly for their use in providing a handle in microscopy. We will also begin deposition of 1<sup>st</sup>-row metal oxides in/on nanostructured supports and probe structure through selective oxidations, diffuse reflectance UV-visible spectroscopy, and EXAFS. These will include materials that combine isolated metal oxides and extended crystalline domains in controlled ratios on the same material, using templating routes.

**Templating via Well-Defined Oxide Precursors.** We have established a collaboration with a synthetic inorganic chemistry group to explore immobilization of a wide range of metal oxide clusters. Further, we will continue to develop oxidation catalysts based on (mixed) alkali-modified Fe, Cu, and Co synthesized by EDTA-precursors.

### Publications

- C. P. Canlas, J. Lu, N. A. Ray, N. A. Grosso-Giordano, J. W. Elam, S. Lee, R. E. Winans, P. C. Stair, R. P. Van Duyne, and J. M. Notestein\*, "Shape-Selective Sieving Layers on an Oxide Catalyst Surface," *Nature Chem.*, **2012**, *4*, 1030-1036.
- D. Prieto-Centurion, A. M. Boston, J. M. Notestein\*, "Structural and electronic promotion with alkali cations of silica-supported Fe(III) sites for alkane oxidation," *J. Catal.*, **2012**, *296*, 77-85.



**Fig. 3.** Benzyl alcohol oxidation was studied over TiO<sub>2</sub>-SiO<sub>2</sub> materials synthesized by different methods and at different surface densities to give a range of 'isolated', polymeric sheets, and crystalline domains, then were titrated with phenylphosphonic acid. Ethoxides (circles) led to near full coverage of the surface with crystalline anatase, whereas a titanocene precursor (squares) never crystallized, but also left a significant fraction of Ti unable to be titrated. Regardless of Ti electronic structure, normalizing rates by the titrated sites gave a single TOF. In contrast, sol-gel materials (stars) followed less predictable behavior in either structure or reactivity.

## Novel Palladium Catalysts for the Oxidative Oligomerization of Methane & Carbon Dioxide Reduction

Postdocs: Julia Khusnutdinova, Bo Zheng  
 Students: Fengzhi Tang, Fengrui Qu, Jia Luo, Jason Schultz  
 Collaborators: Nicolai Lehnert (Univ. of Michigan), Jeffrey T. Miller (Argonne National Lab)  
 Contacts: Liviu M. Mirica, Washington University, Dept. of Chemistry, CB 1134, 1 Brookings Drive, St. Louis, MO 63130; Tel. 314-935-3464; mirica@wustl.edu

### Goal

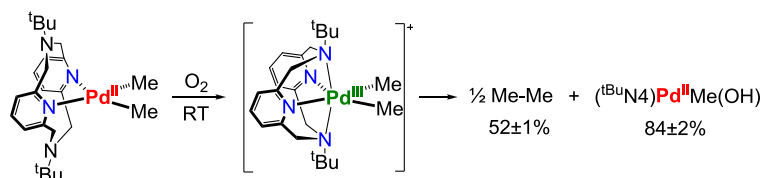
The long term goal of this project is to develop novel catalytic transformations that involve less common Pd<sup>III</sup> and Pd<sup>I</sup> oxidation states and thus expand further the catalytic reactivity of palladium. We are particularly interested in the development of a novel Pd<sup>II</sup>/Pd<sup>III</sup>/Pd<sup>IV</sup> catalytic cycle for the aerobic oxidative oligomerization of hydrocarbons, as well as to establish the redox reactivity of Pd<sup>I</sup> and Pd<sup>III</sup> systems and develop catalysts for the activation of small molecules such as CO<sub>2</sub>.

### DOE Interest

The targeted energy-related chemical transformations would allow for a more efficient use of natural gas reserves as an inexpensive energy resource and thus should have a major impact on our society and the environment. In addition, the development of novel catalytic systems for efficient C-H activation and C-C bond formation and the activation of small molecules such as CO<sub>2</sub> will have far-reaching energy-related implications, in line with the mission of the *Basic Energy Sciences – Catalysis Science Program* of the Department of Energy.

### Recent Progress

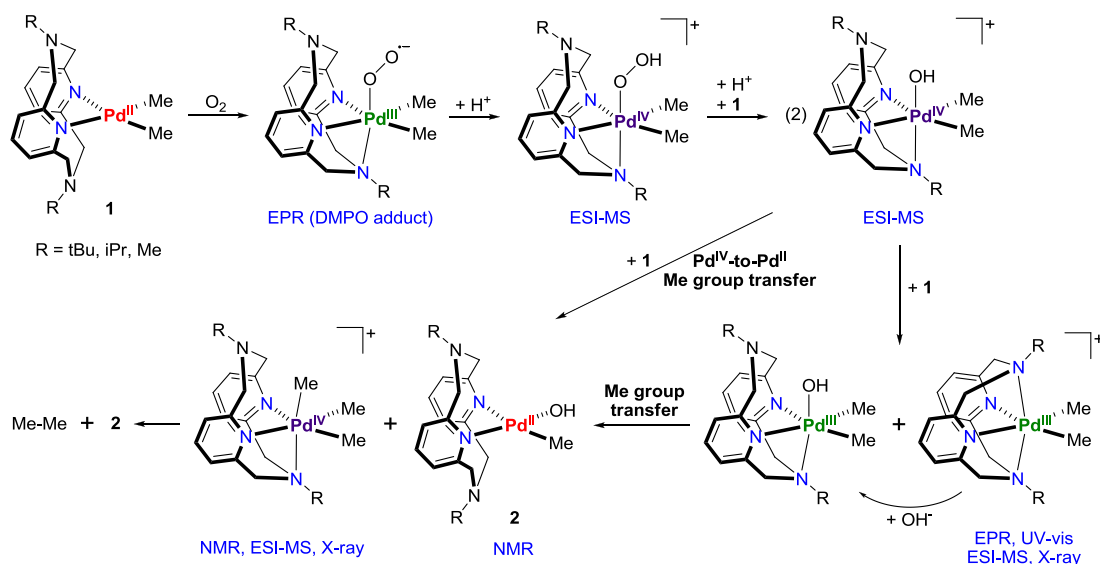
*Mononuclear organometallic Pd<sup>III</sup> complexes.* In 2010 we have employed the flexible tetradentate ligand <sup>t</sup>Bu<sub>4</sub>N4 (N,N'-di-*tert*-butyl-2,11-diaza[3.3](2,6)pyridinophane) to stabilize the first mononuclear organometallic Pd<sup>III</sup> complexes, and we have investigated their C-C and C-heteroatom bond formation reactivity. We have also recently reported that (<sup>t</sup>Bu<sub>4</sub>N4)Pd<sup>II</sup>Me<sub>2</sub> undergoes facile aerobic oxidation to generate the Pd<sup>III</sup> species [(<sup>t</sup>Bu<sub>4</sub>N4)Pd<sup>III</sup>Me<sub>2</sub>]<sup>+</sup>, followed by formation of ethane and the monomethyl complex (<sup>t</sup>Bu<sub>4</sub>N4)Pd<sup>II</sup>Me(OH) (Scheme 1). Overall, this study represented one of the first examples of C-C bond formation upon aerobic oxidation of a Pd<sup>II</sup> dimethyl complex, and provides evidence that (<sup>R</sup>N<sub>4</sub>)Pd systems can undergo aerobic oxidation, C-C bond formation, and C-H bond activation reactions, and thus could be involved in a catalytic cycle for the aerobic oxidative coupling of C-H bonds.



**Scheme 1.** Aerobic oxidative C-C bond formation reactivity of (<sup>t</sup>Bu<sub>4</sub>N<sub>4</sub>)Pd<sup>II</sup>Me<sub>2</sub>.



*Mechanistic studies of aerobic oxidation of Pd<sup>II</sup> complexes.* Continuing our study of high-valent Pd chemistry, we have employed the N-methyl (<sup>Me</sup>N4) and N-isopropyl (<sup>iPr</sup>N4) substituted N4 ligands, which lead to the isolation and characterization of mononuclear Pd<sup>III</sup> and Pd<sup>IV</sup> complexes and allowed a direct structural and reactivity comparison. Importantly, several Pd<sup>III</sup> and Pd<sup>IV</sup> intermediates were detected during the aerobic oxidation of (<sup>Me</sup>N4)Pd<sup>II</sup>Me<sub>2</sub>, including the key Pd<sup>IV</sup> intermediate [(κ<sup>3</sup>-<sup>Me</sup>N4)Pd<sup>IV</sup>Me<sub>3</sub>]<sup>+</sup> leading to ethane elimination, thus providing strong evidence for an inner-sphere O<sub>2</sub> reduction mechanism at a Pd<sup>II</sup> center and sequential C-C reductive elimination from a Pd<sup>IV</sup> center (Scheme 2).



**Scheme 2.** Proposed mechanism for the aerobically induced C-C bond formation of (<sup>R</sup>N4)Pd<sup>II</sup>Me<sub>2</sub> complexes. The intermediate species were detected for <sup>Me</sup>N4 by the techniques listed.

*High-valent Pd complexes stabilized by tridentate ligands.* In addition to the studies using tetradentate ligands, we have shown that the tridentate ligand N,N',N''-trimethyltriazacyclononane (Me<sub>3</sub>tacn) can stabilize both dinuclear Pd<sup>III</sup> and mononuclear Pd<sup>IV</sup> complexes upon sequential one-electron oxidations of mononuclear Pd<sup>II</sup> precursors. We have also recently reported that the dimethyl Pd<sup>II</sup> complex (Me<sub>3</sub>tacn)Pd<sup>II</sup>Me<sub>2</sub> undergoes facile aerobic oxidation to yield the stable [(Me<sub>3</sub>tacn)Pd<sup>IV</sup>Me<sub>3</sub>]<sup>+</sup> species, which eliminates ethane only at elevated temperatures. This system represents one of the first examples of aerobic oxidation of a Pd<sup>II</sup> organometallic precursor to yield a stable Pd<sup>IV</sup> product, supporting the role of Pd<sup>IV</sup> species as viable intermediates in the Pd-mediated aerobic oxidative transformations.

## Future Plans

*Aerobic oxidative coupling of C-H bonds.* Our current research efforts aim to provide further insight into catalyst design for the aerobic oxidative coupling of C-H bonds. We have developed various tetradentate and tridentate ligands whose organometallic Pd<sup>II</sup> complexes exhibit aerobic reactivity to generate high-valent Pd intermediates, and we are investigating a) the C-H activation reactivity of these Pd<sup>II</sup> complexes toward various C-H substrates; b) the detailed mechanism of the aerobic oxidation of Pd<sup>II</sup> precursors to yield Pd<sup>III</sup> and/or Pd<sup>IV</sup> species; and c) the C-C bond formation step from high-valent Pd species.

*Electrocatalytic CO<sub>2</sub> reduction.* Preliminary electrochemical studies show that our flexible tetradentate ligands can stabilize both Pd<sup>I</sup> and Pd<sup>III</sup> species in solution. We are particularly

interested in low-valent Pd complexes due to their proposed involvement in electrocatalytic CO<sub>2</sub> reduction. We are currently employing various tetradentate and tridentate ligands – including ones with soft donor atoms, to stabilize low-valent metal complexes and investigate their reactivity with CO<sub>2</sub>, in order to detect and characterize intermediate species involved in the CO<sub>2</sub> reduction mechanism.

We are also currently expanding our CO<sub>2</sub> and other small molecule activation studies to include first row transition metal complexes stabilized by flexible multidentate ligands.

### Relevant Publications (2010-2013)

*Publications acknowledging DOE support:*

11. Khusnutdinova, J. R.; Luo, J.; Rath, N. P.; Mirica, L. M.\* “Late First Row Transition Metal Complexes of a Tetradentate Pyridinophane Ligand: Electronic Properties and Reactivity Implications”, *Inorg. Chem.*, **2013**, *52*, 3920-3932.
10. Tang, F.; Qu, F.; Khusnutdinova, J. R.; Rath, N. P.; Mirica, L. M.\* “Structural and Reactivity Comparison of Analogous Organometallic Pd(III) and Pd(IV) Complexes”, *Dalton Trans.*, **2012**, *41*, 14046-14050.
9. Tang, F.; Zhang, Y.; Rath, N. P.; Mirica, L. M.\* “Detection of Pd(III) and Pd(IV) Intermediates during the Aerobic Oxidative C-C Bond Formation from a Pd(II) Dimethyl Complex”, *Organometallics*, **2012**, *31*, 6690-6696.
8. Khusnutdinova, J. R.; Mirica, L. M.\* “Organometallic Pd(III) Complexes in C-C and C-Heteroatom Bond Formation Reactions”, invited book chapter in *C-H Activation and Functionalization, Transition Metal Mediation*, Ribas, X., Ed.; Royal Society of Chemistry, 2013, in press.
7. Khusnutdinova, J. R.; Qu, F.; Zhang, Y.; Rath, N. P.; Mirica, L. M.\* “Formation of the Pd(IV) Complex [(Me<sub>3</sub>tacn)Pd<sup>IV</sup>Me<sub>3</sub>]<sup>+</sup> through Aerobic Oxidation of (Me<sub>3</sub>tacn)Pd<sup>II</sup>Me<sub>2</sub> (Me<sub>3</sub>tacn = N,N',N''-trimethyl-1,4,7-triazacyclononane)”, *Organometallics*, **2012**, *31*, 4627-4630. Featured on the cover.
6. Mirica L. M.,\* Khusnutdinova J. R., “Structure and Electronic Properties of Pd(III) Complexes”, *Coord. Chem. Rev.*, **2013**, *257*, 299-314.
5. Khusnutdinova J. R., Rath N. P., Mirica L. M.\* “The Aerobic Oxidation of a Pd(II) Dimethyl Complex Leads to Selective Ethane Elimination from a Pd(III) Intermediate” *J. Am. Chem. Soc.*, **2012**, *134*, 2414-2422.

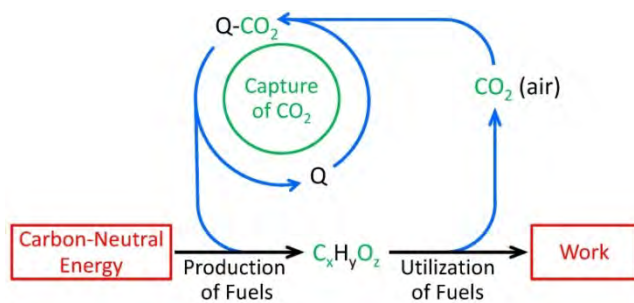
*Earlier Relevant Publications:*

4. Luo, J., Khusnutdinova J. R., Rath N. P., Mirica L. M.\* “Unsupported d<sup>8</sup>-d<sup>8</sup> interactions in cationic Pd<sup>II</sup> and Pt<sup>II</sup> complexes: Evidence for a significant metal-metal bonding character” *Chem. Comm., Emerging Investigators issue* **2012**, *48*, 1532-1534.
3. Luo, J.; Rath, N. P.; Mirica, L. M.\* “Dinuclear Co(II)Co(III) Mixed-Valence and Co(III)Co(III) Complexes with N- and O- Donor Ligands: Characterization and Water Oxidation Studies”, *Inorg. Chem.*, **2011**, *50*, 6152-6157.
2. Khusnutdinova, J. R.; Rath, N. P.; Mirica, L. M.\* “Dinuclear Pd(III) Complexes with a Single Unsupported Bridging Halide Ligand: Reversible Formation from Mononuclear Pd(II) or Pd(IV) Precursors”, *Angew. Chem. Int. Ed.*, **2011**, *50*, 5532-5536.
1. Khusnutdinova, J. R.; Rath, N. P.; Mirica, L. M.\* “Stable Mononuclear Organometallic Pd(III) Complexes and Their C-C Bond Formation Reactivity”, *J. Am. Chem. Soc.*, **2010**, *132*, 7303-7305. Featured as “News of the Week” in *Chem. & Eng. News*, **2010**, *88*, 21, 9.

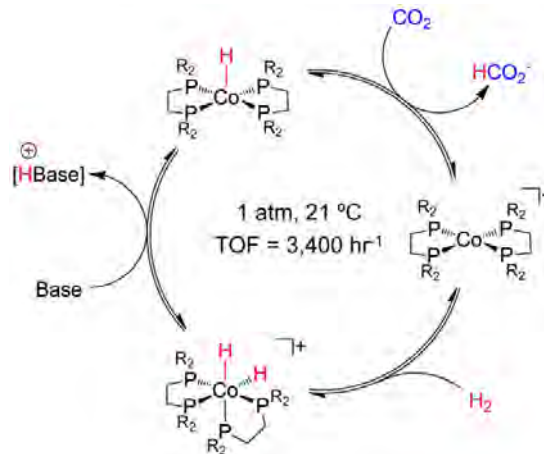
## An Energy-Based Approach to Bifunctional Molecular Catalysis for CO<sub>2</sub> Reduction and Fuel Utilization

Lead PI: Aaron M. Appel  
 Co-PIs: John C. Linehan, Eric S. Wiedner, Donald M. Camaioni, Wendy J. Shaw, R. Morris Bullock  
 Postdocs: Brandon R. Galan, Matthew S. Jeletic, Edwin van der Eide, Sonja M. Peterson, Charles J. Weiss, Nilusha Priyadarshani  
 Contact: Pacific Northwest National Laboratory, PO Box 999, MS K2-57  
 Richland, WA 99352; [aaron.appel@pnnl.gov](mailto:aaron.appel@pnnl.gov)

Due to the intermittent and distributed nature of carbon-neutral energy production, the storage of energy in the form of chemical fuels is highly desirable. The capture and catalytic reduction of CO<sub>2</sub> would allow the production of liquid fuels from this commonly available substrate. While the capture of CO<sub>2</sub> with high energy efficiency remains a challenge, we seek to understand how to rationally design catalysts for the reduction of CO<sub>2</sub> and utilization of the corresponding fuels, using both electrocatalysis and thermal catalysis.



The first step in the reduction of CO<sub>2</sub> can produce either CO or formate. Molecular electrocatalysts based on triphosphine complexes of palladium have been explored with a focus on the incorporation of bifunctionality.<sup>1</sup> For the hydrogenation of CO<sub>2</sub> to formate,<sup>2</sup> the consideration of reaction energetics has been used to design a catalyst system based on a first-row transition metal by specifically considering the hydride donor ability of the resulting metal-hydride and the acidity of the metal-dihydride. For the reverse reaction, the mechanism of electrocatalytic formate oxidation has been studied for a series of bifunctional nickel complexes.<sup>3,4</sup> The resulting proposed mechanism is based on a net transfer of a hydride through a proton-coupled electron transfer reaction.



### References

1. Steffey, B. D.; Curtis, C. J.; DuBois, D. L. *Organometallics* **1995**, *14*, 4937.
2. Getty, A. D.; Tai, C.-C.; Linehan, J. C.; Jessop, P. G.; Olmstead, M. M.; Rheingold, A. L. *Organometallics* **2009**, *28*, 5466.
3. Galan, B. R.; Schöffel, J.; Linehan, J. C.; Seu, C.; Appel, A. M.; Roberts, J. A. S.; Helm, M. L.; Kilgore, U. J.; Yang, J. Y.; DuBois, D. L.; Kubiak, C. P. *J. Am. Chem. Soc.* **2011**, *133*, 12767.
4. Seu, C. S.; Appel, A. M.; Doud, M. D.; DuBois, D. L.; Kubiak, C. P. *Energy Environ. Sci.* **2012**, *5*, 6480.

This page is intentionally blank.

**Sunday Evening**

**Session III**

This page is intentionally blank.

## Center Approach to C-H Functionalization

Huw M. L. Davies

*Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, GA30322, USA*

This presentation will describe a collaborative approach towards achieving new C-H functionalization strategies and our recent advances in the chemistry of donor/acceptor-substituted carbenoids. This class of carbenoids is capable of a range of highly stereoselective C-C bond-forming reactions, such as cyclopropanation and C-H functionalization.<sup>1-3</sup> A series of chiral dirhodium catalysts have been developed for this chemistry and they are capable of very high turnover numbers and can induce high enantioselectivity in a wide range of reactions. The application of these new synthetic methodologies to the synthesis of natural products and pharmaceutical targets will be described.

### References

1. Catalytic C-H Functionalization. An enabling synthetic method for drug development. Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451*, 417-424.
2. Functionalization of Carbon-Hydrogen Bonds Through Transition Metal Carbenoid Insertion, Davies, H. M. L.; Dick, A R., *Top. Curr. Chem.* **2010**, *292*, 303-345.
3. Guiding Principles for Site Selective and Stereoselective C-H Functionalization by Donor/Acceptor-Substituted Rhodium Carbenoids, Davies, H. M. L.; Morton, D. *Chem. Soc. Rev.* **2011**, *40*, 1857-1869.
4. The Combined C-H Functionalization/Cope Rearrangement: Discovery and Applications in Organic Synthesis, Davies, H. M. L.; Lian, Y. *Acc. Chem. Res.* **2012**, *45*, 923-935.

**Selective Reactions of Carbon-Carbon  $\pi$ -Bonds Catalyzed by Cations and Anions**

Lead PI: F. Dean Toste

Postdoc: Dani Peri

Student: Chen Zhao, William M. Hart-Cooper

Collaborators: Kenneth N. Raymond, Robert G. Bergman

Contact: Chemical Sciences Division, Lawrence Berkeley National Laboratory, and  
Department of Chemistry, University of California, Berkeley  
Berkeley, CA 94810-1480; [fdtoste@berkeley.edu](mailto:fdtoste@berkeley.edu)

The past decade has witnessed remarkable development in the use of cationic gold(I) complexes as homogenous catalysts for the transformation of carbon-carbon  $\pi$ -bonds.<sup>1</sup> Several years ago, we demonstrated that the reactivity of these complexes could be controlled by modification of the counter anion to these cationic transition metal complexes.<sup>2</sup> The use of these ionic interactions to control selectivity of cationic species has generally relied on small molecular anions.<sup>3</sup> As an extension of this concept, we have been exploring the use of supramolecular assemblies as the anionic component in reactions catalyzed by cationic transition metal complexes. For example, cationic phosphinegold(I) complexes encapsulated by an anionic  $\text{Ga}_4\text{L}_6$  tetrahedral demonstrated higher turnover numbers, rate acceleration<sup>4</sup> and/or produced different products<sup>5</sup> compared to the unencapsulated catalysts. More recently, we found that cationic catalysts encapsulated in  $\text{Ga}_4\text{L}_6$  tetrahedral supramolecular clusters were well-tolerated by the enzymes and in some cases show improved reactivity and selectivity relative to the free cationic guest.<sup>6</sup> Ultimately, we envision that these concepts can be applied to the design of integrated catalyst networks.<sup>7</sup>

**References**

1. D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395-403.
2. G. A. Hamilton, E. J. Kang, M. M. Blázquez, F. D. Toste, *Science* **2007**, *317*, 496-499.
3. R. J. Phipps, G. L. Hamilton, F. D. Toste, *Nature Chem.* **2012**, *4*, 603-614.
4. Z. J. Wang, C. J. Brown, R. G. Bergman, K. N. Raymond, F. D. Toste, *J. Am. Chem. Soc.* **2011**, *133*, 7358-7360.
5. W. M. Hart-Cooper, K. N. Clary, F. D. Toste, R. G. Bergman, K. N. Raymond *J. Am. Chem. Soc.* **2012**, *134*, 17873-17876.
6. Z. J. Wang, K. N. Clary, R. G. Bergman, K. N. Raymond, F. D. Toste, "A Supramolecular Approach to Combining Enzymatic and Transition Metal Catalysis." *Nature Chem.* **2013**, *5*, 100-103.
7. P. Anbarasan, Z. C. Baer, S. Sreekumar, E. Gross, J. B. Binder, H. W. Blanch, D. G. Clark, F. D. Toste, *Nature* **2012**, *491*, 235-239.



## **Asymmetric Catalysis in Complex Molecular Environments**

**Scott J. Miller**

*Department of Chemistry, 225 Prospect Street, Yale University, New Haven,  
Connecticut 06520-8107, USA  
scott.miller@yale.edu*

Natural products have provided perennial inspiration for the development of synthetic methods, and enzymes have provided an analogous platform for the conception of new catalysts. This lecture will recount an interplay of experiments stimulated by these two major classes of naturally occurring substances. Specifically, the discovery and use of peptides as catalysts for a variety of asymmetric bond formations will be presented. Likewise, applications of these catalysts to the synthesis and selective modification of complex molecules, including biologically active natural products, will be described. A particular emphasis will be placed on reactions that present unusual stereochemical challenges. An analysis of catalyst types that may be brought to bear on complex molecular environments will also be included.

This page is intentionally blank.

**Monday Morning**

**Session IV**

This page is intentionally blank.

# Metal-organic Frameworks as Single Site Solid Catalysts

Wenbin Lin

Department of Chemistry, University of Chicago, 929 E. 57th St., Chicago, IL 60637

e-mail: [wenbin.lin1@gmail.com](mailto:wenbin.lin1@gmail.com)

Metal-organic frameworks (MOFs) have attracted a great deal of interest from the scientific community in recent years.<sup>1,2</sup> As MOFs are typically synthesized under mild conditions, they provide an ideal platform for systematic structural design and property tuning at the molecular level. As a result, MOFs have recently been rationally designed and evaluated for a variety of applications, including nonlinear optics,<sup>1</sup> separation,<sup>3</sup> gas storage,<sup>4,5</sup> chemical sensing,<sup>6</sup> biomedical imaging,<sup>7</sup> drug delivery,<sup>8</sup> and heterogeneous catalysis.<sup>9,10</sup> The single-crystalline nature of many MOFs allows their structures to be precisely determined by single-crystal X-ray crystallography, providing an ideal platform to study single-site catalysis with solid materials. MOF catalysts can combine advantages of both homogeneous catalysts (such as uniform active sites and excellent selectivities) and heterogeneous catalysts (such as easy catalyst separation, recovery, and reuse). The molecular nature of MOF catalysts also allows systematic engineering of the active sites and/or open channel sizes, enabling detailed delineation of the structure-property relationships in MOF catalysts. In this talk, I will present our recent efforts on designing chiral MOFs for asymmetric reactions and exploring photoactive MOFs for solar energy utilization.

1. O. R. Evans and W. Lin, *Acc. Chem. Res.* 2002, **35**, 511-522.
2. N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.* 2005, **38**, 176-182.
3. B. Chen, C. Liang, J. Yang, D. S. Contreras, Y. L. Clancy, E. B. Lobkovsky, O. M. Yaghi and S. Dai, *Angew. Chem. Int. Ed.* 2006, **45**, 1390-1393.
4. J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem. Int. Ed.* 2005, **44**, 4670-4679.
5. M. Dincă and J. R. Long, *Angew. Chem. Int. Ed.* 2008, **47**, 6766-6779.
6. Z. Xie, L. Ma, K. E. deKrafft, A. Jin and W. Lin, *J Am Chem Soc*, 2010, **132**, 922-923.
7. K. E. deKrafft, Z. Xie, G. Cao, S. Tran, L. Ma, O. Z. Zhou and W. Lin, *Angew. Chem. Int. Ed.* 2009, **48**, 9901-9904.
8. W. J. Rieter, K. M. Pott, K. M. Taylor and W. Lin, *J Am Chem Soc*, 2008, **130**, 11584-11585.
9. L. Ma, J. M. Falkowski, C. Abney and W. Lin, *Nature Chemistry*, 2010, **2**, 838-846.
10. F. Song, C. Wang, J. M. Falkowski, L. Ma and W. Lin, *J Am Chem Soc*, 2010, **132**, 15390-15398.

## Bio-inspired Nonheme Iron Catalysts for Hydrocarbon Oxidations

Postdoctoral associate: Williamson Oloo

Graduate students: Young Ju Song, Moly Javadi

Undergraduate student: Shyam Iyer

Collaborators: Miquel Costas (U of Girona, Spain), Eckard Münck (Carnegie Mellon U),  
Sason Shaik (Hebrew U), Yong Wang (Dalian Institute of Chemical Physics)

Contacts: Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota,  
Minneapolis, Minnesota 55455; phone: 612 625 0389; fax: 612 624 7029; e-mail: larryque@umn.edu

### Goal

Inspired by nonheme iron enzymes that catalyze highly stereoselective oxidations of C-H and C=C bonds, we have been developing nonheme iron complexes for use as catalysts for the oxidation of hydrocarbons using H<sub>2</sub>O<sub>2</sub> as an environmentally friendly and atom-efficient oxidant. It is our goal to design and characterize such catalysts for regio- and stereoselective hydrocarbon oxidations and gain mechanistic insights into these novel transformations, particularly into the nature of the high-valent metal-based oxidant(s) involved.

### DOE interest

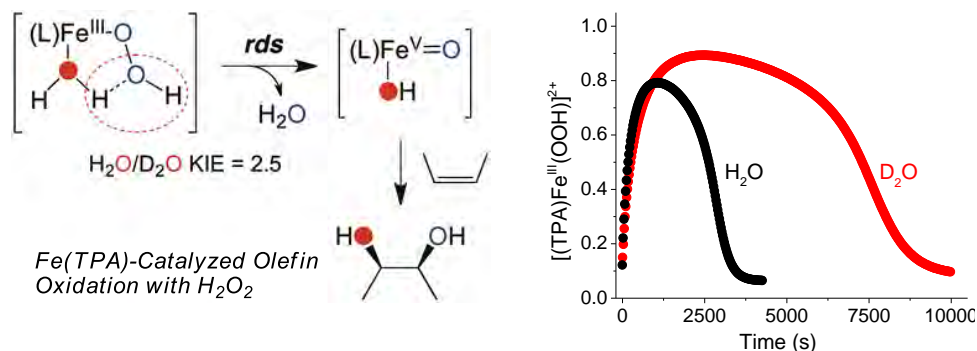
Among the grand challenges in catalysis science identified by the DOE is obtaining a detailed mechanistic understanding of important catalytic transformations. The impending depletion of the earth's petroleum feedstocks makes it wise for us to develop alternative and more environmentally benign strategies for carrying out oxidative transformations of hydrocarbons to fulfill societal demands. Our approach has been to develop bio-inspired hydrocarbon oxidation catalysts based on the reactivity of nonheme iron enzymes such as methane monooxygenase and Rieske dioxygenases that efficiently oxidize methane and naphthalene, respectively. Both enzymes have iron active sites that use amino acid side chains as ligands to produce metal centers that can activate dioxygen and carry out the oxidative transformations under mild reaction conditions. By using tetradentate ligands to mimic these active sites, we have identified nonheme iron catalysts that can oxidize various alkanes and olefins with high stereoselectivity at room temperature using the mild, environmentally benign oxidant, H<sub>2</sub>O<sub>2</sub>. Indeed our efforts led to the first examples of iron-catalyzed *cis*-dihydroxylation of olefins and naphthalene. Our current research efforts are directed towards understanding the mechanistic basis for these transformations, particularly the nature of the high-valent iron oxidant(s) involved in the reactions, in order to advance the design of earth-abundant iron catalysts useful for the selective oxidation of complex organic molecules.

### Recent Progress

#### *1. Kinetic studies of the water-assisted mechanism for bio-inspired Class A nonheme iron catalysts*

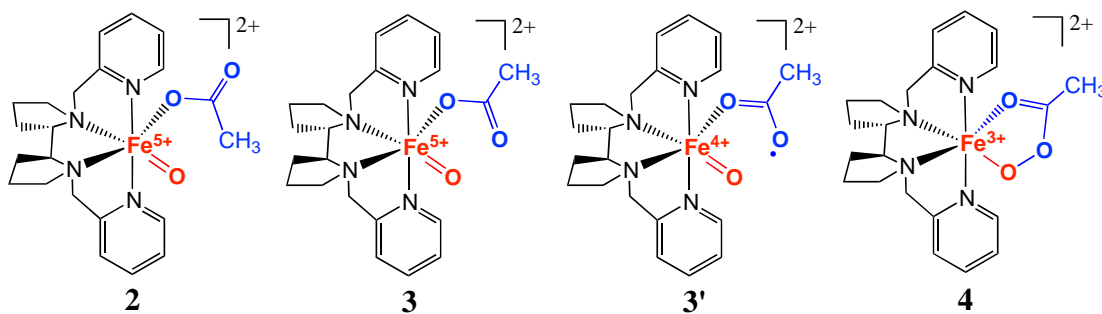
More than 10 years ago, we reported a bio-inspired nonheme iron catalyst that activated H<sub>2</sub>O<sub>2</sub> to oxidize alkanes to the corresponding alcohols (*JACS* **2001**, *123*, 6327) and olefins to a mixture of epoxide and *cis*-diol products (*JACS* **2002**, *124*, 3026). On the basis of <sup>18</sup>O labeling experiments, we proposed a water-assisted mechanism for Fe(TPA) oxidation catalysis where an adjacent water ligand promoted the heterolytic cleavage of the O–O bond of an Fe<sup>III</sup>–OOH intermediate we could trap and characterize at -40 °C to form the Fe<sup>V</sup>(O)(OH) oxidant. We recently obtained persuasive kinetic

evidence for this proposed mechanism. We studied the decay of the key  $\text{Fe}^{\text{III}}\text{-OOH}$  intermediate at  $-40^\circ\text{C}$  and found that its decay rate was unaffected by the addition of substrate but could be accelerated by the addition of water. In addition, this acceleration exhibited a  $\text{H}_2\text{O}/\text{D}_2\text{O}$  isotope effect of 2.5. Furthermore, the decay rate matched the corresponding product formation rate measured under the same conditions. These results support the notion of rate determining O–O bond cleavage of the  $\text{Fe}(\text{III})\text{-OOH}$  intermediate to form an  $\text{Fe}(\text{V})(\text{O})(\text{OH})$  oxidant. This work has just been published in *JACS*.



## 2. DFT-derived insights into the effect of carboxylic acid additives on Class A nonheme iron catalysts

Several groups (Costas, Que, Talsi, White) have noted the beneficial effect of carboxylic acid additives on the performance of this family of nonheme iron catalysts. To account for this effect, we modified our water-assisted mechanism by replacing the water ligand on the observed  $\text{Fe}^{\text{III}}\text{-OOH}$  intermediate with a carboxylic acid and proposed the formation of the analogous  $\text{Fe}^{\text{V}}(\text{O})(\text{O}_2\text{CR})$  oxidant (see structures labeled **2** or **3** below). Indirect evidence supporting this notion was obtained in previously reported experiments (*JACS* **2007**, *129*, 15964). Subsequently, Talsi observed a novel  $S = 1/2$  EPR signal at  $g = 2.7$  that was attributed to the  $\text{Fe}^{\text{V}}(\text{O})(\text{O}_2\text{CR})$  species (*JACS* **2009**, *131*, 10798). To understand the energetics involved in these reactions, we collaborated with Yong Wang and Sason Shaik on DFT calculations on the carboxylic-acid-assisted mechanism. We considered four possible isomers for this high-valent species and found that the acylperoxoiron(III) complex **4** was the most stable electromer, leading us to propose that **4** corresponds to the  $g = 2.7$  species Talsi observed.



As **4** proceeds along the calculated reaction coordinate, it undergoes O–O bond homolysis and converts into **3'** to carry out the initial C–H bond cleavage step. It is interesting to note that the description of **3'** as an oxoiron(IV) moiety with a bound acetoxy radical is analogous to that of Compound I, the oxoiron(IV) porphyrin radical oxidant of cytochrome P450 that carries out hydroxylation of C–H bonds and epoxidation of C=C bonds. This resemblance may change how we view the chemistry of the nonheme iron catalysts and lead to the discovery of new reactivity. This paper has been published in *ACS Catalysis*.

### 3. Spectroscopic characterization of the oxidant formed by the carboxylic-acid-assisted mechanism

In parallel to the DFT work described in #2, we have been working on characterizing the new  $g = 2.7$  species that forms upon addition of acetic acid to the  $\text{Fe}^{\text{III}}\text{-OOH}$  intermediate, assigned by Talsi to the proposed  $\text{Fe}^{\text{V}}(\text{O})(\text{OAc})$  oxidant. However this species represents at best only 15% of the total Fe in the sample under Talsi reaction conditions, making it difficult to determine the oxidation state of the iron center using techniques such as Mössbauer spectroscopy. For such experiments, the  $g = 2.7$  species must represent a much higher fraction in the Fe in the sample. Our ongoing experiments suggest that we now can generate the  $g = 2.7$  species in 50% yield, so its characterization by Mössbauer spectroscopy as well as other techniques such as resonance Raman and X-ray absorption spectroscopy as well as electrospray mass spectrometry is in progress. Kinetic studies parallel to those reported in our just published study of the water-assisted mechanism are planned. Understanding the nature of the oxidant and the overall mechanism of hydrocarbon oxidations in this system will enable appropriate modifications to increase the utility of these reactions in complex organic transformations like those discovered by Christina White.

#### Future plans

*Further kinetic studies:* Carry out detailed kinetic investigations of the reactions of  $\text{H}_2\text{O}_2$  with various members of our family of nonheme iron(II) catalysts to understand the molecular basis for  $\text{H}_2\text{O}_2$  activation by iron that leads to stereospecific olefin oxidation products. Investigate the structural and mechanistic differences that lead to the distinction between Class A and Class B catalytic behavior within this family of nonheme iron catalysts.

*Low temperature trapping and characterization of intermediates:* Use low temperature to prolong the lifetimes of reaction intermediates in order to be able to characterize such species with a variety of spectroscopic techniques (UV-Vis, EPR, Mössbauer, resonance Raman, XAS). Of interest are the oxidants (e.g.  $\text{Fe}^{\text{III}}\text{-OOH}$ ,  $\text{Fe}^{\text{V}}(\text{O})(\text{OH})$ ,  $\text{Fe}^{\text{III}}(\text{O}_2\text{C}(\text{O})\text{R})$  and  $\text{Fe}^{\text{IV}}(\text{O})(\bullet\text{OC}(\text{O})\text{R})$ ) postulated for our iron-catalyzed oxidation reactions.

#### 2013 Publications

1. Oloo, W.; Fielding, A. J.; Que, L., Jr., Rate Determining Water-Assisted O–O Bond Cleavage of a  $\text{Fe}^{\text{III}}\text{-OOH}$  Intermediate in a Bio-inspired Nonheme Iron-Catalyzed Oxidation, *J. Am. Chem. Soc.* **2013**, *135*, 6438-6441.
2. Wang, Y.; Janardanan, D.; Usharani, D.; Han, K.; Que, L., Jr.; Shaik, S., The Nonheme Iron Oxidant Formed in the Presence of  $\text{H}_2\text{O}_2$  and Acetic Acid Is the Cyclic Ferric-peracetate Complex and Not a Perferryl-oxo Complex, *ACS Catal.*, DOI: 10.1021/cs400134g.
3. Prat, I.; Company, A.; Postils, V.; Ribas, X.; Que, L., Jr.; Luis, J. M.; Costas, M., The Mechanism of Stereospecific C–H Oxidation by  $\text{Fe}(\text{Pytacn})$  Complexes: Bioinspired Non-Heme Iron Catalysts Containing *cis*-Labile Exchangeable Sites, *Chem. Eur. J.* DOI: 10.1002/chem.201300110.
4. Oloo, W.; Que, L., Jr., Bio-inspired Metal Catalysts for Hydrocarbon Oxidation, *Comprehensive Inorganic Chemistry*, 2<sup>nd</sup> ed.; Reedijk, J. & Poppelmeier, K., Eds.; Elsevier, Amsterdam, 2013, in press.



**Studies on Homogeneous Catalysis for Efficient Synthesis from Chemical Feedstocks**

Additional PIs: N/A  
Postdoc: Joseph Bair, Wenyong Chen  
Students: Christopher Hill, Christo Sevov  
Collaborators: none  
Contacts: University of California, Berkeley, 718 Latimer Hall MC# 1460, Berkeley, CA 94720-1460; [jhartwig@berkeley.edu](mailto:jhartwig@berkeley.edu)

**Goal**

To identify organometallic complexes that undergo insertions of alkenes into metal-heteroatom and metal-carbon bonds. This research focuses on new fundamental organometallic reactions of organometallic complexes and the translation of these reactions into new catalytic processes.

**DOE Interest**

The work we are conducting under DOE support will allow the direct conversion of alkene feedstocks to alcohols, ethers, amines and alkylarenes directly. Such processes will create a direct route to chemical feedstocks without any waste or side products. By eliminating steps of a synthetic sequence, waste and energy are reduced. In addition to addressing a synthetic goal, our studies will connect new catalyst structures with activity and reveal the mechanisms of new catalytic reactions.

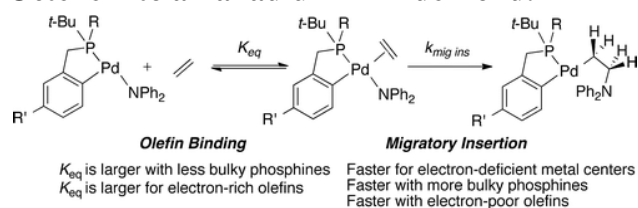
**Recent Progress****Publications (2010-2013)**

1. P. S. Hanley, D. Marković, J. F. Hartwig, "Intermolecular Insertion of Ethylene and Octene into a Palladium–Amide Bond. Spectroscopic Evidence for an Ethylene Amido Intermediate," *J. Am. Chem. Soc.* **132** (2010) 6302–6303.
2. P. S. Hanley, J. F. Hartwig, "Intermolecular Migratory Insertion of Unactivated Olefins into Palladium–Nitrogen Bonds. Steric and Electronic Effects on the Rate of Migratory Insertion," *J. Am. Chem. Soc.* **133** (2011) 15661-15673.
3. D. W. Robbins, J. F. Hartwig, "A Simple, Multidimensional Approach to High-Throughput Discovery of Catalytic Reactions," *Science* **333** (2011) 1423-1427.
4. C. S. Sevov, J. Zhou, J. F. Hartwig, "Iridium-Catalyzed Intermolecular Hydroamination of Unactivated Aliphatic Alkenes with Amides and Sulfonamides," *J. Am. Chem. Soc.* **134** (2012) 11960-11963.
5. C. S. Sevov, J. H. Hartwig, "Iridium-Catalyzed Intermolecular Asymmetric Hydroheteroarylation of Bicycloalkenes," *J. Am. Chem. Soc.* **135** (2013) 2116–2119.
6. C. S. Sevov, J. F. Hartwig, "Iridium-Catalyzed, Intermolecular Hydroetherification of Unactivated Aliphatic Alkenes with Aryl Alcohols," *J. Am. Chem. Soc.* (submitted).

Our work under DOE support has focused on the functionalization of alkenes, the fundamental organometallic chemistry involving the insertions of alkenes into metal-heteroatom bonds, and new approaches to the discovery of catalytic reactions. These studies have led to new classes of insertion reactions and rare examples of the additions of N-H and O-H bonds across unactivated and unstrained alkenes, particularly for late transition metal catalysts. This work has been extended recently to new classes of hydroarylations of alkenes giving rise to methods for the alkylation of both arenes and heteroarenes. We also showed the potential to discover new catalytic processes by analyzing reactions conducted with mixtures of reagents.

## 1. Intermolecular Insertion of Ethylene and Octene into a Palladium–Amide Bond.

We discovered examples of the insertion of completely unactivated alkenes, such as ethylene, into metal-heteroatom bonds. One of the best-characterized examples is the insertion of ethylene into a palladium-amido complex. We conducted a detailed examination of the effect of the steric and electronic properties of the ancillary ligand and the alkene reactant on the rate of migratory insertion of unactivated alkenes into the palladium-nitrogen bond of a series of isolated palladium amido complexes.

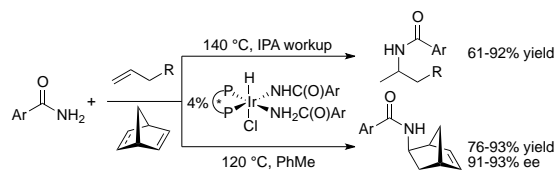


Amidopalladium complexes ligated by cyclometalated benzylphosphine ligands possessing varied steric and electronic properties were synthesized. A version of this complex lacking additional dative ligands react with ethylene at  $-50\text{ }^{\circ}\text{C}$  to form olefin-amido complexes that were observed directly. The olefin amido complex undergoes migratory insertion, followed by  $\beta$ -hydride elimination to generate enamine products.

Studies of the steric properties of the ancillary ligand on the binding of the alkene and the rate of migratory insertion showed that the binding affinity of ethylene vs THF is larger for the less sterically hindered complex than for the more hindered complex, but the less hindered complex undergoes the insertion of ethylene more slowly than does the more hindered complex. Studies on the electronic effects of the ancillary ligand showed that the more electron-poor complexes underwent the migratory insertion step faster than the more electron-rich complexes. Reactions with substituted vinylarenes showed that electron-poor vinylarenes reacted slightly faster than electron-rich vinylarenes. Separation of the energetics of binding and insertion indicate that the complex of an electron-rich vinylarene is more stable in this system than the complex of a more electron-poor vinylarene but that the insertion step of the bound, electron-rich vinylarene is slower than the insertion step with the bound, electron-poor vinylarene.

## 2. Iridium-Catalyzed Intermolecular Additions of Amides, Sulfonamides, and Phenols to Unactivated Aliphatic Alkenes

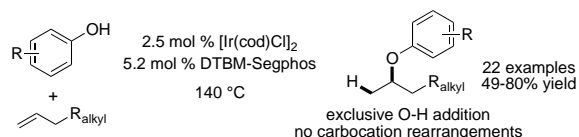
The intermolecular addition of N–H bonds to unactivated alkenes remains a challenging, but desirable, strategy for the synthesis of *N*-alkylamines. We discovered an example of the intermolecular addition of an amide N–H bond



across an unactivated alkene. The intermolecular amination of unactivated  $\alpha$ -olefins and bicycloalkenes with arylamides and sulfonamides generate protected amine products in high yield. Mechanistic studies on this rare catalytic reaction revealed a resting state that is the product of N–H bond oxidative addition and coordination of the amide. Rapid, reversible dissociation of the amide precedes reaction with the alkene, but an intramolecular, kinetically significant rearrangement of the species occurs before this reaction with alkene.

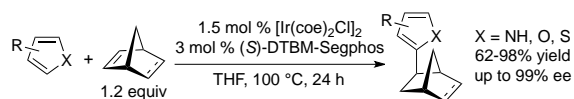
Brønsted acids catalyze the additions of aryl alcohols to alkenes, but these reactions form side products from isomerization of carbocationic intermediates and occur without control of stereochemistry of the product. In contrast, the metal-catalyzed addition of an O–H bond across an alkene could occur with regio-, chemo- and stereocontrol. However, most reported metal-catalyzed hydroetherifications of unsaturated C–C bonds are intramolecular and occur with carbon-carbon multiple bonds that are more reactive than those of unactivated alkenes.

We discovered a catalyst and conditions for the intermolecular additions of aryl alcohols to unactivated  $\alpha$ -olefins in good yields. The combination of  $[\text{Ir}(\text{COD})\text{Cl}]_2$  and the hindered, electron-rich aromatic bisphosphine Segphos catalyzed the additions of phenols to alkenes in good yields. The observation of measurable enantioselectivity shows that the iridium complex, not a proton, catalyzes the addition reaction. Mechanistic studies on this rare catalytic reaction imply that the reaction proceeds by generation an Ir(I) species from the allyl hydride resting states, reversible oxidative addition of the O–H bond of the aryl alcohol, turnover-limiting insertion of the alkene into the Ir–OAr bond and reductive elimination to form the C–H bond.



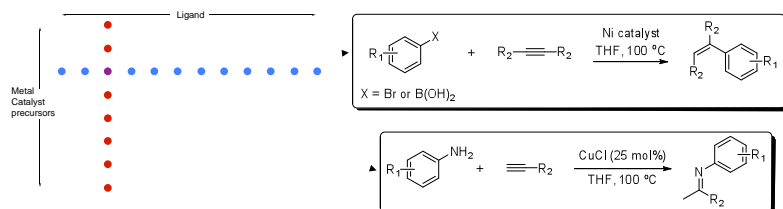
### 3. Iridium-Catalyzed Intermolecular Asymmetric Hydroheteroarylation of Bicycloalkenes

Catalytic hydroarylation of alkenes can occur under neutral conditions with regioselectivity that is complementary to that of acid-catalyzed reactions and stereoselectivity that is derived from the catalyst. We discovered intermolecular asymmetric additions of the C–H bonds of indoles, thiophenes, pyrroles, and furans to bicycloalkenes in high yield with high enantiomeric excess. These heteroarene alkylations occur ortho to the heteroatom. This selectivity is observed even with unprotected indoles, which typically undergo alkylation at the C3 position. Initial mechanistic studies revealed that oxidative addition of a heteroarene C–H bond to a neutral Ir<sup>I</sup> species occurs within minutes at room temperature and occurs in the catalytic cycle prior to the turnover-limiting step. Products from syn addition of the C–H bond across the olefin were observed.



### 4. A Simple, Multidimensional Approach to High-Throughput Discovery of Catalytic Reactions

High-throughput methods for the discovery of catalysts have been the focus of much attention. However, these methods have not been sufficiently general or accessible to typical synthetic laboratories to be adopted widely. We reported a method to evaluate a broad range of catalysts for potential coupling reactions with the use of simple laboratory equipment. Specifically, we assessed an array of catalysts and ligands with a diverse mixture of substrates and then used mass spectrometry to identify reaction products that, by design, exceed the mass of any single substrate. With this method, we discovered a copper-catalyzed alkyne hydroamination and two nickel-catalyzed hydroarylation reactions, each of which displays excellent functional-group tolerance.



#### Future Plans

We plan to continue to evaluate a range of catalysts, including enzymes, for the addition of X–H bonds to alkenes. Our goals include the discovery of additions of X–H bonds to internal alkenes to form linear alkylation products, additions to terminal alkenes without competitive isomerization of the alkene to the internal position, catalysts for additions of X–H bonds to alkenes at lower temperatures than are currently needed, and systems for alkene insertions into higher-valent metal-alkoxides and –amides than the complexes we have currently studied. We also plan to use high-throughput methods to identify new classes of catalysts and the scope of reactions catalyzed by complexes containing new classes of ligands.

This page is intentionally blank.

**Monday Morning**

**Session V**

This page is intentionally blank.

# Design of Polyoxometalate-Based Molecular Catalysts for Bridging the Gap between Homogeneous and Heterogeneous Catalysis

Noritaka Mizuno

Department of Applied Chemistry, School of Engineering, The University of Tokyo

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

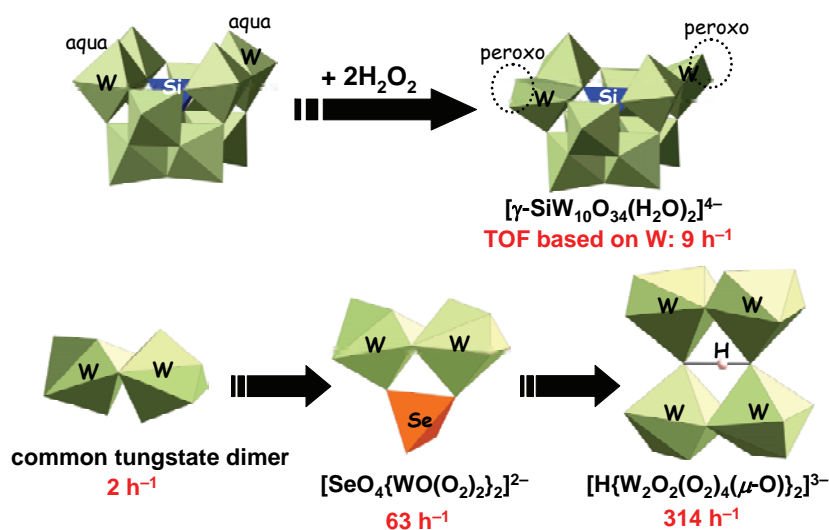
e-mail: tmizuno@mail.ecc.u-tokyo.ac.jp

In this presentation, our recent researches on molecular design of polyoxometalates (POMs) and their related compounds for environmentally-friendly functional group transformations are introduced and discussed. A divacant POM exhibits high catalytic performance for mono-oxygenation-type reactions including epoxidation, sulfoxidation, and hydroxylation with  $\text{H}_2\text{O}_2$ . We have successfully designed and synthesized several POM-based molecular catalysts (metal-substituted POMs) with controlled active sites by the introduction of metal species into the divacant POM as a “structural motif”. These molecular catalysts can efficiently activate various substrates as well as oxidants. In addition, we have developed POM-based “molecular heterogeneous catalysts” by the “solidification” and “immobilization” of catalytically active POMs. The details are below described.

## Design and Synthesis of Polyoxometalate-Based Molecular Catalysts

We have successfully synthesized a novel tetra-*n*-butylammonium (TBA) salt of a protonated divacant silicod decatungstate,  $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$  (**Figure 1**), which efficiently catalyzed mono-oxygenation-type reactions of various substrates including olefins, allylic alcohols, sulfides, and organosilanes using aq.  $\text{H}_2\text{O}_2$ . The high yields and efficiencies of  $\text{H}_2\text{O}_2$  utilization were achieved for epoxidation of various terminal, internal, and cyclic olefins (typically  $\geq 99\%$ ). In addition, we have also synthesized novel highly active peroxotungstate molecular catalysts. For example, a highly active protonated tetranuclear peroxotungstate,  $[\text{H}\{\text{W}_2\text{O}_2(\text{O}_2)_4(\mu\text{-O})\}_2]^{3-}$ , has been synthesized, which showed the highest catalytic activity for oxidation of olefins, allylic alcohols, sulfides, amines, and organosilanes using aq.  $\text{H}_2\text{O}_2$  (**Figure 1**).

By using lacunary POMs as “structural motifs”, we have synthesized several unique POM-based molecular catalysts (metal-substituted POMs) with controlled active sites by introducing metal cations (e.g., V, Fe, Cu, Mn, Ti, Zn, Al, Zr, Hf, lanthanoids) into the vacant sites. With regard to selective oxidation, we have successfully synthesized a divanadium-substituted phosphotungstate,  $[\gamma\text{-PW}_{10}\text{O}_{38}\text{V}_2(\mu\text{-OH})_2]^{3-}$ . This POM could act as an extremely active homogeneous catalyst for hydroxylation of alkanes and aromatics, epoxidation of alkenes including electron-deficient ones, oxidative bromination of alkenes, alkynes, and



**Figure 1.** Functionalization of tungstate-based catalysts for mono-oxygenation-type reactions with aq.  $\text{H}_2\text{O}_2$ .

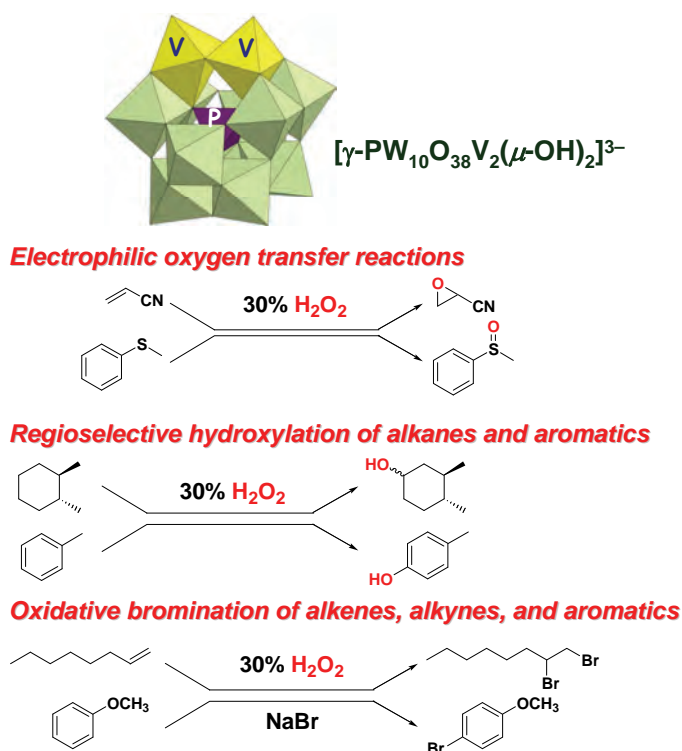
aromatics with  $\text{Br}^-$  as a bromo source, and oxidation of sulfides. In particular, the  $[\gamma\text{-PW}_{10}\text{O}_{38}\text{V}_2(\mu\text{-OH})_2]^{3-}$ -catalyzed chemo-, stereo- and regioselective hydroxylation of alkanes and aromatics are very significant (**Figure 2**).

Generally, metal-substituted POMs have been synthesized by the reaction of alkali-metal salts of lacunary POMs and the corresponding transition-metal salts in aqueous media, while the isomerization and decomposition of lacunary POMs sometimes proceeds in aqueous (acidic) media. We have developed new synthetic procedures for metal-substituted POMs in organic media using appropriate lacunary precursors, which can completely avoid the isomerization and decomposition

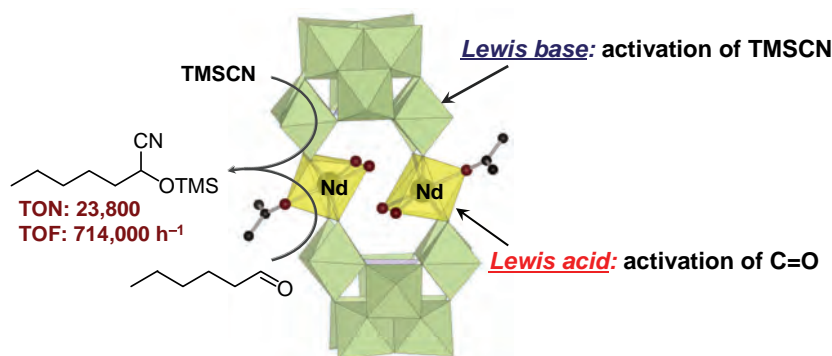
of the original lacunary frameworks. This finding made the design of well-defined active sites with POMs much easier, and various molecular catalysts, which are previously impossible to synthesize in aqueous media, have been synthesized.

The charges and sizes of POMs strongly affect the basicities of the oxygen atoms, and would increase with an increase in the charge densities (i.e., the negative charge per size). On the basis of this concept, we focused for the first time on the basic property of a monomeric tungstate,  $[\text{WO}_4]^{2-}$  that have a high charge density. Indeed,  $[\text{WO}_4]^{2-}$  could act as an efficient base catalyst for chemical fixation of  $\text{CO}_2$  to various substrates such as diamines, monoamines, aminonitriles, and propargylic alcohols, and the activities were the highest level among previously reported systems. We confirmed by various spectroscopic measurements and kinetics that both substrates and  $\text{CO}_2$  could be activated on the same  $[\text{WO}_4]^{2-}$  molecules. This bifunctionality of  $[\text{WO}_4]^{2-}$  is the reason for its high catalytic performance.

POMs anions have bare nucleophilic surfaces due to their external oxygen atoms, which can possibly act as Lewis base sites. In addition, various kinds of metal cations can be introduced into the POMs as Lewis acid sites. By combination of the two important features of POMs, he has designed highly active POM based Lewis acid-base catalysts, i.e., rare-earth-metal-containing POMs (rare-earth-metal



**Figure 2.**  $[\gamma\text{-PW}_{10}\text{O}_{38}\text{V}_2(\mu\text{-OH})_2]^{3-}$ , as an efficient oxidation catalyst with aq.  $\text{H}_2\text{O}_2$ .



**Figure 3.** Design of POM-based Lewis acid-base catalysts for cyanosilylation.

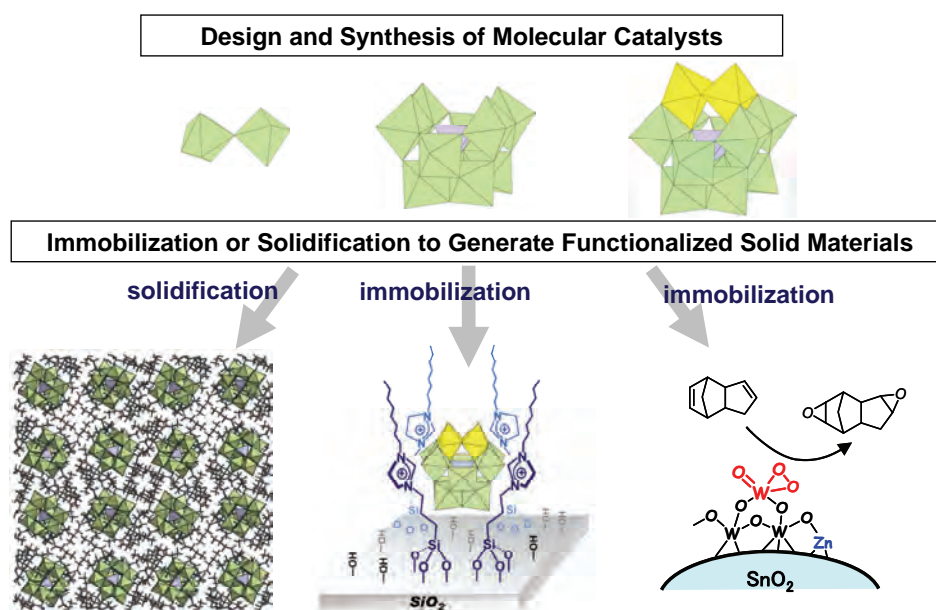


=  $Y^{3+}$ ,  $Nd^{3+}$ ,  $Eu^{3+}$ ,  $Gd^{3+}$ ,  $Tb^{3+}$ , or  $Dy^{3+}$ ). These POMs could easily be synthesized by the above-mentioned in-situ prepared strategy in organic solvents. For example, a neodymium-containing POM showed the remarkable catalytic performance for cyanosilylation of various kinds of structurally diverse ketones and aldehydes, and the turnover frequency ( $714,000\text{ h}^{-1}$ ) and the turnover number (23,800) for the cyanosilylation were of the highest level among those of previously reported catalysts. Both carbonyl compounds and trimethylsilylcyanide can be activated by the Lewis acid (metal cations) and the Lewis base (surface oxygen atoms), respectively, resulting in coexistence of activated coupling partners on the same POM molecules, resulting in acceleration of cyanosilylation (**Figure 3**).

### **Polyoxometalate-Based Molecular Heterogeneous Catalysts**

For the design of POM-based heterogeneous catalysts, we utilized two strategies, i.e., the “solidification” and “immobilization” of catalytically active POMs. The preparation procedures as well as properties of POM-based heterogeneous catalysts are much different from those of classical supported metal catalysts. In the POM-based heterogeneous catalysts, molecular (homogeneous) catalysts are heterogenized with retention of their controlled active sites at the molecular level, preserving the unique catalytic performance of homogeneous POMs by the heterogenization, thus so-called “molecular heterogeneous catalysts” (**Figure 4**).

With regard to “solidification”, we have found that the complexation of POMs with organometallic cations with appropriate charge, size, shape, and hydrophobicity lead to the formation of insoluble fine particles in any solvents. We also used alkali metal and alkyl ammonium cations for solidification of POMs. These



**Figure 4.** Our strategy to design highly active heterogeneous catalysts based on the properties of POMs (“molecular heterogeneous catalysts”).

catalysts have been utilized for the above-mentioned liquid-phase functional group transformations. In addition, we have designed novel anion-exchange materials such as surface-modified silica with ionic liquids and zinc-modified tin oxide for “immobilization” of POMs. Various kinds of POMs could be immobilized onto these supports. The catalytic activities of these molecular heterogeneous catalysts were almost the same as those of the corresponding homogeneous analogues. The catalyst/product separations were very easy, and the recovered catalysts could be reused for many times.

Furthermore, based on the above-mentioned knowledge of POM chemistry, we have successfully developed powerful heterogeneous catalysts (e.g., supported metal hydroxide catalysts) and several new reaction with them.

## References

1. K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, *Science* **300**, 964-966 (2003).
2. Y. Nakagawa, K. Kamata, M. Kotani, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **44**, 5136-5141 (2005).
3. K. Yamaguchi, C. Yoshida, S. Uchida, N. Mizuno, *J. Am. Chem. Soc.* **127**, 530-531 (2005).
4. K. Kamata, S. Yamaguchi, M. Kotani, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **47**, 2407-2410 (2008).
5. K. Kamata, Y. Nakagawa, K. Yamaguchi, N. Mizuno, *J. Am. Chem. Soc.* **130**, 15304-15310 (2008).
6. R. Ishimoto, K. Kamata, N. Mizuno, *Angew. Chem. Int. Ed.* **48**, 8900-8904 (2009).
7. Kamata, T. Hirano, S. Kuzuya, N. Mizuno, *J. Am. Chem. Soc.* **131**, 6997-7004 (2009).
8. N. Mizuno, S. Uchida, K. Kamata, R. Ishimoto, S. Nojima, K. Yonehara, Y. Sumida, *Angew. Chem. Int. Ed.* **49**, 9972-9976 (2010).
9. Y. Kikukawa, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **49**, 6096-6100 (2010).
10. K. Kamata, K. Yonehara, Y. Nakagawa, K. Uehara, N. Mizuno, *Nat. Chem.* **2**, 478-483 (2010).
11. K. Kamata, K. Yonehara, Y. Sumida, K. Hirata, S. Nojima, N. Mizuno, *Angew. Chem. Int. Ed.* **50**, 12062-12066 (2011)
12. K. Kamata, T. Yamaura, N. Mizuno, *Angew. Chem. Int. Ed.* **51**, 7275-7279 (2012)
13. T. Kimura, K. Kamata, N. Mizuno, *Angew. Chem. Int. Ed.* **51**, 6700-6703 (2012)
14. R. Ishimoto, K. Kamata, N. Mizuno, *Angew. Chem. Int. Ed.* **51**, 4662-4665 (2012)
15. T. Hirano, K. Uehara, K. Kamata, N. Mizuno, *J. Am. Chem. Soc.* **134**, 6425-6433 (2012).
16. Y. Kikukawa, K. Suzuki, M. Sugawa, T. Hirano, K. Kamata, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **51**, 3686-3690 (2012)
17. Y. Kikukawa, Y. Kuroda, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **51**, 2434-2437 (2012)

**Nanoconfinement Effects in Heterogeneous Catalysis**

Postdoc: Jung Kyoo Lee, Jingmei Shen  
Students: Michael Missaghi, John Galloway, Delrae Haag  
Collaborators: Mayfair C. Kung (Northwestern)  
Contacts: Northwestern University, Department of Chemical and Biological Engineering,  
Evanston, IL 60208; [hkiung@northwestern.edu](mailto:hkiung@northwestern.edu)

**Goal**

The goal is to develop synthetic strategy and techniques to form artificial catalytic structures that possess functionalities commonly found in enzymes, so as to capture and incorporate their desirable features into abiotic materials, such as cooperativity in a catalytic reaction.

**DOE Interest**

Understanding and demonstrating the feasibility of incorporating enzymatic functionalities into nonbiological systems, so that these systems can be superior to enzymes both in tolerance to process conditions and in ability to tailor the catalytic material to the reaction, could lead to achieving high reaction selectivity and significantly lower energy demand for purification and separation of products. It could result in development of novel catalysts superior to natural enzymes, improve process economics, and reduce environmental impact of chemical and energy conversion processes.

**Recent Progress**

*Precursor molecules for placement of discrete pairings of functional groups on a surface.*

We have successfully developed a new synthesis strategy for simultaneous grafting of discrete functional group pairings onto a surface. The strategy makes use of precursor molecules that possess an internal, easily cleavable silylester, or acyloxysilane, bond. Upon hydrolytic cleavage, this class of molecules would yield a carboxylic acid-organosilanol pairing in which the distance between the groups is a function of the starting compounds chosen and silica pretreatment method. Additionally, the organosilanol represents a highly versatile functional group that can readily undergo heterofunctional condensation with a chlorosilane to make new pairings. We demonstrated this strategy by synthesizing and characterizing precursors that lead to carboxylic acid/organosilanol, carboxylic acid/amine, carboxylic acid/pyridine, and carboxylic acid/phosphine pairings.

*Molecular-size nanocages*

We have developed a new method to synthesize nm-diameter nanocages, using spherosilicates as the core. The core is functionalized first with benzylallylmalonate via hydrosilylation, followed by deprotection of the acid groups and reaction with chlorotriethylsilane to render a core with peripheral vinyl groups. The vinyl groups can be shell-crossed linked with the linker 1,4-bis-dimethylsilylbenzene to result in a structure of core and shell that are linked by cleavable silylester bonds. Cleavage of the silylester bonds generates a bifunctional nanocage containing interior carboxylic acid and silanol groups.

The reactivity of the carboxylic acid groups was examined by their reaction with  $\text{Co}_2(\text{CO})_8$ . The carbonyl reacts readily, losing all CO except one, which is manifested by a singlet at  $1959\text{cm}^{-1}$  in IR. This position of the IR peak suggests the formation of a Co(I) species. This is unusual, and is likely a

consequence of the steric constraint and the limited carboxylate ligands available inside the nanocage. This is another example of unusual properties due to the nanocage environment.

### **Future Plans**

*Discrete pairings of functional groups on a surface:* Begin examining the catalytic consequences of pairing of functional groups.

*Molecular-size nanocages:* The properties of nanocages will be further examined by probing the properties of coordinated transition metal complexes. The chemical reactivity of the bound Co complexes will be examined with respect to their redox behavior and binding of oxygen. Their catalytic properties in oxidation reactions and hydroformylation reactions will be tested. Binding of other transition metal complexes, including Ru, Rh, and Pd complexes will be pursued.

### **Publications (2010-2012)**

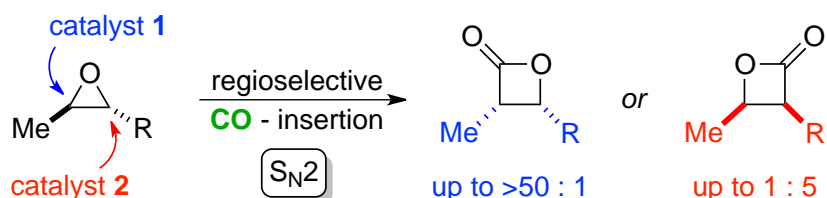
1. "Engineered Polymer for Controlled Metal Nanoparticle Synthesis," Baosong Fu, Michael N. Missaghi, Christopher M. Downing, Mayfair C. Kung, Harold H. Kung, Guomin Xiao, *Chem Mater.* 2010. **22**(7): p. 2181-2183.
2. "Isotope Labelling Study of CO Oxidation-Assisted Epoxidation of Propene. Implication on Oxygen Activation on Au Catalysts," Jian Jiang, Sean M. Oxford, Baosong Fu, Mayfair C. Kung, Harold H. Kung, Jiantai Ma, *Chem Commun.* 46 (2010) 3791 - 3793.
3. "Bis(pyridyl)siloxane-Pd(II) Complex Catalyzed Oxidation of Alcohol to Aldehyde: Effect of Ligand Tethering on Catalytic Activity and Deactivation Behavior," Michael N. Missaghi, John M. Galloway, and Harold H. Kung, *Applied Catalysis A: General*, **391** (2011) 297–304; 10.1016/j.apcata.2010.09.008.
4. "Bis(pyridyl)siloxane Oligomeric Ligands for Palladium(II) Acetate: Synthesis and Binding Properties," Michael N. Missaghi, John M. Galloway, and Harold H. Kung, *Organometallics*, **29** (2010) 3769-3779.
5. "Design and Synthesis of Readily Degradable Acyloxysilane Dendrimers," Christopher M. Downing, Michael N. Missaghi, Mayfair C. Kung, and Harold H. Kung, *Tetrahedron*, (2011), **67**(39), 7502-7509.
6. "Polysiloxanes in Catalysis and Catalyst Preparation: Opportunities for Control of Catalytic Processes," Michael N. Missaghi, Mayfair C. Kung, Harold H. Kung, *Topics in Catalysis*, 2012, **55**, 99-107.

**Development and Application of New Carbonylation Catalysts: Improvements in Regioselectivity, Stereoselectivity, Activity and Exploration of New Reactions**

Additional PIs: None  
 Postdoc: None  
 Students: Erin Dunn, Bryan Whiting, and Michael Mulzer  
 Contacts: Cornell University, Department of Chemistry, Baker Laboratory,  
 Ithaca, NY 14853, gc39@cornell.edu

The goal of this research project is the development of new catalysts for heterocycle carbonylation. The project focuses on three main objectives: 1) the development of a new generation of heterocycle carbonylation catalysts with improved activities and selectivities; 2) the application of heterocycle carbonylation catalysts to access high-value organic synthons and to synthesize monomers for unique polymer architectures; and 3) the study of the mechanisms of heterocycle carbonylation in a range of fundamentally new catalytic transformations.

Our current work is focused on the regioselective carbonylation of disubstituted epoxides. Two new catalysts have been discovered for the carbonylation of *trans*-1,2-disubstituted epoxides to *cis*- $\beta$ -lactones. The two catalysts display high and opposing regioselectivities, which unprecedented for this class of epoxides. The resulting  $\beta$ -lactones are well-defined precursors for a wide variety of aldol-type compounds. Altogether, carbonylation of disubstituted epoxides is established as a viable and economical entry into *syn*- and *anti*-aldol-type products.



### Recent Publications

- Chen, Q.; Mulzer, M.; Shi, P.; Beuning, P. J.; Coates, G. W.; O'Doherty, G. A. "De Novo Asymmetric Synthesis of Fridamycin E" *Org. Lett.* **2011**, *13*, 6592-6595.
- Liang, Y.; Hnatiuk, N.; Rowley, J. M.; Whiting, B. T.; Coates, G. W.; Rablen, P. R.; Morton, M.; Howell, A. R. "Access to Oxetane-Containing psico-Nucleosides from 2-Methyleneoxetanes: A Role for Neighboring Group Participation?" *J. Org. Chem.* **2011**, *76*, 9962-9974.
- Mulzer, M.; Coates, G. W. "A Catalytic Route to Ampakines and Their Derivatives" *Org. Lett.* **2011**, *13*, 1426-1428.

### Moving to Nonprecious Metal Catalysis

Postdoc: Jesus Campos

Student: Mike Manas, Liam Scheringhausen

Collaborators: Balcells (Oslo, computation). Brudvig, Johnson (Yale)

Contact: Yale Chemistry Dept., New Haven, CT, 06520-8107. [robert.crabtree@yale.edu](mailto:robert.crabtree@yale.edu)

#### Goal

Understanding how best to move from precious to nonprecious metal homogeneous catalysts.

#### DOE Interest

Understanding on how to move from our previous very active precious metal catalysts to nonprecious metals may contribute to resolving the widely recognized need to embrace nonprecious elements in catalysis in general. Beyond metallic elements, we now even have a lead case in Main Group catalysis.

#### Recent Progress<sup>1-31</sup>

*Main Group Catalysis* Transition metals (TMs) are more often catalysts than stoichiometric reagents, but the ratio is reversed for the Main Group (MG). We believe that MG catalysis may soon become much better recognized, not just for the classic Lewis Acid catalysis but also for reactions previously only subject to TM catalysis. For example, we showed that MG catalysis was possible for alcohol coupling.<sup>4</sup>

*Redox active ligands* Why are precious metals so good as catalysts? We assume that such metals tend to have 2e redox changes {Ir(I,III,V)} versus the 1e redox changes of the nonprecious TMs {Co(I,II,III)}, resulting in unstable substrate-derived radical intermediates. We are thus moving to redox-active ligands where the M and L each gain or lose 1e, for a total of 2e.<sup>24</sup>

*Outer Sphere Catalysis* An alternative way to avoid the 2e/1e problem mentioned above is to have a catalytic cycle in which there is no oxidation state change at all. Such is the case for Noyori-type outer sphere (OS) cycles. We now have a good OS arene hydrogenation example with Ir that we hope to generalize.<sup>13</sup>

*Nonprecious TMs* We already have some positive results in this area.<sup>3,21,30</sup>

*Mechanism* One of the hazards of working with TMs is the possibility of catalyst decomposition in which case the reaction may be catalyzed by nanoparticles (NPs). We have therefore applied sensitive techniques for solution and for electrochemical detection of NPs or catalyst heterogeneity in general.<sup>16,18</sup> In collaborative mechanistic work we have also applied computation extensively.<sup>3,10,13,21,25,27,31</sup>

*Advanced Physical Techniques* We have collaborated with Mark Johnson to see if his advanced MS techniques can detect catalytic intermediates in operando with promising but not yet decisive results.<sup>29</sup>

*Collaborative work* Our existing catalysts have also been widely requested by other research groups, resulting in numerous collaborative papers in related fields.<sup>19,21,22,23,25,26,29,30</sup> The DOE catalysis grant typically allowed catalyst design, synthesis and initial testing before passing the material to the collaborators.

## **Future Plans**

*Main Group* We have a MG hydrosilylation catalyst in development at present but the details of exactly what is doing the catalysis is still unclear.

*Nonprecious metals* We have a design and screening program in operation to look for OS transfer hydrogenation catalysts, but so far no striking results have emerged.

## **Impact of DOE catalysis program work**

Papers acknowledging the DOE catalysis program continue to be highly cited—636 times just for ones published in 2010-2012. DOE catalysis graduate student Schley won the prize for top 2012 Yale Chemistry thesis and went on to a Caltech postdoc.

## **Publications acknowledging the DOE catalysis grant. (2010-present)**

1. Dobereiner G, Crabtree RH, Dehydrogenation as a substrate-activating strategy in homogeneous transition metal catalysis, *Chem Rev*, 2010, 110, 681-703. [Special Issue on CH Activation ed. Crabtree RH]
2. Hull JF, Hilton ST, Crabtree RH, A Simple Ru Catalyst for the Conversion of Aldehydes or Oximes to Amides, *Inorg Chim Acta*, 2010, 363, 1243-5. [Invited paper for Dilworth Special Issue]
3. Hull, JF; Balcells, D; Sauer, ELO; Raynaud, C; Brudvig, GW; Crabtree, RH; Eisenstein, O, Manganese Catalysts for C-H activation: An Experimental/Theoretical Study Identifies the Stereoelectronic Factor that Controls the Switch between Hydroxylation and Desaturation Pathways, *J. Am. Chem. Soc.*, 2010, 132, 7605-7616.
4. Allen LJ, Crabtree RH, Green alcohol couplings without transition metal catalysts: base mediated  $\beta$ -alkylation of alcohols in aerobic conditions, *Green Chem*, 2010, 12, 1362-1364.
5. Dobereiner G, Crabtree RH, An Acyl Protection Strategy for Synthesis of a Protic NHC Complex via N-Acyl Methanolysis, *Organometallics*, 2010, 29, 5728-5731.
6. Zhou M, Schley ND, Crabtree RH, Cp\* Iridium Complexes Give Catalytic Alkane Hydroxylation with Retention of Stereochemistry, *J. Am. Chem. Soc.*, 2010, 132, 12550-12551.
7. Crabtree RH, Multifunctional Ligands in Transition Metal Catalysis (invited 'Focus' article), *New J Chem*, 2011, 35, 18-23. [Chosen for cover art; top 10 most accessed 5/12]
8. Blakemore JD, Schley ND, Olack G, Incarvito CD, Brudvig GW, Crabtree RH, Anodic Deposition of a Robust Iridium-Based Water-Oxidation Catalyst from Organometallic Precursors, *Chem. Sci*, 2011, 2, 94-98. [Highlighted in: TJ Meyer, *Nature Chem.*, 2011, 757-8.]
9. Crabtree RH, An Organometallic Future in Green and Energy Chemistry?, *Organometallics*, 2011, 30, 17-19.
10. Nova A, Balcells D, Schley ND, Dobereiner GE, Crabtree RH, Eisenstein O, An Experimental-Theoretical Study of the Factors that Affect the Switch between Ruthenium-Catalyzed Dehydrogenative Amide Formation versus Amine Alkylation, *Organometallics*, 2010, 29, 6548-6558.
11. Zhou M, Crabtree RH, C-H Oxidation by Platinum Group Metal Oxo or Peroxo Species” *Chem. Soc. Rev.*, 2011, 40, 1875 - 1884.

12. Brewster TP, Blakemore JD, Schley ND, Incarvito CD, Hazari N, Brudvig GW, Crabtree RH, An Iridium(IV) Species,  $[\text{Cp}^*\text{Ir}(\text{NHC})\text{Cl}]^+$ , Related to a Water-Oxidation Catalyst, *Organometallics*, 2011, 30, 965-973.
13. Dobereiner G, Nova A, Schley N, Hazari N, Miller S, Eisenstein O, Crabtree RH, Iridium-Catalyzed Hydrogenation of N-Heterocyclic Compounds under Mild Conditions by an Outer Sphere Pathway, *J. Am. Chem. Soc.*, 2011, 133, 7547-62.
14. Moore GF, Blakemore JD, Milot RL, Hull JF, Song H, Cai L, Schmuttenmaer CA, Crabtree RH, Brudvig GW, A Visible Light Water-Splitting Cell with a Photoanode formed by Codeposition of a High-Potential Porphyrin and an Iridium Water-Oxidation Catalyst, *EES*, 2011, 4, 2389-2392.
15. Schmeier TJ, Dobereiner GE, Crabtree RH, Hazari N, Secondary Coordination Sphere Interactions Facilitate the Insertion Step in an Iridium(III)  $\text{CO}_2$  Reduction Catalyst, *J Am Chem Soc*, 2011, 133, 9274-9277.
16. Schley ND, Blakemore JD, Subbaiyan NK, Incarvito CD, D'Souza F, Crabtree RH, Brudvig GW, Distinguishing Homogeneous from Heterogeneous Catalysis in Electrode-Driven Water Oxidation with Molecular Iridium Catalysts, *J Am Chem Soc*, 2011, 133, 10473-10481. [Highlighted in: TJ Meyer, *Nature Chem.*, 2011, 757-8.]
17. Schley N, Dobereiner G, Crabtree RH, Oxidative Synthesis of Amides and Pyrroles via Dehydrogenative Alcohol Oxidation by Ruthenium Diphosphine Diamine Complexes, *Organometallics*, 2011, 30, 4174-4179.
18. Crabtree RH, Resolving Heterogeneity Problems and Impurity Artefacts in Operationally Homogeneous Transition Metal Catalysts, *Chem Rev.*, 2012, 112, 1536-1554.
19. Brewster, T; Ding, W; Schley, N; Hazari, N; Batista, V; Crabtree, RH, Thiocyanate Linkage Isomerism in a Ruthenium Polypyridyl Complex, *Inorg. Chem.* 2011, 50, 11938-11946.
20. Zhou, M; Balcells, D; Parent, A; Crabtree, RH; Eisenstein, O,  $\text{Cp}^*$  Iridium Precatalysts for Selective C-H Oxidation via Direct Oxygen Insertion. A Joint Experimental/Computational Study, *ACS Catalysis*, 2012, 2, 208-218. [Chosen for cover art]
21. Guard LM, Palma JL, Stratton WP, Allen LJ, Brudvig GW, Crabtree RH, Batista VS, Hazari N, Synthesis and Computational Studies of Mg Complexes Supported by 2,2':6,2''-Terpyridine Ligands, *Dalton Trans*, 2012, 41, 8098-8110.
22. Vagnini MT, Smeigh AL, Blakemore JD, Eaton SW, Crabtree RH, Brudvig GW, Co DT, and Wasielewski MR, Ultrafast Photodriven Intramolecular Electron Transfer from an Iridium-Based Water-Oxidation Catalyst to Perylene Diimide Derivatives, *Proc Nat Acad Sci USA*, 2012, 109, 15651-6.
23. Blakemore JD, Schley ND, Kushner-Lenhoff MN, Winter AM, D'Souza F, Crabtree RH, Brudvig GW, Comparison of Amorphous Iridium Water-Oxidation Electrocatalysts Prepared from Soluble Precursors, *Inorg Chem*, 2012, 51, 7749-7763.
24. Luca OR, Crabtree, RH, Redox active ligands in catalysis, *Chem. Soc. Rev.*, 2013, 42, 1440 – 1459 (Invited for Werner Special Issue).
25. Dobereiner G, Wu J, Manas M, Schley ND, Takase M, Crabtree RH, Hazari N, Maseras F, Nova A, Mild, Reversible Reaction of Iridium(III) Amido Complexes with Carbon Dioxide, *Inorg. Chem.*, 2012, 51, 9683-9693.
26. Graeupner J, Brewster TP, Blakemore JD, Schley ND, Thomsen JM, Brudvig GW, Hazari N, Crabtree RH, Preparation of Electron-Rich  $\text{CpIr}(\text{biphenyl-2,2'-diyl})$  Complexes with  $\pi$  Accepting Carbon Donor Ligands, *Organometallics*, 2012, 31, 7158-7164.
27. Eisenstein O, Crabtree RH, Outer Sphere Hydrogenation Catalysis, *New J Chem*, 2013, 37, 21-27 (Invited Focus article).
28. Crabtree RH, Abnormal, Mesoionic and Remote N-Heterocyclic Carbene Complexes, *Coord. Chem. Rev.*, 2013, 257, 755-766.
29. Garand, E, Fournier, JA, Kamrath, MZ, Schley, ND, Crabtree, RH, Johnson, MA, Characterization of an activated iridium water splitting catalyst using infrared photodissociation of  $\text{H}_2$ -tagged ions, *Phys Chem Chem Phys*, 2012, 14, 10109-10113.
30. Blakemore, JD, Hull, JF, Crabtree, RH, Brudvig, GW, Aqueous speciation and electrochemical properties of a water-soluble manganese phthalocyanine complex, *Dalton Trans*, 2012, 41, 7681-7688.
31. Schley ND, Halbert S, Raynaud C, Eisenstein O, Crabtree RH, Symmetrical Hydrogen Bonds in Iridium(III) Alkoxides with Relevance to Outer Sphere Hydrogen Transfer, *Inorg. Chem.*, 2013, 42, 3617.



**Monday Afternoon**

**Session VI**

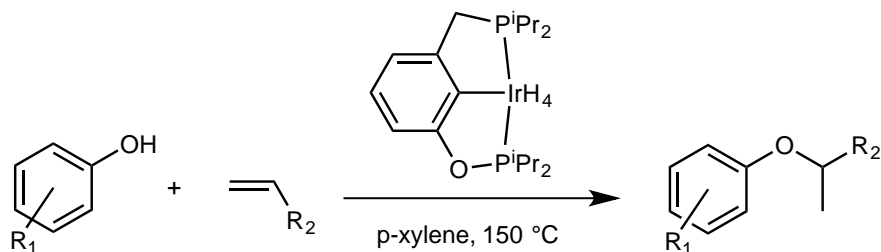
This page is intentionally blank.

## Addition of O-H Bonds to Olefins Catalyzed by Pincer-Iridium Complexes

Michael C. Haibach, David Y. Wang, Changjian Guan, Karsten Krogh-Jespersen and Alan S. Goldman\*

Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, USA

We have reported that alkyl aryl ethers (e.g. EtOAr) react with precursors of the pincer-iridium fragment (<sup>t</sup>BuPCP)Ir (2 mol) to give (<sup>t</sup>BuPCP)Ir(H)(OAr) plus olefin complex, e.g. (<sup>t</sup>BuPCP)Ir(C<sub>2</sub>H<sub>4</sub>).<sup>1</sup> This may be viewed as a dehydroaryloxylation of the ether, thermodynamically driven by the binding of the alcohol and olefin products to the iridium fragment. We elucidated the mechanism of this reaction and considered the possibility that the same reaction steps, in reverse, could be applicable toward catalytic olefin hydroaryloxylation. Although (<sup>t</sup>BuPCP)Ir did not prove to be an effective catalyst, less sterically hindered analogs, e.g. <sup>i</sup>PrPCP, were indeed found to catalyze the addition of phenolic O-H bonds across the double bond of propene and other unactivated olefins. Mechanistic studies in tandem with DFT calculations offer evidence for a pathway proceeding via O-H addition to the iridium center and insertion of olefin into the Ir-OAr bond, followed by C-H elimination; the latter step is, surprisingly, rate-determining. This is the first example of intermolecular O-H addition to a simple olefin bond catalyzed by a well defined “organometallic” mechanism. In particular many transition metals reported to catalyze O-H addition have been shown to act simply by generating Bronsted acids (“hidden acid” mechanism); the pincer-iridium catalysts show regio- and chemo-selectivity very different from these or other acid-based systems. We are currently developing related catalysts that are more active, and exploring the generality of this reaction, particularly with respect to addition of other O-H bonds including that of water. We are also attempting to develop enantioselective catalyses for the ArO-H or related additions.



(1) (a) Choi, J.; Choliy, Y.; Zhang, X.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2009**, *131*, 15627. (b) Kundu, S.; Choi, J.; Wang, D. Y.; Choliy, Y.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2013**, *135*, 5127-5143

## Developing S-block Element Catalysis and New Chemical Transformations

Malcolm H. Chisholm

The Ohio State University, Department of Chemistry and Biochemistry, Columbus, OH 43210

e-mail: [Chisholm.4@osu.edu](mailto:Chisholm.4@osu.edu)

Aside from studies of metal (III) porphyrin complex ( $M=Al, Cr$  or  $Co$ ) in their ability to ring-open and polymerize epoxides and copolymerize epoxides and carbon dioxide, the major thrust of our DOE supported research is in the development of S-block element catalysis and new chemical transformations. Of the group 2 elements, only magnesium has had a significant role in organic synthesis. Indeed, organomagnesium chemistry as exemplified by the Grignard reagent continue to be an area of active research as can be seen by Knochel's development of Turbo-Grignard reagents and Mulvey's development of unprecedented C-H activating systems. To a first order approximation these group 2 elements (excepting Be) do not form covalent bonds: their interactions with ligands are largely electrostatic. They lack well defined directed valency and coordination numbers. Consequently their ions are kinetically labile and coordination numbers and geometries are largely determined by ligand imposed steric factors. In this talk, I will emphasize our use of chelating ligands, particularly  $\beta$ -ketoiminates, dipyrromethenes, and tris-pyrazolylborate ligands, to control the reactivities of these metal centers, notably  $Mg^{2+}$  and  $Ca^{2+}$ . The  $LMgX(THF)$  complexes,  $L = \beta$ -diketoiminate and  $X = Bu^n, NEt_2$  and  $OBu^t$  contain 4-coordinate metal centers and are amongst the most kinetically active single-site catalyst precursors for the ROP of CL ( $k_p = 110m^{-1}s^{-1}$  @  $25^\circ C$ ), and LA ( $k_p = 10.7 M^{-1}s^{-1}$  @  $25^\circ C$ ). When  $X=NEt_2$  or  $OBu^t$  the polymers formed have these groups as end groups consistent with initial attack by X on the ketonic carbon of the monomer. However, for  $Bu^n$  the ring-opening event occurs via a  $\beta$ -H transfer leading 1-butene and polymers of the form H-(PCL)-OH and H-(PLA)-OH upon work up and after quenching with acidic  $H_2O$ .  $LMgBu^n(THF)$  reacts similarly with aldehydes and ketones via H transfer.  $LMgX(THF)$  convert rac-LA to atactic PLA in  $CH_2Cl_2$  or toluene but with added THF the heterotactic PLA containing *isi/sis* tetrads is formed and in neat THF the sequential enchainment of *L*-LA by *D*-LA and vice versa is greater than 95%. The role of THF in the transition-state involving the ring-opening event is clearly implicated and dynamic NMR studies of  $LMgX(THF)$  in toluene- $d_8$  with added THF show that THF exchange occurs by both a dissociative and an associative process when  $X = Bu^n$  and  $OBu^t$  but when  $X = NEt_2$  only a dissociative process is involved. Even though the ROP of CL is 10 times faster than that of LA the presence of LA shuts down the former: only ROP of LA occurs when the two are present. This can be traced to the chelating effect of the lactide polymer during chain growth and the compound  $LMg(OCHMe_2 COEt)$  (THF) models this phenomenon. Bidentrate chelating ligands are not sufficient to suppress ligand scrambling for the larger  $Ca^{2+}$  ion; nor are  $k^3$ -N bulky tris-pyrazolylborates but the use of these ligands with ether appendages that can bind as  $k^3$ -N, $k^3$ -O lead to 7-coordinate calcium alkoxides that are capable of ROP of cyclic esters. The fascinating coordination chemistry of these ligands will also be described.

**Fundamental Understanding and Control of Selectivity and Deactivation in Biomass Conversion Catalysts**

Additional PIs: members of the Institute for Atom-efficient Chemical Transformations-IACT  
Postdocs: Hongbo Zhang and Dongxia Liu  
Contacts: Argonne National Laboratory, Chemical Sciences and Engineering Division,  
Argonne, IL 60439; marshall@anl.gov

**Goal**

Develop a fundamental understanding of the modes of deactivation of biomass conversion catalysts and develop a method for lowering the deactivation rate. In this study, we examine deactivation mechanisms of the copper chromite catalyst for selective hydrogenation of furfural to furfuryl alcohol in vapor phase. In situ X-ray Absorption Fine Structure (XAFS) was used to monitor the active copper oxidation states under reaction conditions. X-ray Photoelectron Spectroscopy (XPS) was used to identify the surface composition as well as the oxidation state. Metallic Cu particle size after different pretreatment/reaction conditions was also examined by XAFS.

**DOE Interest**

Argonne National Laboratory along with its academic partners has established an Energy Frontier Research Center (EFRC), the Institute for Atom-efficient Chemical Transformations (IACT), whose focus is to advance the science of catalysis for the efficient conversion of energy resources into usable forms. IACT is a partnership among world-class scientists at Argonne National Laboratory, Brookhaven National Laboratory, Northwestern University, University of Wisconsin-Madison, and Purdue University. Using a multidisciplinary approach involving integrated catalyst synthesis, advanced characterization, catalytic experimentation, and computation, IACT is addressing key chemistries associated with clean, efficient utilization of the two main chemical energy resources in the United States, namely, biomass. We have identified the efficient removal of oxygen from biomass, as well as the hydrogenation of these systems, as key chemistries and unifying themes for IACT.

**Recent Progress**

Reaction kinetics data were collected under various conditions during vapor-phase hydrogenation of furfural. Selectivity to furfuryl alcohol decreases as a function of conversion level under standard conditions. The overall catalyst activity is highly dependent upon the catalyst pretreatment condition, which strongly affects the deactivation rate.

Several possible deactivation mechanisms have been proposed in the open literature including (a) loss of the active Cu (I) species by reduction, (b) Cu particle sintering, and (c) active Cu site coverage by coke or adsorbed reactants/products. Cu sites may also be covered due to metal migration in bimetallic or alloy catalysts cases. Based on in situ XAFS experiments (Table 1) we conclude that the copper is fully reduced to the metallic state at 200 °C in H<sub>2</sub> and remains zero valent under reaction conditions; no Cu oxide species were detected. X-ray excited spectroscopy (AES) data confirmed the existence of Cu (0) species as

the major surface component (94%) in the reduced sample. Only negligible amounts of Cu (I) and Cu (II) are possible within the experimental error. We therefore believe that Cu (0) is the primary active component for furfural hydrogenation and loss of active Cu (I) species is not the cause of deactivation of copper chromite.

The EXAFS spectrum shows that there is no difference in the catalyst particle size. Average Cu particle sizes are about 6 nm in both the fresh and used catalysts. Therefore, sintering does not appear to be the cause of deactivation (Table 1). The small difference is within the experimental error of the XAFS technique. The reaction temperature was 200 °C, which was relatively low for Cu sintering.

This work shows that catalyst poisoning is due to the adsorption of species derived from furfural and furfuryl alcohol are one of the dominant causes for deactivation when operated at 200 °C, as indicated by XPS data of fresh and used catalysts. In contrast, loss of active Cu (I) sites due to hydrogenation can be ruled out based on in situ XAFS results, which shows that metallic Cu is the active component for the reaction and copper is maintained in the metallic state throughout the process. Cu particle sintering is not a cause for deactivation due the relatively low reaction temperature, as proved by in situ XAFS experiments.

<b>Table 1</b> EXAFS fit of copper chromite after ex situ reduction (200 °C & 300 °C) and fresh and used catalysts ( <i>in situ</i> ).				
	$N_{\text{Cu-Cu}}$ ( $\pm 1$ )	R (Å)	Cu part. size (nm)	Oxidation state
<b><i>Ex situ</i> experiments</b>				
Ex situ (red) 200 °C	10.0	2.54	5.5	Cu <sup>0</sup>
Ex situ (red) 300 °C	9.7	2.55	5.0	Cu <sup>0</sup>
<b><i>In situ</i> experiments</b>				
Fresh	10.0	2.53	5.5	Cu <sup>0</sup>
Used	10.6	2.53	6.3	Cu <sup>0</sup>

## Future Plans

Recent work has shown that the use of ALD overcoating can reduce the rate of deactivation and change the mechanisms of some catalytic reactions. Early work has shown that adding 45 cycles of ALD Al<sub>2</sub>O<sub>3</sub> can dramatically decrease the rate of deactivation while increasing the catalyst selectivity. This promising lead will be further examined in the near future.

## Publications

1. Liu, D.; Zemlyanov, D.; Wu, T.; Lobo-Lapidus, R.; Dumesic, J. A.; Miller, J. T.; and Marshall, C. L.; “Deactivation Mechanistic Studies of Copper Chromite Catalyst for Selective Hydrogenation of 2-Furfuraldehyde,” *J. Catal.*, 2013, 299, 336–345.

## Catalytic Conversion of Glucose and Cellulose into HMF and Subsequent Upgrading to Value-Added Chemicals and Liquid Fuels

**Postdocs:** Yuetao Zhang, Jianghua He  
**Students:** DJ Liu, Eric Dunn  
**Collaborators:** Prof. Zixiang Wang (Graduate University of Chinese Academy of Sciences, DFT calculations on biomass catalysis)  
**Contact:** Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872; [eugene.chen@colostate.edu](mailto:eugene.chen@colostate.edu)

### Goal

Seek a fundamental understanding of the catalytic cellulosic biomass conversion into 5-hydroxymethylfurfural (HMF), a biorefining building block and platform chemical, under mild and homogeneous conditions, and apply the knowledge gained from this study to develop more efficient, selective, environmentally benign, and cost-effective catalyst systems for biomass conversion and upgrading to value-added chemicals and liquid fuels.

### DOE Interest

This project addresses one of the DOE-BES's priority research directions for advancing catalysis sciences: "*understanding the chemistry of lignocellulosic biomass deconstruction and conversion to fuels*". As cellulosic material is the most abundant renewable biomass resource on Earth, it can potentially meet our future renewable energy needs if it can be efficiently converted into platform chemicals and fuels in a technologically and economically competitive fashion, compared to traditional oil refineries. The project's central goal is well aligned with the DOE-BES missions. The DOE's *Catalysis Science* program states that "Particular emphasis is placed on catalysis relevant to the conversion and use of fossil and renewable energy resources and the creation of advanced chemicals...Catalysts are crucial to creating new, energy-efficient routes for the production of basic chemical feedstocks and value-added chemicals. In the immediate future...New strategies for design of selective catalysts for fuel production from both fossil and renewable biomass feedstocks will be explored."

### Recent Progress

*Recyclable polymeric ionic liquid (PIL)-based metal catalysts:* Chromium and aluminum catalysts can be readily supported on PILs to generate recyclable PIL-supported catalysts for effective biomass (glucose or cellulose) conversion into HMF.

*Ubiquitous aluminum alkyl or alkoxy compounds as effective biomass conversion catalysts:* Simple trialkyl and trialkoxy aluminum species, which cost only a fraction (~1%) of the current benchmark catalyst  $\text{CrCl}_2$ , are as effective as  $\text{CrCl}_2$  under the same conditions employed to catalyze the glucose-to-HMF conversion in ionic liquids (ILs).

*Metal(0) nanoparticle (NP) catalysts:* Chromium(0) nanoparticles, Cr(0)-NPs, derived from the zero-valent chromium molecular precursor  $\text{Cr}(\text{CO})_6$ , are highly effective catalysts for the conversion of glucose into HMF in ILs under mild conditions.

*Discrete molecular catalysts:* Several discrete chromium and lanthanide molecular complexes incorporating N-heterocyclic carbene (NHC) ligands have been investigated as potential molecular catalysts for biomass conversion in ILs and the role of NHC ligands as a catalyst poison has been elucidated.

*Organocatalytic coupling of HMF:* A highly selective (98%) and 100% atom-economical catalytic process by a catalytic IL or an NHC has been developed for upgrading of HMF to a promising C<sub>12</sub> kerosene/jet fuel intermediate, 5,5'-di(hydroxymethyl)furoin (DHMF).

*Upgrading of biomass furaldehydes to diesel and premium alkane fuels:* A combination of solvent-free organocatalysis and metal-acid tandem catalysis in water leads to a highly effective new strategy for upgrading bio-derived furaldehydes to value-added chemicals, oxygenated diesel, and high-quality C<sub>10-12</sub> linear alkane jet fuels.

### Future Plans

Future studies will include the development of cost-effective and recyclable catalysts for selective upgrading of biomass furaldehydes into C<sub>10</sub>–C<sub>12</sub> furoin intermediates as well as transformation of such intermediates into value-added chemicals or sustainable materials such as polyols, polyurethanes, and polyesters, as well as oxygenated diesel and high-quality linear alkane fuels.

### Publications (2010–2013)

1. He, J.; Zhang, Y.; Chen, E. Y.-X. "Chromium(0) Nanoparticles as Effective Catalyst for the Conversion of Glucose into 5-Hydroxymethylfurfural", *ChemSusChem* **2013**, *6*, 61–64.
2. Liu, D.; Chen, E. Y.-X. "Polymeric Ionic Liquid (PIL)-Supported Recyclable Catalysts for Biomass Conversion into HMF", *Biomass & Bioenergy*. **2013**, *48*, 181–190.
3. Dunn, E. F.; D. Liu; Chen, E. Y.-X. "Role of N-Heterocyclic Carbenes in Glucose Conversion into HMF by Cr Catalysts in Ionic Liquids", *Appl. Catal. A: Gen.* **2013**, in press.
4. D. Liu; Chen, E. Y.-X. "Upgrading Biomass Furaldehydes to Diesel and Premium Alkane Fuels by Solvent-Free Organocatalytic Coupling and Metal-Acid Tandem Catalysis", **2013**, manuscript under review.
5. Nakarit, C.; Kelland, M. A.; Liu, D.; Chen, E. Y.-X. "The Effect on Structure II Kinetic Hydrate Inhibitor Performance of Incorporating Synergist-Related Cationic Monomers into N-Vinyl Lactam Copolymers", **2013**, manuscript under review.
6. Liu, D.; Zhang, Y.; Chen, E. Y.-X. "Organocatalytic Upgrading of the Key Biorefining Building Block by a Catalytic Ionic Liquid and N-heterocyclic Carbenes", *Green Chem.* **2012**, *14*, 2738–2746 (cover article).
7. Liu, D.; Chen, E. Y.-X. "Ubiquitous Aluminum Alkyls and Alkoxides as Effective Catalysts for Glucose to HMF Conversion in Ionic Liquids", *Appl. Catal. A: Gen.* **2012**, *435/436*, 78–85.
8. Zhang, Y., Du, H.; Qian, X.; Chen, E. Y.-X. "Ionic Liquid–Water Mixtures: Enhanced  $K_w$  for Efficient Cellulosic Biomass Conversion", *Energy & Fuels* **2010**, *24*, 2410–2417.



## Selective Catalytic Dehydration and Hydrodeoxygenation Reactions for the Production of Fuels and Chemicals from Biomass

Additional co-PIs: Paul Dauenhauer, Wei Fan and Dionisios Vlachos

Postdoc: Jung Ho Jae, Phong Do

Students: Eyas Mahmoud, Williams Luke

Contact: Catalysis Center for Energy Innovation, Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, lobo@udel.edu

The reduction of the oxygen content of biomass-derived molecules is an essential step towards upgrading these molecules into blend-ready fuel additives and 'green' chemicals. These reactions can be difficult to accomplish selectively as biomass-derived molecules often have multiple and chemically similar oxygen-containing groups. Generally it is also not desired to remove all oxygen groups as the products (alkanes) have low commercial value other than their energy content. In this talk I will discuss four different approaches to accomplish the hydrodeoxygenation of biomass-derived oxygenates. The first two examples are the hydrodeoxygenation of m-cresol with hydrogen gas [1] and the hydrodeoxygenation of furfural using the propanol-to-acetone reaction as a source of hydrogen atoms.[2] Both processes rely on the use of bifunctional catalysts that make possible a new fast reaction channel that combines hydrogenation and dehydration steps to form the final product. The use of a 'liquid' source of hydrogen atoms such as propanol allows for a more controllable one-phase reaction system and relatively low temperatures. We will discuss the optimization of the catalysts properties to achieve both high selectivity and acceptable rates of reaction. The two other examples take advantage of the Diels-Alder reaction to form intermediates that can be transformed into useful aromatic molecules. First we will look at the formation of p-xylene by the addition of ethylene to dimethylfurfural and investigate the network of reactions that control the selectivity of the overall reaction and how to control reaction conditions to maximize the yield.[3] Finally, we will study the synthesis of phthalic anhydride by the dehydration of the Diels-Alder adduct of furan and maleic anhydride. Because this Diels-Alder reaction is exothermic and reversible, and effective catalyst has to operate at low temperatures otherwise the adduct will decompose before the dehydration reaction can take place. We found that mixed anhydrides (acetic and methylsulphonate) are very effective at opening the oxo-bridge of the Diels-Alder adduct, avoiding the retro-Diels-Alder reaction and producing phthalic anhydride in high yields. Other opportunities to apply this chemistry to other furans derived from biomass will be discussed.

### References:

1. Foster, A. J.; Do, P. T. M.; Lobo, R. F. *Topics in Catalysis* **2012**, 55, 118.
2. Jae, J., Zhen W., Lobo R.F. and Vlachos, D.G., *ChemSusChem*, submitted.
3. Do, P.T.M., McAtee, J.R., Watson, D.A., Lobo, R.F., *ACS Cat.*, **2013**, 3, 41-46.

This page is intentionally blank.

**Monday Evening**

**Session VII**

This page is intentionally blank.

**Understanding elementary steps of catalytic conversions in water to achieve complex transformations**

Lead PI: Johannes A. Lercher  
Co-PI's: Yong Wang, Donald Camaioni, and Donghai Mei  
Contact: Institute for Integrated Catalysis, Pacific Northwest National Laboratory,  
P.O. Box 999, K2-12, Richland, WA 99352; [johannes.lercher@pnnl.gov](mailto:johannes.lercher@pnnl.gov)

The chemical instability of the constituents of deconstructed lignocellulose requires conducting hydrodeoxygenation and the reactions to cleave and form C-C bonds in an aqueous environment. Water influences not only the mode of adsorption and stabilization of the reactants and products on the catalysts; it also influences the transition state. Inevitably, the presence of water may also chemically modify the surface and potentially also the bulk of the catalytic phase. The lecture describes how the state of the catalyst elements and the individual reaction steps are being investigated and how the information can be used to design and synthesize catalysts that allow complex multistep transformations.

Two catalytic functions dominate the liquid/solid/gas reactions, i.e., the metal function, responsible for hydrogenation/dehydrogenation, hydrogenolysis and hydrolysis and the acid function catalyzing dehydration, isomerization, alkylation, oligomerization as well as decarbonylation/decarboxylation. In addition to analyzing the reaction kinetics under steady state and transient conditions, the metal catalyst properties and its influence on the interaction with the reactants is studied under reaction conditions using in situ X-ray absorption and molecular spectroscopy in order to better understand the nature of the catalytically active sites, the conversions of the molecules as well as irreversible changes to the catalyst. Acid base reactions of alcohols in zeolites are analyzed in the presence and absence of water. It will be discussed, how the competition of molecules and water for acid sites influences rates and selectivities inducing positive and negative effects for the targeted catalytic reactions leading eventually to the controlled conversion of lignocellulose. It will be shown how the properties of the individual steps can be adjusted so that the desired selectivity is combined with higher catalyst stability.

### Photo-Catalysis on Plasmonic Metal Nanoparticles

Department of Chemical Engineering, University of Michigan  
(email: linic@umich.edu)

Metals are used as catalysts for many chemical transformations, including ammonia synthesis, hydrocarbon reforming, oxidation, hydrogenation, etc. All these reactions are triggered by coupling of metal nanoparticle phonon modes (excited by thermal heating of the metal) with adsorbates, which results in the evolution of the adsorbate from the reactant to the product state on the ground state potential energy surface. As such, these reactions usually require high temperature and due to the untargeted nature of bond activation they are not very selective towards targeted products. These reactions can be modeled very well with classical transition state theory.

An alternative way to activate chemical reactions on metal surfaces is to use energetic electrons, which can scatter through unpopulated adsorbate states, inducing forces on atoms and resulting in chemical transformations. This electron-mediated mechanism of bond activation was elucidated in experiments that involved extended surfaces of metal single crystals illuminated by short pulses of high intensity light (ie, lasers at intensity  $\sim 10^9$  times higher than the intensity of solar flux). While this electron-driven process offers a number of advantage compared to the phonon mediated mechanism (specific chemical bonds can be selectively targeted by the energy of electrons), the required use of high intensity light made this process of bond activation irrelevant from the practical application perspective.

We showed recently that nanoparticles of noble metals (plasmonic nanoparticles) can activate electron-driven chemical reactions even when illuminated with low intensity light.(1) Plasmonic metallic nanostructures (Ag, Au, and Cu are of particular interest) are characterized by their strong resonant interaction with UV-vis light through the excitation of localized surface plasmon resonance (LSPR).(2,3) LSPR results in strong, spatially non-homogeneous oscillating electric fields in the neighborhood of the nanostructure. These fields are several orders of magnitude larger than the field associated with the incoming photon flux, i.e., the electro-magnetic energy of UV-vis radiation is concentrated in very small volumes (essentially the surface of the nanostructure).(2,3) It is this high local field that increases the absorption cross-section of the nanostructures of these metals compared to extended surfaces.

I will discuss our findings with particular emphasis on critical experimental signatures of these reactions and the molecular models used to explain the chemical transformations.(4) I will outline the main advantages associated with these electron-mediated photo-chemical reactions on metals in a case study focusing on the development of solid, silver-based catalysts for epoxidation or propylene to form propylene oxide.(5)

1. P. Christopher, H. Xin, S. Linic, "Visible light enhanced catalytic oxidation reactions on plasmonic silver nanostructures", **Nature Chemistry**, 3, 467, 2011.
2. D. B. Ingram, S. Linic, "Water splitting on composite plasmonic-metal/semiconductor photo-electrodes: Evidence for selective plasmon induced formation of charge carriers near the semiconductor surface", **Journal of the American Chemical Society**, 133, 5202, 2011
3. S. Linic, P. Christopher, D. B. Ingram, "Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy", **Nature Materials**, 10, 911, 2011.
4. P. Christopher, H. Xin, M. Andiappan, S. Linic, "Singular characteristics and unique chemical bond activation mechanisms of photocatalytic reactions on plasmonic nanostructures", **Nature Materials**, 11, 1044–1050, 2012
5. M. Andiappan, S. Linic, "Tuning selectivity in propylene epoxidation by plasmon mediated photo-switching of Cu oxidation state", **Science**, 339, 1590, 2013

## Theoretical Investigation of Heterogeneous Catalysis at the Solid-Liquid Interface for the Conversion of Lignocellulosic Biomass Model Molecules

Postdoc: Jianmin Lu  
Students: Muhammad Faheem  
Contacts: University of South Carolina, 301 S. Main, Columbia, SC 29208;  
[heyden@cec.sc.edu](mailto:heyden@cec.sc.edu)

### Goals

Develop and validate highly efficient and accurate computational methodologies for predicting elementary reaction rates of processes occurring at solid-liquid interfaces relevant for the conversion of lignocellulosic biomass model molecules. We aim at identifying the importance of an aqueous reaction environment on reaction mechanisms, activity, and selectivity for C-O versus C-C bond cleavage in polyalcohols and reductive deoxygenation versus hydrogenation of guaiacol over transition metal catalyst surfaces. As a result, we move towards the design and discovery of improved catalysts for a future biorefining industry that converts lignocellulosic biomass in a liquid phase environment into renewable fuels and chemicals.

### DOE Interest

Our desire to better understand chemical reactions at the solid-liquid interface is motivated by the fact that various recently proposed catalytic processes for the conversion of oxygenated hydrocarbons into fuels or chemicals occur in a liquid-phase environment. A key advantage of liquid-phase catalytic processing is that thermally unstable reactant molecules, such as carbohydrates, can be processed at relatively low temperatures at which undesirable thermal degradation reactions are slow and targeted product selectivities are high. In particular, aqueous-phase processing (APP) of biomass-derived oxygenated hydrocarbons represents a promising catalytic liquid-phase technology for the renewable production of fuels and chemicals. At the same time, our understanding of heterogeneous catalysis in the liquid phase is very limited. And while it is generally known that solvent effects can dramatically change a catalyst's activity and selectivity by changing the free energies of reactants, products, and transition states by stabilizing or destabilizing charged intermediates and transition states, it is currently hardly possible to predict the specific effects of a complex liquid environment on a catalyst's activity and selectivity. This again severely inhibits the rational design of heterogeneous catalysts for the conversion of lignocellulosic biomass into chemicals and fuels.

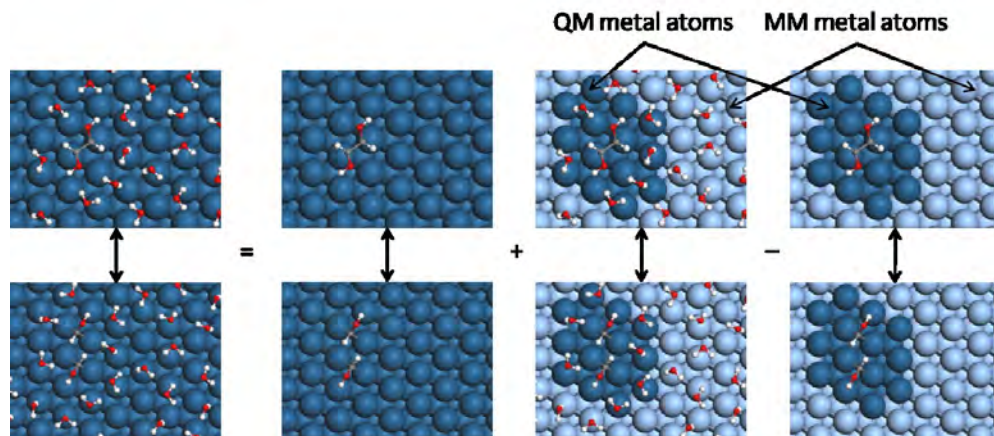
### Recent Progress

We developed, implemented, and validated explicit and implicit solvation schemes for metal surfaces, *eSMS* and *iSMS*, respectively, that are highly accurate although they are at least 6-8 orders of magnitude faster than current approaches that sample the reaction system and use a full

quantum chemical description of the system. This improvement in performance was achieved by noticing that while the electrostatic interaction of water molecules with adsorbed reactants and transition states is long ranged requiring very large unit cells with hundreds of water molecules and transition metal atoms, the indirect effect of water molecules on free energy differences by changing the electron density of transition metal atoms is short ranged. As a result, we can use a simple subtraction scheme and partition the reaction system in a quantum mechanical (QM) and a molecular mechanical (MM) (or implicit solvation) region similar to what is possible and commonly done in the homogeneous and enzyme catalysis communities. Equation 1 and Figure 1 illustrate our procedure,

$$\Delta G_{\text{surface/water}} = \Delta E_{\text{surface/vacuum}} + \Delta G_{\text{cluster/water}} - \Delta E_{\text{surface/vacuum}} \quad (1)$$

where  $\Delta G_{\text{surface/water}}$  is the desired reaction free energy of an elementary process occurring at the metal-water interface,  $\Delta E_{\text{surface/vacuum}}$  is the corresponding gas-phase reaction energy in the absence of all water molecules that are not part of the reaction coordinate,  $\Delta G_{\text{cluster/water}}$  is the free energy of reaction at the metal-water interface with all metal atoms far away from the adsorbed reactant and all water molecules not part of the reaction coordinate modeled classical (or with an implicit solvation model), and  $\Delta E_{\text{surface/vacuum}}$  is the gas-phase reaction energy corresponding to  $\Delta G_{\text{cluster/water}}$  after removal of all classical (implicit) water molecules. For the *eSMS* method we validated the use of the “fixed charge approximation” and investigated the C-C cleavage reaction in dehydrogenated ethylene glycol. We observe that an aqueous environment hinders the C-C cleavage by both increasing the activation barrier and reaction free energy. Our *iSMS* method with COSMO-RS solvation model is qualitatively and quantitatively in good agreement with our *eSMS* method. Computed activation barriers and reaction free energies differ between *eSMS* and *iSMS* by less than 0.1 eV.



**Fig. 1:** Schematic representation of our *eSMS* methodology for calculation of the free energy of reaction for, e.g., C-C bond scission in dehydrogenated ethylene glycol ( $C_2H_4O_2 + H_2O \rightleftharpoons 2CHOH + H_2O$ ) over Pt (111) in water. Arrows connect reactant (up) to cleavage products (down) in the respective models. H, O, C and Pt atoms are shown, in white, red, gray and blue (dark blue for QM, light blue for MM), respectively.

A first application of the *iSMS* method to the decarbonylation and decarboxylation of propanoic acid over Pd (111) suggests that while a non-polar solvent such as octane does not significantly affect the activity of the Pd surface, water increases the decarboxylation rate by 2-3 orders of



magnitude and the decarbonylation rate by a factor of 30. O-H, C-H, and C-O bond cleavages are all facilitated in the presence of liquid water.

### **Future Plans**

*Method development, implementation, and validation:* Development of a highly efficient computational procedure for predicting free energies of adsorption and desorption at metal-water interfaces within our *eSMS* methodology.

*Biomass model molecule applications:* Computation of reaction free energies for various processes in the conversion of ethylene glycol, glycerol, and guaiacol over Pt (111) and Ru (0001) catalyst surfaces in both vapor and aqueous environments. Development of microkinetic reaction models based on parameters obtained from first principles, study of the effect of reaction environment on a catalyst's activity and selectivity, and investigation of the differences of the effect of water on Pt and Ru catalysts.

### **Publications (2012-2013)**

M. Faheem, S. Suthirakun, A. Heyden, "New implicit solvation scheme for solid surfaces," *J. Phys. Chem. C* **116** (2012) 22458-22462.

J. Lu, S. Behtash, A. Heyden, "Theoretical investigation of the reaction mechanism of the decarboxylation and decarbonylation of propanoic acid on Pd (111) model surfaces," *J. Phys. Chem. C* **116** (2012) 14328-14341.

J. Lu, S. Behtash, M. Faheem, A. Heyden, "Microkinetic Modeling of the Decarboxylation and Decarbonylation of Propanoic Acid over Pd (111) Model Surfaces Based on Parameters Obtained from First Principles," *J. Catal.* IN PRESS (2013).

This page is intentionally blank.

**Tuesday Morning**

**Session VIII**

This page is intentionally blank.

## Theoretical description of CO<sub>2</sub> reduction

Additional PIs: Felix Studt, Frank Abild-Pedersen, Thomas Bligaard  
Additional Staff: Aleksandra Vojvodic, Jens Hummelshøj, Chris O'Grady  
Postdocs: Adam Lausche, Zaoshi Yuan, Hanne Falsig, Hongliang Xin, Jess Wellendorf, Jun Yan, Rasmus Brogaard  
Students: Aidan Klobuchar, Andrew Doyle, Tuhin Khan, Keld Lundgaard, Andrew Medford, Andreas Mogelhoff, Charlie Tsai, Jong-Suk Yoo, Lin Li, Venkat Vishwanathan  
Contact: SLAC National Accelerator Laboratory,  
Menlo Park, CA 94025, USA  
[norskov@stanford.edu](mailto:norskov@stanford.edu)

### Goal

We aim to develop an understanding of catalytic CO<sub>2</sub> reduction to hydrocarbons and alcohols. Thermal processes, (photo-) electrochemical processes and combinations thereof are considered. The factors that determine the catalytic activity of catalysts are identified and used to design new catalysts. The thermal catalysis project is part of the DOE-BES FWP in the SUNCAT Center for Interface Science and Catalysis, which has a number of other projects, see list of participants above and list of publications 2011-13 below.

### DOE Interest

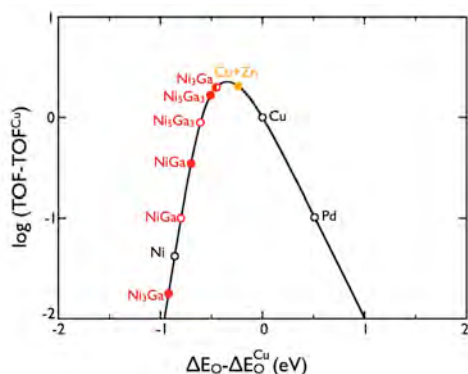
Storing solar energy (from photovoltaics or wind turbines, for instance) in the form of hydrocarbons or alcohols is extremely attractive because it means that the current energy infrastructure can be utilized. This calls for chemical, electrochemical or photo-electrochemical methods to reduce CO<sub>2</sub>. The accessibility of suitable catalysts is a major roadblock in developing such opportunities. The work described here addresses the fundamental challenges associated with the atomic-scale design of such catalysts.

### Recent Progress and challenges for the future

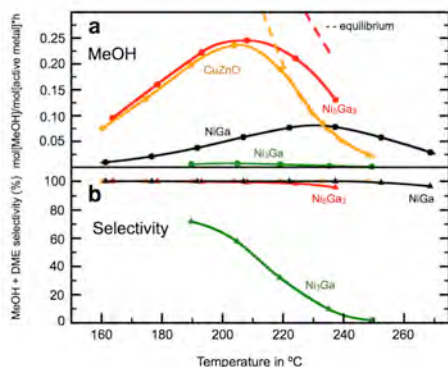
We have analyzed the methanol synthesis process in detail, identified the active site of the industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, and identified descriptors of catalytic activity. We have used this insight to design new catalysts that would be able to facilitate CO<sub>2</sub> reduction to methanol at ambient pressures. Such a process could be interesting in connection with a decentralized use of solar or wind-generated hydrogen. Since all reaction intermediates bind through oxygen, the resulting activity volcano is one-dimensional, only depending on the oxygen adsorption energy,  $\Delta E_0$  (see Figure 1). Ni-Ga intermetallic compounds are predicted to be active and stable. Subsequent synthesis, characterization and test by the group of Ib Chorkendorff and Søren Dahl at the Technical University of Denmark shows remarkable activity and selectivity towards methanol, comparable or larger than the industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst (see Figure 2). Interestingly, the reverse Water-Gas-Shift activity of the

new catalysts is significantly lower than that of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, an important property if one wants to employ these catalysts in small scale devices.

In a separate project we have studied the (photo-) electrochemical reduction of CO<sub>2</sub>. Using the same methodology, but adding in the effect of applied potential and solvation by the electrolyte, trends in activity can be mapped out as indicated in Figure 3. Shown is an activity volcano for the first step in CO<sub>2</sub> reduction, the formation of CO.

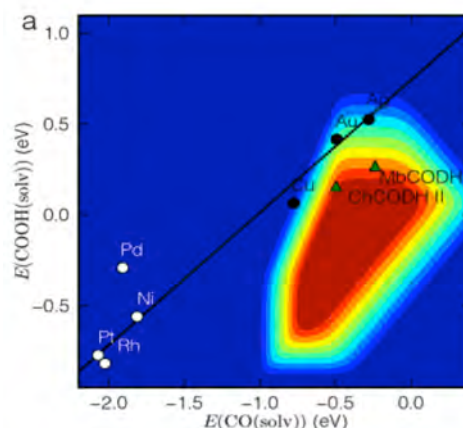


**Figure 1.** Theoretical activity volcano for CO<sub>2</sub> hydrogen to methanol as a function of  $\Delta E_0$  at 500 K, 1 bar and a H<sub>2</sub>:CO<sub>2</sub> ratio of 3:1. (Studt et al., to be published)

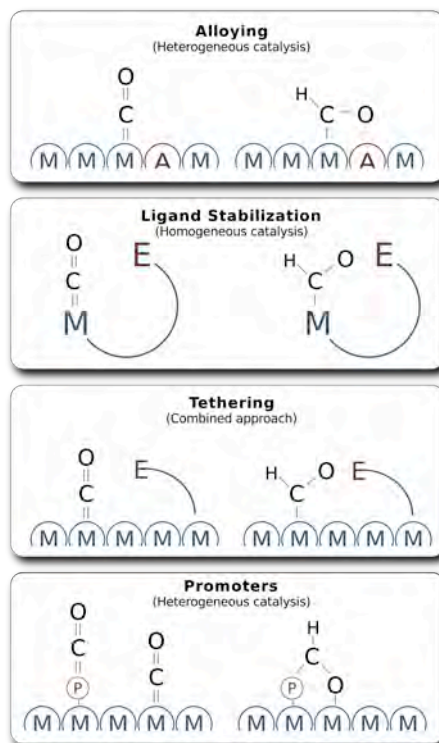


**Figure 2.** (a) Activity towards methanol of a series of Ni<sub>x</sub>Ga<sub>y</sub> catalysts compared to Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> as a function of temperature at atmospheric pressures. Equilibrium towards methanol is depicted as dotted lines. (b) CO free selectivity towards methanol and DME in %. (Studt et al., to be published)

The problem with elemental metal catalysts is clear: The energies of different intermediates scale so that the optimum in activity is not captured. The fact the active sites of CODH enzymes are calculated to be



**Figure 3.** Kinetic volcanoes for CO evolution at 0.3 V overpotential. The specific CO evolution current calculated from ChCODH II and MbCODH enzyme models are included for comparison. (Hansen et al. J. Phys. Chem. Lett. 4, 388 (2013))



**Figure 4.** Strategies for enhancing the rate of CO hydrogenation. (Pederson et al. J. Phys. Chem. Lett. 3, 251 (2012))

closer to optimum gives some hope. It points to the need for finding methods to go beyond planar, single site catalysts for these difficult reactions. Various strategies including the possibility of combining heterogenous and (anchored) homogeneous catalysts is included in Figure 4, addressing the similar problem for the further reduction of CO: The scaling between the bonding of CHO (or COH for the more reactive metals) and CO need to be broken by adding new components to the surface.

### SUNCAT-DOE Publications (2011-2013)

V. Viswanathan, J. K. Nørskov, A. Speidel, R. Scheffler, S. Gowda and A. C. Luntz: *Li-O-2 Kinetic Overpotentials: Tafel Plots from Experiment and First-Principles Theory*, J Phys Chem Lett **4**: 556-560 (2013)

F. Viñes, A. Vojvodic, F. Abild-Pedersen and F. Illas: *Brønsted–Evans–Polanyi Relationship for Transition Metal Carbide and Transition Metal Oxide Surfaces*, The Journal of Physical Chemistry C **117**: 4168-4171 (2013)

L. Li, A. H. Larsen, N. A. Romero, V. A. Morozov, C. Glinsvad, F. Abild-Pedersen, J. Greeley, K. W. Jacobsen and J. K. Nørskov: *Investigation of Catalytic Finite-Size-Effects of Platinum Metal Clusters*, J Phys Chem Lett **4**: 222-226 (2013)

A.C. Lausche, F. Abild-Pedersen, R. J. Madix, J. K. Nørskov and F. Studt: *Analysis of sulfur-induced selectivity changes for anhydrous methanol dehydrogenation on Ni(100) surfaces*, Surface Science **613**: 58-62 (2013)

J. S. Hummelshoj, A. C. Luntz and J. K. Nørskov: *Theoretical evidence for low kinetic overpotentials in Li-O-2 electrochemistry*, Journal of Chemical Physics **138** (2013)

M. Dell'Angela, T. Anniyev, M. Beye, R. Coffee, A. Fohlich, J. Gladh, T. Katayama, S. Kaya, O. Krupin, J. LaRue, A. Mogelhoj, D. Nordlund, J. K. Nørskov, H. Oberg, H. Ogasawara, H. Ostrom, L. G. M. Pettersson, W. F. Schlotter, J. A. Sellberg, F. Sorgenfrei, J. J. Turner, M. Wolf, W. Wurth and A. Nilsson: *Real-Time Observation of Surface Bond Breaking with an X-ray Laser*, Science **339**: 1302-1305 (2013)

J. Yan, K. Jacobsen and K. Thygesen: *Optical properties of bulk semiconductors and graphene/boron nitride: The Bethe-Salpeter equation with derivative discontinuity-corrected density functional energies*, Phys Rev B **86** (2012)

J. Wellendorff, K. T. Lundgaard, A. Mogelhoj, V. Petzold, D. D. Landis, J. K. Nørskov, T. Bligaard and K. W. Jacobsen: *Density functionals for surface science: Exchange-correlation model development with Bayesian error estimation*, Phys Rev B **85** (2012)

A. Vojvodic: *Steam Reforming on Transition-Metal Carbides from Density-Functional Theory*, Catalysis Letters **142**: 728-735 (2012)

V. Viswanathan, H. A. Hansen, J. Rossmeisl and J. K. Nørskov: *Unifying the 2e- and 4e- Reduction of Oxygen on Metal Surfaces*, The Journal of Physical Chemistry Letters **3**: 2948-2951 (2012)

V. Viswanathan, H. A. Hansen, J. Rossmeisl and J. K. Nørskov: *Universality in Oxygen Reduction Electrocatalysis on Metal Surfaces*, Acs Catal **2**: 1654-1660 (2012)

V. Viswanathan, H. A. Hansen, J. Rossmeisl, T. F. Jaramillo, H. Pitsch and J. K. Nørskov: *Simulating Linear Sweep Voltammetry from First-Principles: Application to Electrochemical Oxidation of Water on Pt(111) and Pt3Ni(111)*, Journal of Physical Chemistry C **116**: 4698-4704 (2012)

Valdes, J. Brillet, M. Gratzel, H. Gudmundsdottir, H. A. Hansen, H. Jonsson, P. Klupfel, G.-J. Kroes, F. Le Formal, I. C. Man, R. S. Martins, J. K. Nørskov, J. Rossmeisl, K. Sivula, A. Vojvodic and M. Zach: *Solar hydrogen production with semiconductor metal oxides: new directions in experiment and theory*, Physical Chemistry Chemical Physics **14**: 49-70 (2012)

- A. Toftelund, I. C. Man, H. A. Hansen, F. Abild-Pedersen, T. Bligaard, J. Rossmeisl and F. Studt: *Volcano Relations for Oxidation of Hydrogen Halides over Rutile Oxide Surfaces*, *Chemcatchem* **4**: 1856-1861 (2012)
- F. Studt, F. Abild-Pedersen, Q. Wu, A. D. Jensen, B. Temel, J.-D. Grunwaldt and J. K. Nørskov: *CO hydrogenation to methanol on Cu-Ni catalysts: Theory and experiment*, *J. Catal.* **293**: 51-60 (2012)
- F. Studt, F. Abild-Pedersen, J. B. Varley and J. K. Nørskov: *CO and CO<sub>2</sub> Hydrogenation to Methanol Calculated Using the BEEF-vdW Functional*, *Catalysis Letters* **143**: 71-73 (2012)
- F. Studt: *The Oxygen Reduction Reaction on Nitrogen-Doped Graphene*, *Catalysis Letters* (2012)
- E. Skulason, T. Bligaard, S. Gudmundsdottir, F. Studt, J. Rossmeisl, F. Abild-Pedersen, T. Vegge, H. Jonsson and J. K. Nørskov: *A theoretical evaluation of possible transition metal electro-catalysts for N<sub>2</sub> reduction*, *Physical Chemistry Chemical Physics* **14**: 1235-1245 (2012)
- C.B. Rasmussen, T. V. W. Janssens, B. Temel, T. Bligaard, B. Hinnemann, S. Helveg and J. Sehested: *The energies of formation and mobilities of Cu surface species on Cu and ZnO in methanol and water gas shift atmospheres studied by DFT*, *J. Catal.* **293**: 205-214 (2012)
- S. Rajasekaran, S. Kaya, F. Abild-Pedersen, T. Anniyev, F. Yang, D. Stacchiola, H. Ogasawara and A. Nilsson: *Reversible graphene-metal contact through hydrogenation*, *Phys Rev B* **86** (2012)
- V. Petzold, T. Bligaard and K. W. Jacobsen: *Construction of New Electronic Density Functionals with Error Estimation Through Fitting*, *Topics in Catalysis* **55**: 402-417 (2012)
- A. A. Peterson, L. C. Grabow, T. P. Brennan, B. G. Shong, C. C. Ooi, D. M. Wu, C. W. Li, A. Kushwaha, A. J. Medford, F. Mbuga, L. Li and J. K. Nørskov: *Finite-Size Effects in O and CO Adsorption for the Late Transition Metals*, *Topics in Catalysis* **55**: 1276-1282 (2012)
- A. Peterson, M. Dreher, J. Wambach, M. Nachtegaal, S. Dahl, J. K. Nørskov and F. Vogel: *Evidence of Scrambling over Ruthenium-based Catalysts in Supercritical-water Gasification*, *Chemcatchem* **4**: 1185-1189 (2012)
- A.J. Medford, A. Vojvodic, F. Studt, F. Abild-Pedersen and J. K. Nørskov: *Elementary steps of syngas reactions on Mo<sub>2</sub>C(001): Adsorption thermochemistry and bond dissociation*, *J. Catal.* **290**: 108-117 (2012)
- B. D. McCloskey, A. Speidel, R. Scheffler, D. C. Miller, V. Viswanathan, J. S. Hummelshøj, J. K. Nørskov and A. C. Luntz: *Twin Problems of Interfacial Carbonate Formation in Nonaqueous Li-O<sub>2</sub> Batteries*, *J Phys Chem Lett* **3**: 997-1001 (2012)
- A.C. Lausche, J. S. Hummelshøj, F. Abild-Pedersen, F. Studt and J. K. Nørskov: *Application of a new informatics tool in heterogeneous catalysis: Analysis of methanol dehydrogenation on transition metal catalysts for the production of anhydrous formaldehyde*, *J. Catal.* **291**: 133-137 (2012)
- D. Landis, J. S. Hummelshøj, S. Nestorov, J. Greeley, M. Dulak, T. Bligaard, J. K. Nørskov and K. W. Jacobsen: *The Computational Materials Repository*, *Computing in Science and Engineering* (2012)
- E. M. Karp, C. T. Campbell, F. Studt, F. Abild-Pedersen and J. K. Nørskov: *Energetics of Oxygen Adatoms, Hydroxyl Species and Water Dissociation on Pt(111)*, *The Journal of Physical Chemistry C*: 121128143844003 (2012)
- J. S. Hummelshøj, F. Abild-Pedersen, F. Studt, T. Bligaard and J. K. Nørskov: *CatApp: A Web Application for Surface Chemistry and Heterogeneous Catalysis*, *Angew Chem Int Ed Engl* **51**: 272-274 (2012)
- Y. D. Hou, B. L. Abrams, P. C. K. Vesborg, M. E. Bjorketun, K. Herbst, L. Bech, B. Seger, T. Pedersen, O. Hansen, J. Rossmeisl, S. Dahl, J. K. Nørskov and I. Chorkendorff: *Photoelectrocatalysis and electrocatalysis on silicon electrodes decorated with cubane-like clusters*, *J Photon Energy* **2** (2012)



- C.Friebel, V. Viswanathan, D. J. Miller, T. Anniyev, H. Ogasawara, A. H. Larsen, C. P. O'Grady, J. K. Nørskov and A. Nilsson: *Balance of Nanostructure and Bimetallic Interactions in Pt Model Fuel Cell Catalysts: In Situ XAS and DFT Study*, J Am Chem Soc **134**: 9664-9671 (2012)
- C.E. Doronkin, T. S. Khan, T. Bligaard, S. Fogel, P. Gabrielsson and S. Dahl: *Sulfur poisoning and regeneration of the Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for H<sub>2</sub>-assisted SCR of NO<sub>x</sub> by ammonia*, Applied Catalysis B: Environmental **117-118**: 49-58 (2012)
- C.E. Doronkin, S. Fogel, S. Tamm, L. Olsson, T. S. Khan, T. Bligaard, P. Gabrielsson and S. Dahl: *Study of the "Fast SCR"-like mechanism of H<sub>2</sub>-assisted SCR of NO<sub>x</sub> with ammonia over Ag/Al<sub>2</sub>O<sub>3</sub>*, Appl Catal B-Environ **113**: 228-236 (2012)
- S. H. Chou, J. Voss, I. Bargatin, A. Vojvodic, R. T. Howe and F. Abild-Pedersen: *An orbital-overlap model for minimal work functions of cesiated metal surfaces*, Journal of physics. Condensed Matter **24**: 445007 (2012)
- R. Y. Brogaard, P. G. Moses and J. K. Nørskov: *Modeling van der Waals Interactions in Zeolites with Periodic DFT: Physisorption of n-Alkanes in ZSM-22*, Catalysis Letters **142**: 1057-1060 (2012)
- M. Behrens, F. Studt, I. Kaatkin, S. Kuhl, M. Havecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B. Knief, M. Tovar, R. W. Fischer, J. K. Nørskov and R. Schlogl: *Methanol Synthesis over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>: The Active Site in Industrial Catalysis*, Science **336** 893-897 (2012)
- J. Wellendorff and T. Bligaard: *On the Importance of Gradient-Corrected Correlation for van der Waals Density Functionals*, Topics in Catalysis **54**: 1143-1150 (2011)
- S. Wang, B. Temel, J. Shen, G. Jones, L. C. Grabow, F. Studt, T. Bligaard, F. Abild-Pedersen, C. H. Christensen and J. K. Nørskov: *Universal Bronsted-Evans-Polanyi Relations for C-C, C-O, C-N, N-O, N-N, and O-O Dissociation Reactions*, Catalysis Letters **141**: 370-373 (2011)
- S. Wang, V. Petzold, V. Tripkovic, J. Kleis, J. G. Howalt, E. Skulason, E. M. Fernandez, B. Hvolbaek, G. Jones, A. Toftelund, H. Falsig, M. Bjorketun, F. Studt, F. Abild-Pedersen, J. Rossmeisl, J. K. Nørskov and T. Bligaard: *Universal transition state scaling relations for (de)hydrogenation over transition metals*, Physical chemistry chemical physics : PCCP **13**: 20760-20765 (2011)
- A. Vojvodic and J. K. Nørskov: *Optimizing Perovskites for the Water-Splitting Reaction*, Science **334**: 1355-1356 (2011)
- A. Vojvodic, F. Calle-Vallejo, W. Guo, S. Wang, A. Toftelund, F. Studt, J. I. Martinez, J. Shen, I. C. Man, J. Rossmeisl, T. Bligaard, J. K. Nørskov and F. Abild-Pedersen: *On the behavior of Bronsted-Evans-Polanyi relations for transition metal oxides*, The Journal of chemical physics **134**: 244509 (2011)
- V. Viswanathan, K. S. Thygesen, J. S. Hummelshøj, J. K. Nørskov, G. Girishkumar, B. D. McCloskey and A. C. Luntz: *Electrical conductivity in Li(2)O(2) and its role in determining capacity limitations in non-aqueous Li-O(2) batteries*, J Chem Phys **135**: 214704 (2011)
- G. A. Tritsarlis, J. K. Nørskov and J. Rossmeisl: *Trends in oxygen reduction and methanol activation on transition metal chalcogenides*, Electrochimica Acta **56**: 9783-9788 (2011)
- G. A. Tritsarlis, J. Greeley, J. Rossmeisl and J. K. Nørskov: *Atomic-Scale Modeling of Particle Size Effects for the Oxygen Reduction Reaction on Pt*, Catalysis Letters **141**: 909-913 (2011)
- S. Saadi, B. Hinnemann, C. C. Appel, S. Helveg, F. Abild-Pedersen and J. K. Nørskov: *First-principles investigations of Ni(3)Al(111) and NiAl(110) surfaces at metal dusting conditions*, Surface Science **605**: 582-592 (2011)
- J. K. Nørskov, F. Abild-Pedersen, F. Studt and T. Bligaard: *Density functional theory in surface chemistry and*

*catalysis*, P Natl Acad Sci USA **108**: 937-943 (2011)

A. Møgelhøj, A. K. Kelkkanen, K. T. Wikfeldt, J. Schiøtz, J. J. Mortensen, L. G. M. Pettersson, B. I. Lundqvist, K. W. Jacobsen, A. Nilsson and J. K. Nørskov: *Ab Initio van der Waals Interactions in Simulations of Water Alter Structure from Mainly Tetrahedral to High-Density-Like*, The Journal of Physical Chemistry B **115**: 14149-14160 (2011)

A. Larsen, J. Kleis, K. Thygesen, J. Nørskov and K. Jacobsen: *Electronic shell structure and chemisorption on gold nanoparticles*, Phys Rev B **84** (2011)

J. Kleis, J. Greeley, N. A. Romero, V. A. Morozov, H. Falsig, A. H. Larsen, J. Lu, J. J. Mortensen, M. Dulak, K. S. Thygesen, J. K. Nørskov and K. W. Jacobsen: *Finite Size Effects in Chemical Bonding: From Small Clusters to Solids*, Catalysis Letters **141**: 1067-1071 (2011)

G. Jones, F. Studt, F. Abild-Pedersen, J. K. Nørskov and T. Bligaard: *Scaling relationships for adsorption energies of C2 hydrocarbons on transition metal surfaces*, Chemical Engineering Science **66**: 6318-6323 (2011)

Y. Hou, B. L. Abrams, P. C. K. Vesborg, M. E. Bjorketun, K. Herbst, L. Bech, A. M. Setti, C. D. Damsgaard, T. Pedersen, O. Hansen, J. Rossmeisl, S. Dahl, J. K. Nørskov and I. Chorkendorff: *Bioinspired molecular co-catalysts bonded to a silicon photocathode for solar hydrogen evolution*, Nature Materials **10**: 434-438 (2011)

L. C. Grabow, F. Studt, F. Abild-Pedersen, V. Petzold, J. Kleis, T. Bligaard and J. K. Nørskov: *Descriptor-Based Analysis Applied to HCN Synthesis from NH(3) and CH(4)*, Angewandte Chemie-International Edition **50**: 4601-4605 (2011)

M. Garcia-Mota, A. Vojvodic, H. Metiu, I. C. Man, H. Y. Su, J. Rossmeisl and J. K. Nørskov: *Tailoring the Activity for Oxygen Evolution Electrocatalysis on Rutile TiO(2)(110) by Transition-Metal Substitution*, Chemcatchem **3**: 1607-1611 (2011)

W. J. Durand, A. A. Peterson, F. Studt, F. Abild-Pedersen and J. K. Nørskov: *Structure effects on the energetics of the electrochemical reduction of CO(2) by copper surfaces*, Surface Science **605**: 1354-1359 (2011)

A. J. Churchard, E. Banach, A. Borgschulte, R. Caputo, J.-C. Chen, D. Clary, K. J. Fijalkowski, H. Geerlings, R. V. Genova, W. Grochala, T. Jaron, J. C. Juanes-Marcos, B. Kasemo, G.-J. Kroes, I. Ljubic, N. Naujoks, J. K. Nørskov, R. A. Olsen, F. Pendolino, A. Remhof, L. Romanszki, A. Tekin, T. Vegge, M. Zach and A. Zuetzel: *A multifaceted approach to hydrogen storage*, Physical Chemistry Chemical Physics **13**: 16955-16972 (2011)

J. Chen, J. S. Hummelshøj, K. S. Thygesen, J. S. G. Myrdal, J. K. Nørskov and T. Vegge: *The role of transition metal interfaces on the electronic transport in lithium-air batteries*, Catalysis Today **165**: 2-9 (2011)

M. E. Bjorketun, G. S. Karlberg, J. Rossmeisl, I. Chorkendorff, H. Wolfschmidt, U. Stimming and J. K. Nørskov: *Hydrogen evolution on Au(111) covered with submonolayers of Pd*, Phys Rev B **84** (2011)

E. Skulason, V. Tripkovic, M. E. Bjorketun, S. Gudmundsdottir, G. Karlberg, J. Rossmeisl, T. Bligaard, H. Jonsson and J. K. Nørskov: *Modeling the Electrochemical Hydrogen Oxidation and Evolution Reactions on the Basis of Density Functional Theory Calculations*, Journal of Physical Chemistry C **114**: 18182-18197 (2010)

A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl and J. K. Nørskov: *How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels*, Energy & Environmental Science **3**: 1311-1315 (2010)

## One-pot catalytic conversion of biomass and alkanes: Kinetically coupling deoxygenation and dehydrogenation pathways

Additional PIs: None  
Postdoc: None  
Students: Jeremy Bedard, Mark Sullivan  
Collaborators: None  
Contact: University of Minnesota, 421 Washington Ave SE, Minneapolis, MN 55455; [abhan@umn.edu](mailto:abhan@umn.edu)

### Goal

Develop mechanistic understanding of heterogeneous catalytic processes for alkane dehydrogenation and biomass deoxygenation with a focus on kinetically coupling dehydrogenation and deoxygenation pathways.

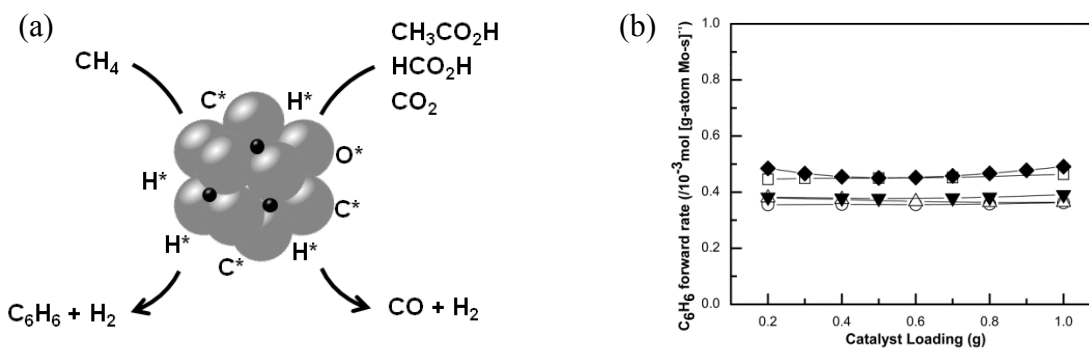
### DOE Interest

As raw materials for liquid fuels, biomass and natural gas lie at opposite ends of the chemical spectrum – natural gas is hydrogen rich while biomass-derived oxygenates are hydrogen deficient. A critical underlying challenge for the conversion of these emerging carbon-based feedstocks to hydrocarbon fuels lies in the development of catalytic processes for inter- and intra- molecular hydrogen transfer. An understanding of the structure and function of catalytic solids in hydrogen transfer processes will play a critical role in determining the viability of alternative carbon sources for the synthesis of liquid hydrocarbon fuels.

### Recent Progress

*Dehydroaromatization of CH<sub>4</sub> and CH<sub>4</sub>/H<sub>2</sub> mixtures:* Forward rates ( $R_{\text{for}}$ ) of C<sub>6</sub>H<sub>6</sub> synthesis via CH<sub>4</sub> pyrolysis were calculated to be  $0.47 \pm 0.08 \times 10^{-3}$  mol/(g-atom Mo-s) and shown to be invariant with catalyst loading. Independent experiments with H<sub>2</sub>/CH<sub>4</sub> mixtures (0.0-0.1 molar ratio) show that  $R_{\text{for}}$  for benzene synthesis is invariant ( $0.38 \pm 0.05 \times 10^{-3}$  mol/(g-atom Mo-s)) with hydrogen pressures and catalyst loading confirming that H<sub>2</sub> inhibition of CH<sub>4</sub> DHA net rates is due to thermodynamic reversibility.

*Co-processing CH<sub>4</sub> and oxygenates with  $(C/H)_{\text{eff}} < 0.25$ :* Co-processing acetic acid, formic acid, or carbon dioxide with methane on Mo/ZSM-5 catalysts at 950 K resulted in reforming of the CH<sub>4</sub>/oxygenate co-feed to produce CO and H<sub>2</sub> upstream while concurrently oxidizing a part of the catalyst bed deeming it unavailable for CH<sub>4</sub> dehydroaromatization. CH<sub>4</sub> dehydroaromatization occurs downstream of the oxygenate reforming zone in the presence of CO and H<sub>2</sub> produced upstream. Co-processing oxygenates with CH<sub>4</sub> causes an increase in the H<sub>2</sub> to CH<sub>4</sub> ratio which acts to shift the thermodynamic equilibrium towards the reactants, but does not have any kinetic consequences on the forward rate of C<sub>6</sub>H<sub>6</sub> production (Figure 1(b)). Oxygen is stoichiometrically removed as CO irrespective of the concentration or identity of the oxygenate and no change in the forward rate of benzene synthesis is observed at varying CO concentrations in the effluent.



**Figure 1** (a) Schematic representation of  $\text{CH}_4$  pyrolysis and  $\text{C}_1$ - $\text{C}_2$  deoxygenation on Mo/ZSM-5 catalysts; and (b) Average forward rate of  $\text{C}_6\text{H}_6$  production as a function of catalyst loading at 950 K,  $\text{CH}_4$  flow rate  $12.0 \text{ cm}^3 \text{ min}^{-1}$ , 1 atm,  $\text{CH}_4:\text{Ar} = 9:1$ , and catalyst weight 0.2-1.0 g with  $\text{Mo}:\text{Al}_f = 0.25$ .  $\text{HCOOH}/\text{CH}_4$  ( $\circ$ ),  $\text{CO}_2/\text{CH}_4$  ( $\Delta$ ),  $\text{CH}_3\text{COOH}/\text{CH}_4$  ( $\square$ ),  $\text{H}_2/\text{CH}_4$  ( $\blacktriangledown$ ), and  $\text{CH}_4$  ( $\blacklozenge$ ).

Co-processing  $\text{CH}_4$  and oxygenates with  $(\text{C}/\text{H})_{\text{eff}} \geq 0.25$ : The effective hydrogen index as proposed by Chen et al. (Chemtech 16 (1986) 506) accurately describes the stoichiometric hydrogen deficiency of carbohydrate feedstocks.

$$\text{EHI} = (\text{H}/\text{C})_{\text{eff}} = (\text{H} - 2(\text{O}))/\text{C}$$

This definition, however, considers that O removal occurs via the formation of water which is not the observation we report. Instead, we propose the  $(\text{C}/\text{H})_{\text{eff}}$  which accurately accounts for the preferential selectivity to remove oxygen as CO instead of  $\text{H}_2\text{O}$ .

$$(\text{C}/\text{H})_{\text{eff}} = (\text{C} - \text{O})/\text{H}$$

$\text{CO}_2$ ,  $\text{HCOOH}$ , and  $\text{CH}_3\text{COOH}$  possess  $(\text{C}/\text{H})_{\text{eff}} < 0.25$ ; the addition of these co-feeds to  $\text{CH}_4$  therefore, results in a net reduction of the  $(\text{C}/\text{H})_{\text{eff}}$  of the process feed and thereby reduces the net synthesis rate of aromatic compounds. In preliminary results, we report that the addition of co-feeds with  $(\text{C}/\text{H})_{\text{eff}} > 0.25$ , for example,  $\text{CH}_3\text{COCH}_3$  results in an increase in the net rate of benzene synthesis.

### Future Plans

*Reactions of  $\text{CH}_4$ /oxygenates with  $(\text{C}/\text{H})_{\text{eff}} > 0.25$ :* Develop kinetic and mechanistic understanding of reactions of  $\text{CH}_4$  and oxygenates with  $(\text{C}/\text{H})_{\text{eff}} > 0.25$  to assess the role of stoichiometry and chemical functionality in deoxygenation pathways.

*Hydrodeoxygenation on self-supporting metal carbide catalysts:* Explore the potential for selective, low temperature hydrodeoxygenation of  $\text{C}_2$ - $\text{C}_3$  oxygenates on metal carbide catalyst formulations.

### **Publications (2012-2013)**

1. J. W. Bedard, D-Y. Hong, A. Bhan (2013) "Co-processing CH<sub>4</sub> and oxygenates on Mo/H-ZSM-5: 2. CH<sub>4</sub>/CO<sub>2</sub> and CH<sub>4</sub>/HCOOH Mixtures" *Phys. Chem. Chem. Phys.* Accepted.
2. J. W. Bedard, D-Y. Hong, A. Bhan (2013) "CH<sub>4</sub> dehydroaromatization on Mo/H-ZSM-5: 1.Effects of co-processing H<sub>2</sub> and CH<sub>3</sub>COOH" *In Review*.
3. J. W. Bedard, A. Bhan (2013) "Co-processing CH<sub>4</sub> and CH<sub>3</sub>COOH on Mo/H-ZSM-5 Catalysts: Coupling Deoxygenation and Dehydrogenation Pathways" 23<sup>rd</sup> North American Catalysis Society Meeting, Louisville, KY (June 2013). [Poster]

**Catalysis: Reactivity and Structure**

Additional PIs: Ping Liu, Dario Stacchiola, Sanjaya D. Senanayake, Jonathan C. Hanson

Post-docs: Rui Si, Wenqian Xu, Kumudu Mudiyansele

Students: Zongyuan Liu, Si Luo

Contact: The PI and Co-PIs are at the Chemistry Department of Brookhaven National Laboratory, Upton, NY 11973-5000  
Jose A. Rodriguez; [rodriguez@bnl.gov](mailto:rodriguez@bnl.gov)  
Ping Liu, [pingliu3@bnl.gov](mailto:pingliu3@bnl.gov)  
Dario Stacchiola, [djs@bnl.gov](mailto:djs@bnl.gov)  
Sanjaya Senanayake, [ssenanay@bnl.gov](mailto:ssenanay@bnl.gov)  
Jonathan C. Hanson, [hanson1@bnl.gov](mailto:hanson1@bnl.gov)

**Goal:**

The goal of this program is to provide an improved understanding of chemical catalysis by elucidating details of the fundamental properties of molecules, surfaces, and their reactions that are critical to catalysis and energy conversion. Reactivity-structure correlations explored and unraveled by utilization of synchrotron radiation are a key aspect of these studies. Complexities stemming from the inherent multi-component aspects of heterogeneous catalysis are explored using both ultra-high-vacuum surface science investigations of well-defined model systems, and powder diffraction and x-ray absorption studies of "real-world" systems. Quantum-chemical calculations based on density-functional theory are performed to help in interpretation of experimental results and to study basic aspects of catalytic reactions.

**DOE interest:**

We are engaged in fundamental studies examining the behavior of catalysts used for the production of clean fuels and the prevention of environmental pollution. Basic correlations between surface structure and chemical reactivity, necessary for a rational design of heterogeneous catalysts, are being explored. The program is heavily involved in the development of new techniques for the characterization of heterogeneous catalysts and in the operation of the Synchrotron Catalysis Consortium (SCC). Proximity to the National Synchrotron Light Source (NSLS) and Center for Functional Nanomaterials (CFN) greatly enhances program impact and scope. Our work greatly influences other programs in the areas of catalysis and surface science through collaborative research. The project contributes to the DOE long term goal of understanding and controlling chemical processes for energy-related applications.

## Recent Progress

### Activation of Noble Metals on Metal-Carbide Surfaces: Novel Catalysts for CO Oxidation, Desulfurization and Hydrogenation Reactions

In the continuous search for new catalysts, one may wonder whether metals deposited on supports other than metal oxides may provide alternative catalysts with increased activity or selectivity. Transition-metal carbides exhibit broad and amazing physical and chemical properties. These properties may be viewed as resulting from a combination of those of covalent solids, ionic crystals and transition metals. As compounds, the metal carbides are less ionic than the metal oxides. High-resolution photoemission, scanning tunneling microscopy (STM) and first-principles periodic density-functional (DF) calculations have been used to study the interaction of metals of

Groups 9, 10 and 11 with MC(001) (M= Ti, Zr, V, Mo) surfaces. DF calculations give adsorption energies that range from 2 eV (Cu, Ag, Au) to 6 eV (Co, Rh, Ir). STM images show that Au, Cu, Ni and Pt grow on the carbide substrates forming two-dimensional islands at very low coverage, and three-dimensional islands at medium and large coverage. In many systems, the results of DF calculations point to the preferential formation of admetal-C bonds with significant electronic perturbations in the admetal, see Figure 1. TiC(001) and ZrC(001) transfer some electron density to the admetals facilitating bonding of the adatom with electron-acceptor molecules (CO, O<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, SO<sub>2</sub>, thiophene, etc). For example, the Cu/TiC(001) and Au/TiC(001) systems are able

to cleave both S-O bonds of SO<sub>2</sub> at a temperature as low as 150 K, displaying a reactivity much larger than that of TiC(001) or extended surfaces of bulk copper and gold. At temperatures below 200 K, Au/TiC is able to dissociate O<sub>2</sub> and perform the 2CO + O<sub>2</sub> → 2CO<sub>2</sub> reaction. Furthermore, in spite of the very poor hydrodesulfurization performance of TiC(001) or Au(111), a Au/TiC(001) surface displays an activity for the hydrodesulfurization of thiophene higher than that of conventional Ni/MoS<sub>x</sub> catalysts. In general, the Au/TiC system is more chemically active than systems generated by depositing Au nanoparticles on oxide surfaces. Thus, metal carbides are excellent supports for enhancing the chemical reactivity of noble metals.

Among all greenhouse gases in the atmosphere, carbon dioxide plays a special role due to the magnitude of the emissions generated by human activities involving the combustion of carbonaceous fuels, principally wood, coal, oil and natural gas. CO<sub>2</sub>

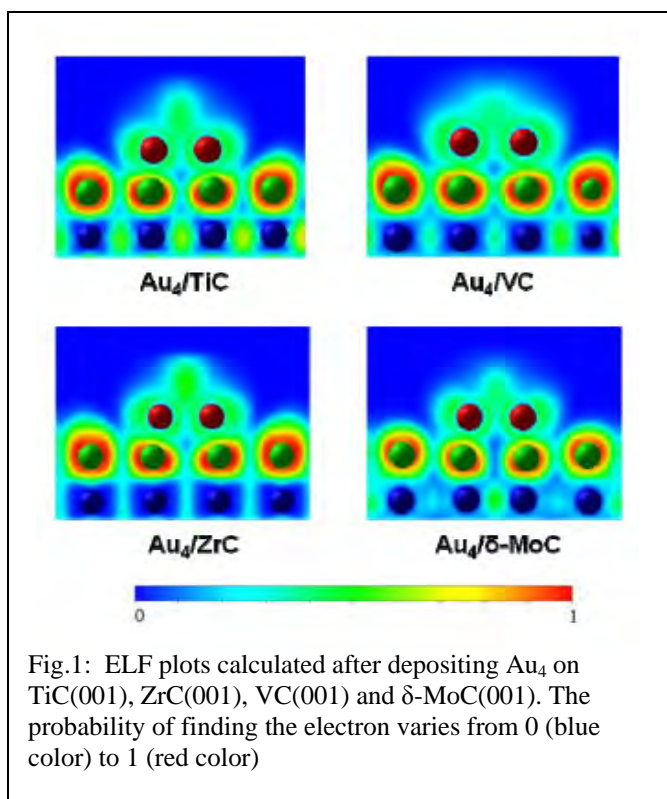
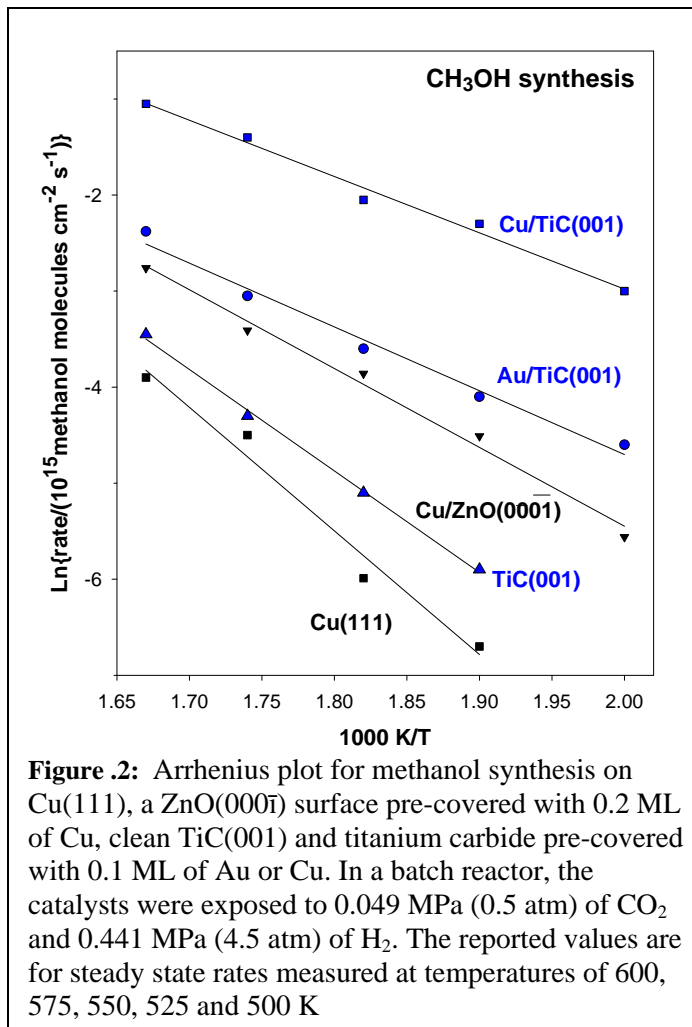


Fig.1: ELF plots calculated after depositing Au<sub>4</sub> on TiC(001), ZrC(001), VC(001) and δ-MoC(001). The probability of finding the electron varies from 0 (blue color) to 1 (red color)

chemistry has become a very attractive area of research not only because environmental concerns but also due to the potential use of CO<sub>2</sub> as an alternative and economical feedstock. The recovery of CO<sub>2</sub> for its hydrogenation to alcohols or other hydrocarbon compounds is an important approach to recycle the released carbon dioxide. This is a difficult task due to the challenges associated with the chemical activation of CO<sub>2</sub>. In the area of heterogeneous catalysis, a lot of attention has been focused on the synthesis of methanol through the hydrogenation of carbon dioxide ( $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$ ) on metal and metal/oxide catalysts. Commercially, methanol is synthesized from syngas (CO-CO<sub>2</sub>-H<sub>2</sub>) over Cu-ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts at 493-573 K and 5-10 MPa. Can metals deposited on carbide supports be active enough for methanol synthesis? Our studies indicate that small Cu and Au particles in contact with a TiC(001) surface undergo a charge polarization which makes them very active for CO<sub>2</sub> activation and the catalytic synthesis of methanol. The binding energy of CO<sub>2</sub> on these systems is in the range of 0.6 to 1.1 eV, much larger than those observed on surfaces or nanoparticles of Cu and Au. Thus, in spite of the poor CO<sub>2</sub> hydrogenation performance of Cu(111) and Au(111), the Cu/TiC(001) and Au/TiC(001) systems display a catalytic activity for methanol synthesis substantially higher than that of conventional Cu/ZnO catalysts., see Figure 2. The turnover frequencies for methanol production on Cu/TiC(001) are 170-500 times much larger than on Cu(111). Thus, the present study illustrates the advantages of using a metal carbide as a support for noble metals for CO<sub>2</sub> hydrogenation.



### CO Oxidation of Well-defined Surfaces of Mixed-Metal Oxides

In automotive exhaust emission control, the complete oxidation of carbon monoxide is of prime importance to meet increasingly stringent environmental regulations in a practical way. Our group have found that mixed-metal oxides of the CeO<sub>2</sub>/CuO<sub>x</sub> and RuO<sub>2</sub>/TiO<sub>2</sub> types are quite active for the oxidation of CO. A Cu(111) surface displays a low activity for the oxidation of carbon monoxide ( $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ ). The supported nanoparticles of CeO<sub>2</sub> and RuO<sub>2</sub> have special structural and



chemical properties that make them quite active for the dissociation of O<sub>2</sub> and they do not bind the atomic O generated very strongly.

### **Electronic Metal-Support Interactions and the Production of Hydrogen through Ethanol Steam Reforming on Ni/CeO<sub>2</sub>**

The electronic properties of Ni deposited on CeO<sub>2</sub>(111) have been examined using photoemission and DFT calculations. The experimental and theoretical results point to a new type of metal-support interaction which produces large electronic perturbations for small Ni particles in contact with ceria. The Ni/CeO<sub>2</sub> systems exhibited a density of metal d states near the Fermi level that was much smaller than that expected for bulk metallic Ni. The electronic perturbations induced by ceria on Ni made this metal a very poor catalyst for CO methanation, but transformed Ni into an excellent catalyst for the production of hydrogen through the steam reforming of ethanol. The behaviour seen for the Ni/CeO<sub>2</sub> systems illustrates the positive effects derived from electronic metal-support interactions and points to a promising approach for improving or optimizing the performance of metal/oxide catalysts.

### **Development of techniques for *in-situ* characterization of powder catalysts: Time-resolved PDF, XAFS/XRD and XAFS/IR**

In the last two years, the Catalysis Group at BNL has been very active in developing instrumentation for the characterization of catalysts with pair-distribution function (PDF) analysis and the integration of XAFS and XRD or XAFS and IR. The development of techniques for characterizing the structural properties of catalysts under the high-pressure conditions of industrial processes is widely recognized as a top priority in the area of heterogeneous catalysis. *In-situ* PDF have been used to study the structure of amorphous metal and metal oxide nanoparticles. Using a XAFS/IR combination, we have investigated reaction mechanisms and correlations between structure/reactivity for CO oxidation and ethanol steam reforming on Cu-ceria and Ni-ceria catalysts.

### **Future plans**

In the future, the focus of this research program will be on obtaining a fundamental understanding of catalytic processes associated with the cleaning of fossil-derived fuels (desulfurization), the activation and utilization of CO<sub>2</sub>/CO (alcohol synthesis) and the use of ethanol as fuel (partial oxidation and reforming of the molecule). We will take advantage of the knowledge and expertise of the PI's for the preparation of well-defined model catalysts, the development of techniques for *in-situ* characterization, and the implementation on quantum-chemical methods for the study of reaction mechanisms. In a comprehensive research program, we will examine the effects of size, morphology and chemical environment, providing a truly atomistic view for explaining/predicting catalytic activity.

## **Publications (2011-2013)**

### **2011**

1. J.A. Rodriguez, P. Liu, Y. Takahashi, F. Viñes, L. Feria, E. Florez, K. Nakamura, and F. Illas, *Novel Au-TiC Catalysts for CO Oxidation and Desulfurization Processes*, Catal. Today, 166 , 2-9 (2011).

2. T. Gomez, E. Florez, J. A. Rodriguez and F. Illas, *Reactivity of transition metals (Pd, Pt, Cu, Ag, Au) towards molecular hydrogen dissociation: extended surfaces versus particles supported on TiC(001) or small is not always better and large is not always bad*, J. Phys. Chem. C, 115, 11666-11672 (2011).
3. F. Yang, J. Graciani, J. Evans, P. Liu, J. Hrbek, J. Fdez. Sanz, and J.A. Rodriguez, *CO Oxidation on Inverse CeO<sub>x</sub>/Cu(111) Catalysts: High Catalytic Activity and Ceria-Promoted Dissociation of O<sub>2</sub>*, J. Am. Chem. Soc. 133, 3444-3451 (2011).
4. L. Feria, J. A. Rodriguez, T. Jirsak, F. Illas, *Interaction of SO<sub>2</sub> with Cu/TiC(001) and Au/TiC(001): Towards a New Family of DeSO<sub>x</sub> Catalysts*, J. Catal., 279, 352-360 (2011).
5. F. Yang, Y.M. Choi, P. Liu, D. Stacchiola, J. Hrbek and J.A. Rodriguez, *Identification of 5-7 Defects in a Copper Oxide Surface*, J. Am. Chem. Soc. 133 11474-11477 (2011).
6. E. Florez, T. Gomez, J. A. Rodriguez, and F. Illas, *On the Dissociation of Molecular Hydrogen by Au Supported on Transition Metal Carbides: Choice of the Most Active Support*, Phys. Chem. Chem. Phys., 13, 6865-6871 (2011).
7. J. Ciston, R. Si, J.A. Rodriguez, J.C. Hanson, A. Martínez-Arias, M. Fernandez-García, and Y. Zhu, *Morphological and Structural Changes during the Reduction and Reoxidation of CuO/CeO<sub>2</sub> and Ce<sub>1-x</sub>Cu<sub>x</sub>O<sub>2</sub> Nanocatalysts: In-situ Studies with Environmental TEM, XRD and XAS*, J. Phys. Chem. C, 115, 13851-13859 (2011).
8. A. Frenkel, Q. Wang, N. Marinkovic, J.G. Chen, L. Barrio, R. Si, A. Lopez-Camara, A.M. Estrella, J.A. Rodriguez and J.C. Hanson, *Combining X-ray Absorption and X-ray Diffraction Techniques for in Situ Studies of Chemical Transformations in Heterogeneous Catalysis: Advantages and Limitations*, J. Phys. Chem. C, 115, 17884-17890 (2011).
9. F. Yang, S. Kundu, A.B. Vidal, P.J. Ramírez, S.D. Senanayake, D. Stacchiola, J. Evans, P. Liu and J.A. Rodriguez, *Unravelling the Behaviour of RuO<sub>x</sub> nanoparticles in Mixed-Metal Oxides: Special Structural and Catalytic Properties of RuO<sub>2</sub>/TiO<sub>2</sub>(110) Surfaces*, Angew. Chem. Int. Ed., 50, 10198-10202 (2011).
10. G.G. Asara, L. Feria, E. Florez, J. M. Ricart, P. Liu, J. A. Rodriguez, and F. Illas, *Theoretical study of the interaction of CO on TiC(001) and Au nanoparticles supported on TiC(001): probing the nature of the Au/TiC interface*, J. Phys. Chem. C, 115, 22495-22504 (2011).
11. F. Yang, Y.M. Choi, S. Agnoli, P. Liu, D. Stacchiola, J. Hrbek and J.A. Rodriguez, *CeO<sub>2</sub>↔CuO<sub>x</sub> Interactions and the Controlled Assembly of CeO<sub>2</sub>(111) and CeO<sub>2</sub>(100) Nanoparticles on an Oxidized Cu(111) Substrate*, J. Phys. Chem. C, 115, 23062-23066 (2011).
12. G. G. Asara, L. Feria, E. Florez, J. M. Ricart, P. Liu, J.A. Rodriguez, and F. Illas, *Theoretical Study of the Interaction of CO on TiC(001) and Au Nanoparticles Supported on TiC(001): Probing the Nature of the Au/TiC Interface*, J. Phys. Chem. C, 115 (2011) 22495-22504

## 2012

13. J. A. Rodriguez and F. Illas, *Activation of Noble Metals on Metal-Carbide*

- Surfaces: Novel Catalysts for CO Oxidation, Desulfurization and Hydrogenation Reactions*, Phys. Chem. Chem. Phys., 14, 427-428 (2012). **(invited)**
14. J.A. Rodriguez, Supported Gold in CO Oxidation, the Water-gas Shift, and DeSO<sub>x</sub> Reactions book chapter for *Supported Metals in Catalysis*, 2<sup>nd</sup> Edition (Editors: James Anderson and Marcos Fernandez-Garcia), Imperial College Press, London, 2012 **(invited book chapter)**.
  15. S. D. Senanayake<sup>1</sup>, J. Sadowski, Jaime Evans, S. Kundu, S. Agnoli, F. Yang, D. Stacchiola, J.I. Flege, J. Hrbek, and J.A. Rodriguez, *Nanopatterning in CeO<sub>2</sub>/Cu(111): A New Mechanism for Surface Reconstruction and Enhancement of Catalytic Activity*, J. Phys. Chem. Letters, 3, 839-843 (2012).
  16. A.B. Vidal, L. Feria, J. Evans, Y. Takahashi, P. Liu, K. Nakamura, F. Illas, and J.A. Rodriguez, *CO<sub>2</sub> Activation and Methanol Synthesis on Novel Cu/TiC and Au/TiC Catalysts*, J. Phys. Chem. Lett., 3, 2275-2280 (2012).
  17. T. Yan, D. W. Redman, W.-Y. Yu, D. W. Flaherty, J. A. Rodriguez, and C. B. Mullins, *CO Oxidation on Inverse Fe<sub>2</sub>O<sub>3</sub>/Au(111) Model Catalysts*, J. Catal. 294 216-222 (2012).
  18. J.A. Rodriguez, J.C. Hanson and P.J. Chupas, Goals and Challenges for the *In-situ* Characterization of Heterogeneous Catalysts, in: *In-situ Characterization of Heterogeneous Catalysts*, Editors: J.A. Rodriguez, J.C. Hanson and P.J. Chupas; Wiley: New York, 2012.
  19. A. I. Frenkel, J. A. Rodriguez, and J. G. Chen, *Synchrotron Techniques for In-situ Catalytic Studies: Capabilities, Challenges and Opportunities*, ACS Catalysis, 2, 2269-2280 (2012) **(invited)**.

### 2013

20. J. Carrasco, L. Barrio, P. Liu, J.A. Rodriguez, and M.V. Ganduglia-Pirovano, *Theoretical studies for the adsorption of CO and C on Ni(111) and Ni/CeO<sub>2</sub>(111): Evidence for a strong metal-support interaction*, J. Phys. Chem. C, 117, 8241-8247 (2012).
21. S. D. Senanayake, D. Stacchiola, and Jose A. Rodriguez, *Unique Properties of Ceria Nanoparticles Supported on Metals: Novel Inverse Ceria/Copper catalysts for CO Oxidation and the Water-Gas Shift Reaction*, Accounts of Chemical Research, in press DOI: 10.1021/ar300231p (2013) **(invited)**.
22. W. Xu, Z. Liu, A. Johnston-Peck, S.D. Senanayake, G. Zhou, D. Stacchiola, E. Stach and J.A. Rodriguez, *Steam Reforming of Ethanol on Ni/CeO<sub>2</sub>: Reaction Pathway and Interaction between Ni and the CeO<sub>2</sub> Support*, ACS Catalysis, in press, DOI: 10.1021/cs4000969 (2013).
23. D. J. Stacchiola, S. Senanayake, P. Liu and J. A. Rodriguez, *Fundamental studies of well-defined surfaces of mixed-metal oxides: Special properties of MO<sub>x</sub>/TiO<sub>2</sub>(110) {M= V, Ru, Ce or W}*, Chemical Reviews, in press, DOI: 10.1021/cr300316v (2012) **(invited)**.
24. H.Wang, W. Zhou, J.-X. Liu, R. Si, G. Sun, M.-Q. Zhong, H.-Y. Su, H.-B. Zhao, J. A. Rodriguez, S. J. Pennycook, J. C. Idrobo, W.-X. Li, Y. Kou, and D. Ma, *Platinum-Modulated Cobalt Nanocatalysts for Low-Temperature Aqueous-Phase Fischer–Tropsch Synthesis*, J. Am. Chem. Soc. 135, 4149-4158 (2013).

This page is intentionally blank.

**Tuesday Morning**

**Session IX**

This page is intentionally blank.

**Revealing the Surface Structure of Ceria Nanocrystals with Well-defined Facets**

Leading PI: Steven Overbury

Postdoc: Meijun Li, Amanda K. Mann

Contact: Chemical Science Division, Oak Ridge National Laboratory. 1 Bethel Valley Rd, Oak Ridge, TN 37831. Email: [wuzl@ornl.gov](mailto:wuzl@ornl.gov); [overburysh@ornl.gov](mailto:overburysh@ornl.gov)

Heterogeneous catalysis takes place on the surface of catalytic materials and undoubtedly the surface structure plays an essential role in catalysis. Establishing the structure-catalysis relationship is the Holy Grail in fundamental catalysis research and the basis for designing better catalytic materials. However, the structural complexity and heterogeneity of traditional catalysts prevents a full understanding of the interplay between the surface structure and catalytic behaviors. Recent advances in nanomaterials synthesis make it possible to achieve nanocrystals with crystallographically defined surface facets and high surface area, which can be considered as ideal model catalysts for catalytic studies under realistic conditions. Application of these well-faceted nanocrystals in catalysis has generated interesting catalytic function that is dependent on the surface structure of the nanomaterials. To understand the structure dependence, a prerequisite is the full characterization of the surface sites of these nanocrystals during the catalytic process. In our project, we have investigated the surface structure of a typical metal oxide nanocrystal, ceria nanoshapes (rods (mainly {110} facet), cubes ({100}), and octahedra ({111})) *via* two different approaches, i.e., direct visualization *via* high resolution electron microscopy, indirect probing *via* model molecules and model reactions.<sup>1-5</sup> We found that although the ceria nanoshapes seem well-faceted on the surface, they are not perfectly structured but contain various defects on the surface and in the bulk that can have a profound effect on the catalytic chemistry during ceria catalysis. It is suggested that the surface structure of ceria controls the catalytic performance through the structure-dependent surface sites geometry, surface vacancy formation energy, defect sites and coordinatively unsaturated sites on ceria. The insights provide bases for rational design of better and novel catalytic materials.

**References:**

1. Wu, Z. L.; Li, M. J.; Howe, J.; Meyer, H. M.; Overbury, S. H. *Langmuir* **26**, 16595 (2010).
2. Wu, Z. L.; Li, M. J.; Overbury, S. H. *J. Catal.* **285**, 61 (2012).
3. Wu, Z. L.; Li, M. J.; Mullins, D. R.; Overbury, S. H. *ACS Catal.* **2**, 2224 (2012).
4. Qiao, Z. A.; Wu, Z. L.; Dai, S. *ChemSusChem*, invited submission (2013).
5. Li, M. J.; Wu, Z. L.; Overbury, S. H. *J. Catal.*, submitted (2013).

**Acknowledgements:** This Research is sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy. Part of the work was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the User Facility Division, Office of Basic Energy Science, U.S. Department of Energy.

**Selectivity Control through Modification of Metal Catalysts with Organic Monolayers**

Additional PI: Daniel K. Schwartz

Students: Carolyn Schoenbaum, Rudy Kahsar

Collaborators: Jeroen van Bokhoven (ETH-Zurich)

Contacts: University of Colorado, Dept. of Chemical and Biological Engineering  
UCB 424, ECCH 111; Boulder, CO 80309-0424; [will.medlin@colorado.edu](mailto:will.medlin@colorado.edu)

**Goal**

Investigate structure-reactivity relationships for supported metal catalysts modified by self-assembled monolayers of organic thiolates, as a method for understanding the role of the near-surface environment in controlling surface reactivity.

**DOE Interest**

By tailoring the properties of the monolayer-forming species, one can alter adsorbate-adsorbate interactions to control activity and selectivity in heterogeneous catalysis. Self-assembled monolayers represent a useful model platform for understanding how the properties of a metal-solution interface alter reactivity. A combination of catalyst screening experiments and surface characterization is being used to understand mechanisms by which monolayers can influence catalyst activity and selectivity in several probe reactions.

**Recent Progress**

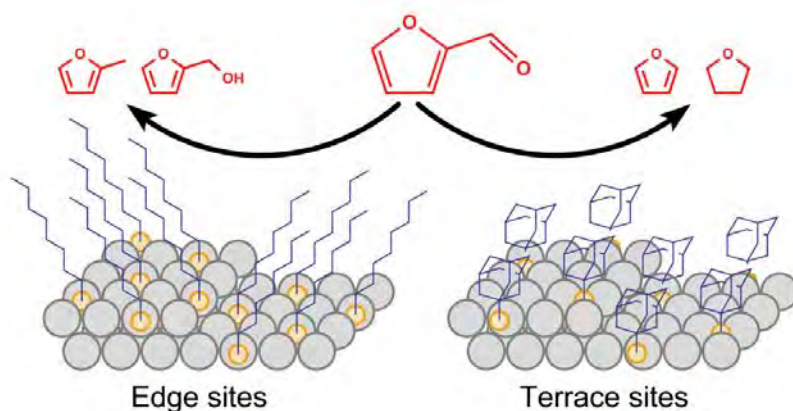
We have studied several reactions on supported metal catalysts modified by self-assembled monolayers, focusing on mechanisms by which SAMs modify selectivity. In general, we have found that SAMs can modify surface reactivity by at least two mechanisms. The first involves controlling *surface crowding*, by using the self-organizing properties of the SAM to generate overlayers with differing surface densities to control ensemble size and/or the magnitude of electronic effects. The second mechanism involves direct, *non-covalent interactions* between the organic function of the tail and the organic reactant; these interactions can change the preferred alignment of adsorbed reactants.

The relationship between surface crowding and catalytic activity was recently investigated using SAMs on Pd/Al<sub>2</sub>O<sub>3</sub> catalysts. The surface density of the thiolate modifier was controlled by varying the steric bulk of the organic substituent. Acetylene hydrogenation, which results in uncontrolled crowding due to carbonaceous “coke” formation on the catalyst, was found to be insensitive to modification by the thiols. For hydrogenation reactions less associated with uncontrolled coking, crowding – and therefore reactivity – could be controlled systematically using SAMs. In particular, ethylene hydrogenation was 17 times faster on AT-coated surfaces than on C18-coated surfaces, consistent with the additional accessibility to specific sites



unavailable on C18-modified surfaces. The effect of modifier density on reactivity was found to be dramatically different for several mono- and bi-functional reactants, suggesting that controlled crowding with SAMs can be used to understand reaction structure sensitivity and active site requirements in catalysis.

Surface crowding effects have also been probed in the hydrogenation of furfural over Pd catalysts (Scheme 1). Vibrational spectroscopy studies demonstrate that the selectivity improvement is achieved by controlling the availability of specific sites for the hydrogenation of furfural on supported Pd catalysts through the selection of an appropriate SAM. Increasing SAM density by controlling the steric bulk of the organic tail ligand restricts adsorption on terrace sites and dramatically increases selectivity to desired products furfuryl alcohol and methylfuran. This technique of active-site selection simultaneously serves both to enhance selectivity and provide insight into the reaction mechanism. We have similar selectivity-control effects that are mainly due to surface crowding and electronic modification with sulphur for the selective hydrogenation of 1-epoxy-3-butene and 4-nitrostyrene.



**Scheme 1.** Using steric bulk to control SAM density strongly affects selectivity in the hydrogenation of furfural on Pd catalysts.

In general, we have found that non-covalent interactions between SAM modifiers and reactants are more prevalent in reactions involving larger reactant molecules, where there is a more extensive opportunity for such interactions. For example, Pd/Al<sub>2</sub>O<sub>3</sub> catalysts coated with various thiolate self-assembled monolayers (SAMs) were used to direct the partial hydrogenation of eighteen-carbon polyunsaturated fatty acids, yielding a product stream enriched in monounsaturated fatty acids (with low saturated fatty acid content), a favorable result for increasing the oxidative stability of biodiesel. The uncoated Pd/Al<sub>2</sub>O<sub>3</sub> catalyst quickly saturated all fatty acid reactants under hydrogenation conditions, but the addition of alkanethiol SAMs markedly increased the reaction selectivity to the monounsaturated product oleic acid, to a level of 80–90% even at conversions >70%. This effect, which is attributed to steric effects between the SAMs and reactants, was consistent with the relative consumption rates of linoleic and oleic acid using alkanethiol coated and uncoated Pd/Al<sub>2</sub>O<sub>3</sub> catalysts. With an uncoated catalyst, each fatty acid, regardless of its degree of saturation had a similar turnover frequency. Using

alkanethiol coated Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, the activity was reduced by a factor of 4 for polyunsaturated reactants and by a factor of 100 for the monounsaturated reactants. In contrast to the hydrophobic alkanethiol modifiers, hydrophilic thioglycerol SAM modifiers were found to strongly inhibit reaction kinetics for all fatty acid reactants.

### Future Plans

*Tuning non-covalent interactions using SAMs.* We have recently observed that non-covalent interactions between alkanethiols and SAMs can yield dramatic improvement in the selectivity for hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes on Pd and Pt catalysts. Structure-property relations for such systems are currently being investigated.

*Variation of supported metal composition.* To date, we have focused on using SAMs to control selectivity on a select group of metals (Pd, Pt, Cu). A key question is whether the effects of SAMs are generalizable to many other systems, and in particular whether metal catalysts that have been optimized in the absence of SAMs can be further improved by SAM addition.

*Variation of attachment chemistry.* We are exploring how variation of the surface attachment chemistry (e.g., with dithiols and siloxane-based species) can influence SAM modifying effects.

### Publications (2011-2013)

S.T. Marshall, D.K. Schwartz, J.W. Medlin, “Adsorption of oxygenates on alkanethiol-functionalized Pd(111) surfaces: Mechanistic insights into the role of self-assembled monolayers on catalysis”, *Langmuir*, **27** (2011) 6731-6737.

K.R. Kahsar, D.K. Schwartz, J.W. Medlin, “Liquid- and Vapor-Phase Hydrogenation of 1-Epoxy-3-butene Using Self-Assembled Monolayer Coated Palladium and Platinum Catalysts”, *Applied Catalysis A: Chemical*, **445-446** (2012) 102-106.

M. Makosch, V. Bumbálek, J. Sá, W.-I. Lin, M. Rovezzi, J.W. Medlin, K. Hungerbühler, J.A. van Bokhoven, “Organic thiol modified Pt/TiO<sub>2</sub> catalysts to control chemoselective hydrogenation of substituted nitroarenes”, *ACS Catalysis* **2** (2012) 2079-2081.

C.A. Schoenbaum, D.K. Schwartz, J.W. Medlin, “Controlling surface crowding on a Pd catalyst with thiolate self-assembled monolayers”, *Journal of Catalysis* **303** (2013) 92-99.

J.W. Medlin, “Understanding and controlling reactivity of unsaturated oxygenates and polyols on metal catalysts”, *ACS Catalysis*, **1** (2011) 1284-1297.

S.T. Marshall, J.W. Medlin, “Surface-level mechanistic studies of adsorbate–adsorbate interactions in heterogeneous catalysis by metals”, *Surface Science Reports*, **66** (2011) 173-184.

# Poster Presentations

This page is intentionally blank.

## Oxo Rhenium and Molybdenum Catalysts for C-O Cleavage and Deoxygenation

Postdocs: Dr. Kothanda Rama Pichaandi and Dr. Aysegul Senocak  
Students: Mr. Isaac Corn, Ms. Jing Yi, and Ms. Shuo Liu  
Affiliations: Department of Chemistry, Purdue University  
Contacts: Purdue University, Department of Chemistry, 560 Oval Drive, West Lafayette, IN 47907. E-mail: mabuomar@purdue.edu

### Goal

Develop efficient and selective catalytic processes that remove oxygen atoms from biomass derived compounds.

### DOE Interest

Limited supply of nonrenewable crude oil and its impact on climate change necessitate a shift towards renewable resources. Plants are solar factories that utilize CO<sub>2</sub>, H<sub>2</sub>O, and sunlight to make lignocellulosic matter. However, biomass components, xylans, cellulose, and lignin are rich in oxygen. One of the major obstacles in utilizing biomass is the challenge of removing oxygen atoms from carbohydrates and polyols to increase the energy content and decrease the boiling point. A desirable catalytic system would operate under reasonably mild conditions, tolerate water and air, use robust and recyclable catalyst, and give high product selectivity. Our approach has been to develop catalysts for the deoxydehydration (DODH) of polyols using alcohols as the reductants because alkenes are valuable feedstock and they can easily be transformed to longer hydrocarbon chains via olefin metathesis. The use of high boiling alcohols provides safer conditions in comparison to hydrogen and allows for the coupling of two important chemical reactions into one transformation as the oxidation of alcohols to ketones is a highly sought after process. The fundamental chemistry we are studying in combination with quantitative kinetics will provide the foundation for future designs and use of catalysts in biomass conversions.

### Recent Progress

*Rhenium-Catalyzed DODH of Biomass-Derived Polyols to Small and Useful Organics.* We described a catalytic method that uses neat glycerol to make small and useful organics (SUO). The catalyst, methyltrioxorhenium (MTO), is tolerant to water and air. The substrate, glycerol, participates in transfer hydrogenation and deoxygenation to give volatile products, allyl alcohol, propanal, and acrolein, leaving the non-volatile dihydroxyacetone (DHA) by-product in the residue. This reaction can also be carried out in the presence of an alcohol as a solvent and transfer hydrogenation agent. Other biomass-derived polyols (erythritol and threitol) can be used to make small organic molecules. Allyl alcohol and 2,5-dihydrofuran are valuable building-block chemicals that have received wide use in the pharmaceutical and polymer industries.

*Kinetics and Mechanism of MTO-Catalyzed DODH of Diols to Alkenes.* Catalytic deoxydehydration (DODH) of vicinal diols is carried out employing methyltrioxorhenium (MTO) as the catalyst and a sacrificial alcohol as the reducing agent. The reaction kinetics feature an induction period when MTO is added last, and show zero-order in [diol] and half-order dependence on [catalyst]. The rate-determining step involves reaction with alcohol as

evidenced by a KIE of 1.4 and a large negative entropy of activation ( $\Delta S^\ddagger = -154 \pm 33 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The active form of the catalyst is methyldioxorhenium(V) (MDO), which is formed by reduction of MTO by alcohol or via a novel C-C bond cleavage of an MTO-diolate complex. The majority of the MDO-diolate complex is present in dinuclear form giving rise to the  $[\text{Re}]^{1/2}$  dependence. The MDO-diolate complex undergoes further reduction by alcohol in the RDS to give rise to a putative rhenium(III) diolate. The latter is the active species in DODH extruding stereoselectively trans-stilbene from (R,R)-(+)-hydrobenzoin to regenerate MDO and complete the catalytic cycle.

*Atomic Rhenium Nanoparticles (NP) as Catalysts in Alcohol Dehydrogenation.* Small rhenium nanocrystalline particles (2nm) are formed from  $\text{NH}_4\text{ReO}_4$  at 180 °C in neat aqueous-phase alcohol without any support. The Re NP catalyze the direct dehydrogenation of different secondary and benzyl alcohols to ketones or aldehydes. The NP catalyst can be employed at 0.10 mol % loading and is recyclable without loss of activity 9 times. The metallic Re nanocrystallines are formed by reduction of Re(VII) oxide by alcohols and are tolerant with over 10 equiv. mercury. Transmission electron microscopy (TEM)/high resolution-TEM is shown in Figure 1 below.

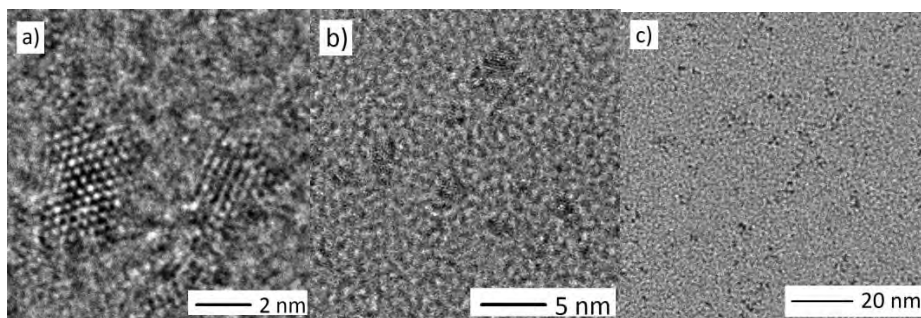


Figure 1. TEM/HR-TEM of Black-Solid Re Nanocrystalline from  $\text{NH}_4\text{ReO}_4$  in neat 3-Octanol at 180 °C for 10 h.

### Future Plans

*Spectroscopy and characterization of Re NP catalyst:* Complete the characterization of the Re NP catalyst in collaboration with Dr. Jeff Miller at ANL using XANES and EXAFS (in situ and operando). Study the reactions kinetics, and characterize the rhenium species under operando conditions.

*Catalysis with unusual metal oxo carbonyl complexes:* Our successful preparation of rhenium(III) and (V) containing a  $\pi$ -donor oxo and  $\pi$ -acceptor carbonyl ligands opens the door to very exciting new chemistry for us to explore in the context of deoxygenation of biomass-derived compounds as well as new electrochemical reduction of  $\text{CO}_2$ .

### Publications (2012-2013)

1. Basudeb Saha, Saikat Dutta, and Mahdi M. Abu-Omar, "Aerobic oxidation of 5-hydroxymethylfurfural with homogeneous and nanoparticulate catalysts " *Catal. Sci. Technol.* **2012**, 2, 79-81.

2. Kothanda Rama Pichaandi, Phillip E. Fanwick, and Mahdi M. Abu-Omar, "Trioxorhena(VII)carborane Anion and Its Methyl-Substituted Analogue: Synthesis, Structure, DFT, and Catalytic Studies" *Organometallics* **2012**, *31*, 1888-1896.
3. Jing Yi, Shuo Liu, and Mahdi M. Abu-Omar, "Rhenium-Catalyzed Transfer Hydrogenation and Deoxygenation of Biomass-Derived Polyols to Small and Useful Organics" *ChemSusChem* **2012**, *5*, 1401-1404.
4. Basudeb Saha, Dinesh Gupta, Mahdi M. Abu-Omar, Arindam Modak, and Asim Bhaumik, "Porphyrin based porous organic polymer supported iron(III) catalyst for efficient aerobic oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid" *J. Cat.* **2013**, *299*, 316-320.
5. Isaac R. Corn, Pablo D. Astudillo-Sánchez, Michael J. Zdilla, Phillip E. Fanwick, Michael J. Shaw, Jeffery T. Miller, Dennis H. Evans, and Mahdi M. Abu-Omar, "Synthesis and electrochemical reactivity of molybdenum dicarbonyl supported by redox active  $\alpha$ -diimine ligand" *Inorg. Chem.* **2013**, ASAP (DOI: 10.1021/ic400348j).
6. Shuo Liu, Aysegul Senocak, Jessica L. Smeltz, Linan Yang, Benjamin Wegenhart, Jing Yi, Hilka Kenttämä, Elon A. Ison, and Mahdi M. Abu-Omar, "Mechanism of MTO-Catalyzed Deoxydehydration (DODH) of Diols to Alkenes" *Organometallics* **2013**, in press.

## Bridging Homogeneous and Heterogeneous Catalysis through Ion-Exchangeable Materials

Students: Tanya M. Breault, Joseph E. Yourey, Benjamin M. Klepser  
 Contacts: University of Michigan Department of Chemistry, 930 N. University Avenue, Ann Arbor, MI 48109, bartmb@umich.edu

### Goal

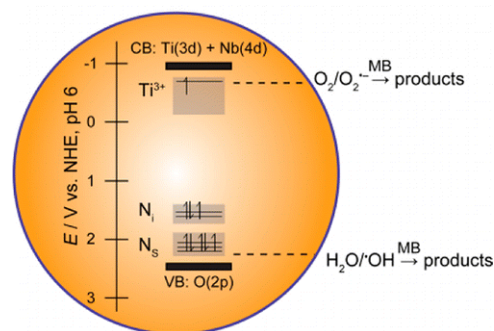
To use solar radiation to accomplish energy-relevant redox transformations such as water-oxidation using titania-based (anatase and ion-exchangeable perovskite) materials and molecular catalysts together *under working reaction conditions*.

### DOE Interest

Developing materials that generate charge carriers over as broad of the solar spectrum as possible is a key requirement for increasing the efficiencies of photocatalytic chemical reactions such as pollutant dye degradation and water splitting. Titania-based materials have been widely explored for these reactions, and the sol-gel methods developed and rationale behind the selected ions are quite general and will influence other energy-based programs. For example 2-D perovskites oxides are studied as solid-oxide fuel cell electrolytes. Ionic conductivity, just like electronic conductivity, is a sensitive function of defect structure. Therefore, the ability to control and eliminate vacancies at the level of synthesis has broad impact in catalysis science.

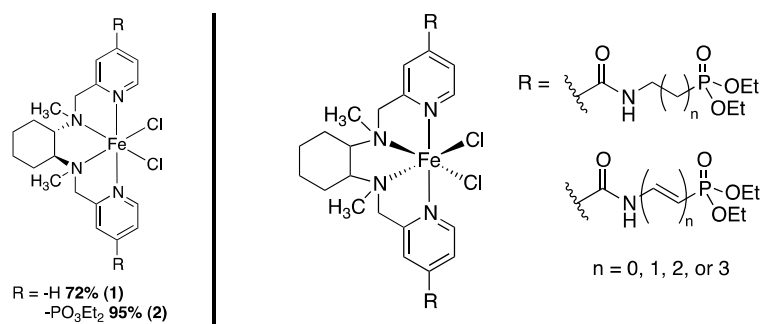
### Recent Progress

*Synthesis, electron structure, and photocatalysis on visible-light absorbing  $\text{TiO}_2:(\text{Nb},\text{N})$  compositions:* A series of co-incorporated compounds,  $\text{TiO}_2:(\text{Nb},\text{N})$ , were synthesized via a facile sol-gel process.<sup>1</sup> This technique allows us to synthesize mono-alloyed compositions,  $\text{Ti}_{1-(5x/4)}\text{Nb}_x\text{O}_2$ , which are converted to co-incorporated forms by annealing under flowing ammonia to afford  $\text{Ti}_{1-(5x/4)}\text{Nb}_x\text{O}_{2-y-\delta}\text{N}_y$ , referred to as NbN-x, where  $x = 1 - 30$  % niobium. The series of compounds crystallize in the anatase structure, determined by powder X-ray diffraction. Diffuse reflectance UV-vis spectroscopy shows that the optical gap ranges from 2.37 eV ( $x = 1$ ) to 2.20 eV ( $x = 30$ ). It is noted that without the nitridation treatment, the absorption edge is 3.1 eV regardless of Nb content. At hole mole-% Nb, these compounds degrade monolayer coverage of methylene blue due at a rate that  $\sim 7$  times faster than  $\text{TiO}_2$  alone.<sup>2</sup> We also show that in addition to redox chemistry leading to dye degradation by active oxygen species, our champion compound, NbN-25, acts as a *visible-light* responsive water oxidation photocatalyst in the presence of a  $\text{RuO}_2$  co-catalyst and  $\text{IO}_3^-$  sacrificial electron acceptor.<sup>3</sup>



**Figure 1.** Electronic structure of  $\text{TiO}_2:(\text{Nb},\text{N})$ -25 photocatalyst.





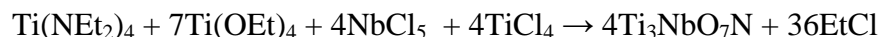
**Figure 2.** Phosphonate-modified iron water-oxidation catalysts.

*Phosphonate-modified Fe water-oxidation catalysts:* In 2011, Fillol *et al.* showed that the complex  $\text{Fe}(\text{bpmcn})\text{Cl}_2$  ( $\text{bpmcn} = N,N'$ -bis(2-methyl-pyridyl)- $N,N'$ -dimethyl-cyclohexane diamine) oxidizes water with concomitant reduction of  $\text{Ce}^{4+}$  in the dark. We have prepared a phosphonate-modified version of the catalyst to tether to anatase-structured  $\text{TiO}_2$  electrodes. We show that we can covalently link the molecule to  $\text{TiO}_2$ , and that the rest potential of the unmodified electrode (-0.4 V vs. RHE) shifts to more positive potentials once the surface has been modified with catalyst **2** (0.35 V vs. RHE), suggesting that holes are

oxidizing the Fe catalyst. The phosphonate group gives a chemically stable catalyst bound to the surface, however the current density observed for the modified electrodes prepared to date is less than what is observed on a bare  $\text{TiO}_2$  electrode. Back  $e^-$  transfer from the conduction band of  $\text{TiO}_2$  to the catalyst is believed to hinder activity.

### Future Plans

*Non-hydrolytic sol-gel processing methods to generate oxynitrides.* Non-hydrolytic sol-gel chemistry that uses metal halides, alkoxides, and amides in non-aqueous solution may allow for simultaneously incorporating both nitrogen and oxygen on the anion sublattice in a single chemical reaction, giving a true co-alloy. An example reaction is:



All of these precursors are soluble in THF and toluene; therefore this reaction can be carried out under an inert  $\text{N}_2$  atmosphere to prevent oxidation of the amido groups. Constructing photoanodes with good Ohmic contact in order to elucidate the electronic structure of this composition (and other future co-incorporated compositions) becomes feasible. With well contacted photoelectrodes in hand, co-catalyst loading and necking treatments with  $\text{TiCl}_4$  will be performed to optimize the performance of these electrodes as we continue to study these visible-light harvesting compounds for photocatalytic water splitting.

*Modifying the covalent tether to inhibit potential back electron transfer.* We can retard back electron transfer from our iron-based catalysts by elongating and conjugating the covalent tether, similar to what has been done in DSSCs. Currently, we are synthesizing derivatives of **2** with the modified tethers illustrated in Scheme 2. Modifying the tether length can be rapidly achieved from the carboxylate modified ligand simply by adding amines with various chain lengths

attached to the desired anchor; all of this chemistry is compatible with what we have developed in in the previous work illustrated in Figure 2.

### **Publications (2011 – 2013)**

1. Breault, T. M.; Bartlett, B. M. Lowering the Band-gap of Anatase-structured TiO<sub>2</sub> by Co-alloying with Nb and N: Electronic Structure and Photocatalytic Degradation of Methylene Blue Dye. *J. Phys. Chem. C* **2012**, *116*, 5986-5994.
2. Breault, T. M.; Bartlett, B. M. Composition-Dependence of TiO<sub>2</sub>:(Nb,N)-*x* Compounds on the Rate of Photocatalytic Methylene Blue Dye Degradation. *J. Phys. Chem. C* **2013**, Just Accepted, DOI: 10.1021/jp312199t.
3. Breault, T. M.; Bartlett, B. M. Visible Light Water Oxidation Using a Co-Catalyst Loaded Anatase-Structured Ti<sub>1-(5*x*/4)</sub>Nb<sub>*x*</sub>O<sub>2-*y*-*δ*</sub>N<sub>*y*</sub> Compound. Submitted to *Inorg. Chem.*

**Photocatalysis of modified transition metal oxide surfaces**

Post docs: Junguang Tao, James Lallo  
Students: Tim Luttrell, Alan Kramer, Sandamali Halpegamage  
Contact: Department of Physics, University of South Florida, Tampa, FL 33620;  
[mbatzill@usf.edu](mailto:mbatzill@usf.edu)

**Goal:**

The goal is to establish a cause-effect relationship for photocatalytic activity variations of different structures of the same material; and furthermore gain fundamental understanding on modification of photocatalysts by compositional or surface modifications. Gaining atomic scale understanding of how surface and bulk modifications alter the (photo) reactivity will lead to design principles for next generation photocatalysts.

In the current funding period the research objectives have been: (a) Preparation of epitaxial anatase  $\text{TiO}_2$  samples by pulsed laser deposition. (b) Comparison of hydrogen diffusion on the rutile  $\text{TiO}_2(011)\text{-}2\times 1$  with that of the (110) surface. (c) Determining the stability of the  $\text{TiO}_2(011)\text{-}2\times 1$  reconstruction upon interactions with adsorbates. (d) Characterization of adsorption and (thermal and photo) reaction of molecules with nitro-endgroups, (e) Exploring the possibility of modifying planar model photocatalyst surfaces with graphene to enable fundamental studies on reported enhanced photocatalytic activities of graphene modified transition metal oxides.

**DOE interest:**

Understanding the structure property relationship of surfaces is a central scheme for chemical transformation reactions at surfaces.  $\text{TiO}_2$  is the model system for chemical properties of transition metal oxides. Our studies have given new insight in this widely studied material and thus significantly contribute to the understanding of this material and the surface science of transition metal oxides in general. Making photocatalysts more efficient is an important goal for DOE. Our studies explore the fundamentals of how, by modifying simple oxides with dopants or through interfaces with dissimilar materials, this may be achieved.

**Recent Progress:**

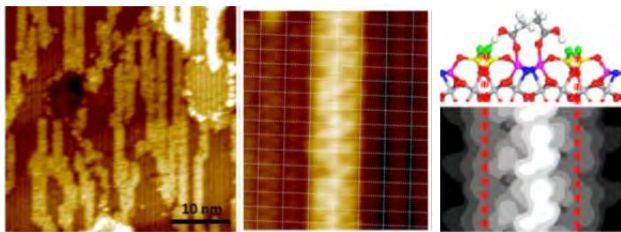
***Improvement of epitaxial  $\text{TiO}_2$  film preparation by PLD and characterization of their photoactivity:*** A central aspect of this project has been the preparation of well-defined  $\text{TiO}_2$  films, which then can be modified by dopants and/or heterostructures. Additionally, we hoped to establish from which region in the sample away from the surface charge carriers can be extracted to contribute in surface reactions. For the latter we evaluate the photoactivity as a function of film thickness. Using photocatalytic decomposition of organic dyes we measure photocatalytic activity of our prepared films to decrease in the order of anatase (001) > anatase (101) > rutile (011). Also the photoactivity appears to saturate for anatase films with a thickness of ~15 nm suggesting that in any  $\text{TiO}_2$ -photocatalyst only the topmost ~15 nm contribute charge carriers for reactions. For rutile the film thickness at which saturation occurs is even shorter and this may contribute to the lower photocatalytic activity of rutile compared to anatase.

**Characterization of adsorption nitro-endgroup molecules on  $TiO_2$ :**

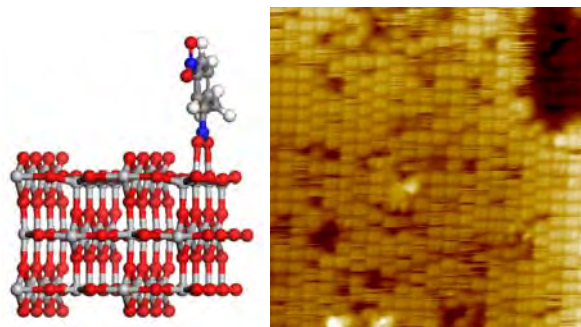
In order to characterize photoreactions in UHV good probe molecules are needed. In the past mainly carboxylic acids were used for this purpose. However, this is a dissociatively adsorbed molecule which also leads to the adsorption of hydrogen at the surface, which may play an important role in charge trapping at the surface. In this study we characterized the adsorption of 2-4 dinitrotoluene (DNT) on rutile  $TiO_2(110)$ .

We show in combination of STM and DFT simulations (by our collaborators) that DNT adsorbs strongly and molecularly intact through one of its two nitro-groups at the surface. At the saturation coverage an ordered  $2 \times 1$  adsorbate overlayer is formed. Fig. 1 shows the adsorption configuration and STM results. At elevated temperatures ( $>300$  C) the molecules react with sub-surface excess titanium on the slightly reduced substrates. In-situ UV radiation desorbs the molecule from the surface thus showing promise for model photocatalyst studies.

**Adsorbate induced restructuring of  $TiO_2(011)-2 \times 1$  and the formation of 1D adsorbate clusters:** Metal oxide surfaces have been thought to be fairly rigid. On the example of rutile  $TiO_2(011)$  we show that this is not necessarily the case. This surface restructures by interacting with molecules. The synergic effect of adsorbates causes a strictly directional reorganization of the substrate,



**Fig. 2: Adsorbate induced restructuring of the substrate results in formation of 1D adsorbate clusters of acetate adsorbed on  $TiO_2(011)-2 \times 1$ . Left STM images and right DFT simulations of adsorbate structure.**

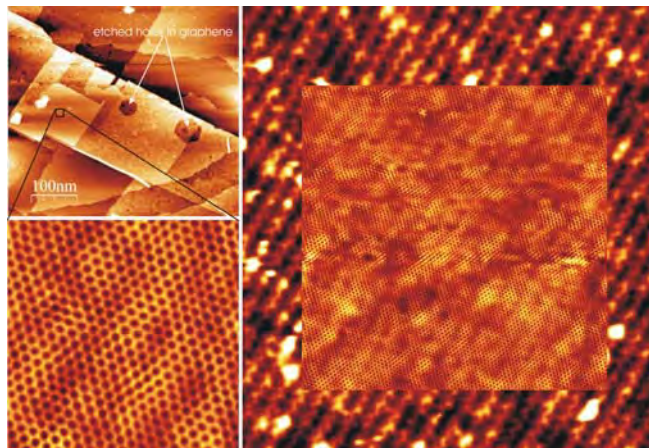


**Fig. 1: Adsorption of DNT on  $TiO_2(110)$ . Left, model of the most stable adsorption configuration of calculated by DFT. Right, STM image of a  $2 \times 1$  overlayer structure of adsorbed DNT.**

which results in one-dimensional adsorbate cluster formation, see Fig. 2. The increase in the surface energy of the restructured surface is compensated for by the larger molecular adsorption energy. The reversible change of the surface structure suggests a dynamic surface that may change its properties in response to adsorbed molecules. These results are published in *Phys. Rev. Lett.* 108, 106105 (2012).

**Exploring the possibility of modifying planar model photocatalyst surfaces with graphene:**

In recent years, a significant body of work has appeared in the literature that suggests that the photocatalytic properties of transition metal oxides can be enhanced by modifying their surfaces with graphene. In practical materials this is accomplished by adsorbing graphene oxide in solution and subsequent reduction of the graphene oxide. In order to prepare planar model systems that will enable us to do surface science characterizations of the graphene/metal oxide interface we transferred graphene to a metal oxide surface. Initial studies, shown in Fig. 3, show the successful transfer onto a  $\text{SrTiO}_3(001)$  surface.



**Fig. 3:** STM images of graphene transferred to  $\text{SrTiO}_3(001)$  substrate. Upper left shows a large scale image with hexagonal holes indicating the onset of etching of the graphene by release of oxygen from the substrate. On flat areas atomic resolved images of the graphene honeycomb are possible (lower left) The right image shows a superposition of an STM image of graphene ( $20 \times 20 \text{ nm}$ ) on an STM image of the clean  $\text{SrTiO}_3(001)$  surface ( $30 \times 30 \text{ nm}$ ).

**Publications (2010-2013):**

- “Scanning tunneling microscopy and photoemission studies of graphene supported on  $\text{SrTiO}_3(001)$ ” R. Addou, H. Coy-Diaz, M. Batzill, **submitted**
- “A combined surface science and DFT study of the adsorption of dinitrotoluene (2,4-DNT) on rutile  $\text{TiO}_2(110)$ : Molecular scale insight for sensing of explosives” J. Tao, Q. Cuan, S. Halpegamage, R. Addou, X.Q. Gong, M. Batzill, **submitted**
- “Diffusion and Reaction of Hydrogen on Rutile  $\text{TiO}_2(011)-2 \times 1$ : The Role of Surface Structure” J. Tao, Q. Cuan, X.Q. Gong, M. Batzill **J. Phys. Chem. C** 116, 20438 (2012).
- “Adsorbate Induced Restructuring of  $\text{TiO}_2(011)-(2 \times 1)$  Leads to One-Dimensional Nanocluster Formation” Q. Cuan, J. Tao, X.Q. Gong, M. Batzill **Phys. Rev. Lett.** 108, 106105 (2012).
- “Fundamental aspects of surface engineering of transition metal oxide photocatalysts” M. Batzill, **Energy and Environ. Sci.** 4, 3275-3286 (2011).
- “Adsorption of Acetic Acid on Rutile  $\text{TiO}_2(110)$  vs  $(011)-2 \times 1$  Surfaces” J. Tao, T. Luttrell, J. Bylsma, M. Batzill **J. Phys. Chem. C** 115, 3434-3442 (2011).
- “A two dimensional phase of  $\text{TiO}_2$  with a reduced band gap” J.G. Tao, T. Luttrell, M. Batzill **Nature Chemistry** 3, 296-300 (2011).
- “Role of Surface Structure on the Charge Trapping in  $\text{TiO}_2$  Photocatalysts” J.G. Tao, M. Batzill **J. Phys. Chem. Lett.** 1, 3200 (2010).
- “Nano-ripple formation on  $\text{TiO}_2(110)$  by low-energy grazing incidence ion sputtering” T. Luttrell, M. Batzill **Phys. Rev. B** 82, 035408 (2010).

## Metal-Metal Bonded Reaction Intermediates in Catalytic C–H Functionalization

Students: Amanda K. M. Long, George Timmer, Katherine Kornecki,  
Collaborators: Huw Davies (Emory University), Tobias Ritter (Harvard University)  
Contact: Department of Chemistry, University of Wisconsin – Madison, 1101 University Ave., Madison, WI 53706; [berry@chem.wisc.edu](mailto:berry@chem.wisc.edu)

**Goal**

To define the fundamental coordination chemistry and mechanisms of C–H functionalization by metal-metal bonded compounds of Ru and Rh of the general formula  $M_2(\text{ligand})_4$ , where M = Ru or Rh and ligand = a monoanionic, bridging ligand.

**DOE Interest**

Direct functionalization of C–H bonds has the potential to greatly improve the efficiency of chemical synthesis. Rather than relying on energy-intensive and atom un-economical functional group transformations, useful organic molecules or materials can instead be prepared more rapidly by utilizing ubiquitous C–H bonds as latent functional groups.  $Rh_2$  and  $Ru_2$  complexes are some of the best catalysts for promoting these reactions, but the reaction mechanisms are poorly understood. Mechanistic insight into these processes can lead to further improved catalyst development.

**Recent Progress**

*Mechanistic Studies of  $Rh_2$ -Catalyzed C–H Amination:* We have recently discovered a new, single-electron transfer mechanism that is operable in intermolecular C–H amination catalyzed by the dirhodium catalyst  $Rh_2(\text{esp})_2$ , where  $\text{esp} = \alpha, \alpha, \alpha', \alpha'$ -tetramethyl-1,3-benzenedipropanoate [1]. This mechanism accounts for about 60 % of the yield of the product from these reactions, and relies upon the ability of the  $Rh_2(\text{esp})_2$  catalyst to be oxidized to the  $Rh_2(\text{II,III})$  oxidation state. By preparing  $Rh_2$  complexes that are structurally analogous to  $Rh_2(\text{esp})_2$  but that bear redox non-innocent dicarboxylate ligands, we found that  $Rh_2(\text{esp})_2$  and its analogs perform equivalently in intramolecular C–H amination reactions [2]. However, the  $Rh_2$  compounds bearing redox non-innocent ligands could not access the single-electron transfer mechanism in intermolecular C–H amination and were thus poor catalysts for these reactions. These results suggest that  $Rh_2$ -centered oxidation (rather than ligand-centered oxidation) is essential for the accessibility of the single-electron transfer mechanism. In further work, we have utilized an amidate analog of the  $\text{esp}$  ligand to stabilize a mixed-valent  $Rh_2(\text{II,III})$  complex that is an exceptional catalyst for intramolecular C–H amination [3]. The added stability of the complex that stems from its higher oxidation state leads to an increase in the catalyst turnover numbers (vs  $Rh_2(\text{esp})_2$ ) by about a factor of three.

*Isolation of a Donor/Acceptor Carbene Complex:* We have observed a new, metastable intermediate species upon reaction of dirhodium complexes with organic diazo compounds and are currently employing several spectroscopic methods (NMR



spectroscopy, resonance Raman spectroscopy, and X-ray absorption spectroscopy), in attempt to identify this novel species. Currently available data are highly suggestive that this intermediate is a dirhodium carbene complex, a long sought after species whose characterization has remained elusive for decades. The chemical reactivity of this new species is consistent with its formulation as a carbene complex, as it is shown to affect cyclopropanation of alkenes as well as insertion of the carbene moiety into C–H bonds.

*Diruthenium Nitride Chemistry:* We have characterized an unprecedented intramolecular aryl C–H amination reaction involving a nitrido compound that occurs under surprisingly mild conditions [4]. We used variable temperature kinetic measurements to determine activation parameters and the kinetic isotope effect of aryl C–H functionalization, and we determined the overall reaction enthalpy via calorimetric techniques. These experimental benchmarks were used to calibrate DFT calculations of the reaction coordinate pathway, with the result that C–H amination occurs via an electrophilic aromatic substitution mechanism [5,6]. Recently, we have used a new ligand design to disfavor intramolecular C–H amination to promote intermolecular C–H amination, as evidenced by the conversion of  $\text{PPh}_3$  to  $\text{H}_2\text{NPPh}_3$  [7]. This N atom transfer reaction can be incorporated into a synthetic cycle that allows for regeneration of the precursor complexes. Current efforts are focused on achieving catalytic N atom transfer from this system.

*Review Articles:* We have recently written two major review articles that serve to integrate our knowledge of how metal-metal multiply bonded compounds perform C–H functionalization reactions. In the first article, three-center/four-electron bonds within a  $\text{M}=\text{M}=\text{E}$  framework (here, E = carbene, nitrene, or nitride) are described in detail. The bonding manifold in these species, which are the presumed reactive intermediates in C–H functionalization reactions, is particularly well suited to lead to *superelectrophilic* reactivity [8]. In the second review article, we discuss the similarities and differences between C–H functionalization by  $\text{Rh}_2(\text{II},\text{II})$  compounds and their isoelectronic  $\text{Pd}_2(\text{III},\text{III})$  counterparts. While  $\text{Rh}_2$  complexes utilize a group transfer mechanism to achieve C–H functionalization,  $\text{Pd}_2$  compounds achieve C–H functionalization via an organometallic mechanism [9].

### **Future Plans:**

*Further Characterization of  $\text{Rh}_2$  Intermediates:* We plan to continue our mechanistic studies of  $\text{Rh}_2$ -catalyzed reactions, with a specific emphasis on isolating and characterizing new  $\text{Rh}_2$  intermediates: new types of  $\text{Rh}_2$  carbene compounds,  $\text{Rh}_2$  nitrene compounds, and  $\text{Rh}_2$  amido species.

*Exploration of First-Row Transition Metal Compounds as  $\text{Rh}_2$  Mimics:* Focusing on the metal-metal bond as the defining feature of  $\text{Rh}_2$  catalysts, we plan to prepare first row transition metal analogs of  $\text{Rh}_2$  species and to test their catalytic activity.

*Exploration of the Scope of Intermolecular N Atom Transfer from  $\text{Ru}_2$  Nitrides:* Having achieved N atom transfer to phosphine substrates, we wish to attempt N atom transfer to olefins (aziridination) or insertion of the N atom into C–H bonds to afford amination products.

### Publications (2010-2013)

- [1] Kornecki, K. P.; Berry, J. F. "Evidence for a One-Electron Mechanistic Regime in Dirhodium Catalyzed Intermolecular C–H Amination" *Chem. Eur. J.* **2011**, *17*, 5827-5832.
- [2] Kornecki, K. P.; Berry, J. F. "Dirhodium Catalysts Bearing Redox Non-Innocent Chelating Dicarboxylate Ligands and their Performance in Intra- and Intermolecular C–H Amination" *Eur. J. Inorg. Chem.* **2012**, 562-568.
- [3] Kornecki, K. P.; Berry, J. F. "A Mixed-Valent Dirhodium(II,III) Catalyst with Increased Longevity in Intramolecular C–H Amination" *Chem. Commun.*, **2012**, *48*, 12097-12099.
- [4] Long, A. K. M.; Yu, R. P.; Timmer, G. H.; Berry, J. F. "Aryl C–H Amination by an Electrophilic Diruthenium Nitride" *J. Am. Chem. Soc.* **2010**, *132*, 12228-12230.
- [5] Long, A. K. M.; Timmer, G. H.; Pap, J. S.; Snyder, J. L.; Yu, R. P.; Berry, J. F. "Aryl C–H Amination by Diruthenium Nitrides in the Solid State and in Solution at Room Temperature: An Experimental/Computational Study of the Reaction Mechanism" *J. Am. Chem. Soc.* **2011**, *133*, 13138-13150.
- [6] Timmer, G. H.; Berry, J. F. "Electrophilic Aryl C–H Amination by Dimetal Nitrides: Correlating Electronic Structure with Reactivity" *Chem. Sci.*, **2012**, *3*, 3038-3052.
- [7] Corcos, A. R.; Long, A. K. M.; Guzei, I. A.; Berry, J. F. „A Synthetic Cycle for Nitrogen Atom Transfer Featuring a Diruthenium Nitride Intermediate“ *Eur. J. Inorg. Chem.* ASAP.
- [8] Berry, J. F. "The Role of Three-Center/Four-Electron Bonds in Superelectrophilic Dirhodium Carbene and Nitrene Catalytic Intermediates" *Dalton Trans.* **2012**, *41*, 700-713.
- [9] Kornecki, K. P.; Powers, D. C.; Ritter, T.; Berry, J. F. "Metal-Metal Bonded Compounds as Catalysts for C–H Functionalization" *Prog. Inorg. Chem.* Accepted



**Early Career: Catalyst design for small molecule activation of energy consequence**

Raúl Hernández Sánchez, Theodore A. Betley\*

Harvard University, Department of Chemistry and Chemical Biology, Cambridge, MA 02138

email: betley@chemistry.harvard.edu

We are targeting homogeneous polynuclear complexes to model the reaction sites found in the active sites found in heterogeneous catalysts. Through the inclusion of multiple redox-active metal ions in the same reaction site, the cooperative reaction chemistry of these reaction sites on small molecule substrates can be systematically examined. Using this approach, we seek to develop a general methodology for transforming ubiquitous small molecules (e.g., N<sub>2</sub>, CO<sub>2</sub>) into viable building blocks for synthetic fuels. Our efforts in catalyst development will be described in the following contexts: (1) design ligand platforms to proximally accommodate multiple metal centers; (2) establish the ability of the polynuclear complexes to mediate multi-electron redox transformations, both electrochemically and via small-molecule activation processes; and (3) develop the multi-electron, stoichiometric reactivity discovered into viable catalytic processes to transform small molecule substrates into value-added chemicals (e.g. fuels).

We have used simple polyamine-based ligands to construct polynuclear reaction sites with the capability to control the local metal ion coordination environment while proximally orienting the metal ions to induce cooperative redox reactivity. This strategy allows numerous permutations permitting a high degree of generality to this approach with many synthetic handles to tune redox and reaction chemistry. Our first published reports showcase the expanded redox flexibility, spin-state tunability, and the capacity to effect multi-electron small molecule activation. The open-shell configuration induced by the weak-field superstructure permits facile functionalization of bound substrates. Future research will primarily focus on incorporating the stoichiometric reactivity into viable catalytic sequences for the breakdown of small molecule substrates.

**References**

1. Zhao, Q.; Betley, T. A. *Angew. Chem. Int. Edit.* **2011**, *50*, 709-712.
2. Powers, T. M.; Fout, A. R.; Zheng, S.-L.; Betley, T. A. *J. Am. Chem. Soc.* **2011**, *133*, 4917-4923.
3. Zhao, Q.; Harris, T. D.; Betley, T. A. *J. Am. Chem. Soc.* **2011**, *133*, 8293-8306.
4. Harris, T. D.; Betley, T. A. *J. Am. Chem. Soc.* **2011**, *133*, 13582-13585.
5. Eames, E. V.; Harris, T. D.; Betley, T. A. *Chem. Sci.* **2012**, *3*, 407-415.

**Bayesian Error Ensemble Functionals for Catalysis Studies**

Lead PI: Jens K. Nørskov  
Postdoc: Jess Wellendorff  
Student: Keld T. Lundgaard, Tuhin S. Khan  
Contact: SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025; [bligaard@slac.stanford.edu](mailto:bligaard@slac.stanford.edu)

A methodology for semi-empirical density functional optimization, using regularization and cross-validation methods from machine learning, is developed. We demonstrate that such methods enable well-behaved exchange correlation approximations in very flexible model spaces, thus avoiding the overfitting found when standard least-squares methods are applied to high-order polynomial expansions. A general-purpose density functional for surface science and catalysis studies should accurately describe bond breaking and formation in chemistry, solid state physics, and surface chemistry, and should preferably also include van der Waals dispersion interactions. Such a functional necessarily compromises between describing fundamentally different types of interactions, making transferability of the density functional approximation a key issue. We investigate this trade-off between describing the energetics of intramolecular and intermolecular, bulk solid, and surface chemical bonding, and the developed optimization method explicitly handles making the compromise based on the directions in model space favored by different materials properties. The approach is applied to designing the Bayesian error estimation functional with van der Waals correlation (BEEF-vdW), a semi-local approximation with an additional nonlocal correlation term. Furthermore, an ensemble of functionals around BEEF-vdW comes out naturally, offering an estimate of the computational error. An extensive assessment on a range of data sets validates the applicability of BEEF-vdW to studies in chemistry and condensed matter physics. Applications of the approximation and its Bayesian ensemble error estimate to a number of surface science problems and a catalytic reaction support this.[1,2,3]

**References**

1. V. Petzold et al., *Top Catal.* **55**, 402 (2012)
2. J. Wellendorff et al., *Phys. Rev. B* **85**, 235149 (2012)
3. T.S. Khan et al., *Submitted* (2013)

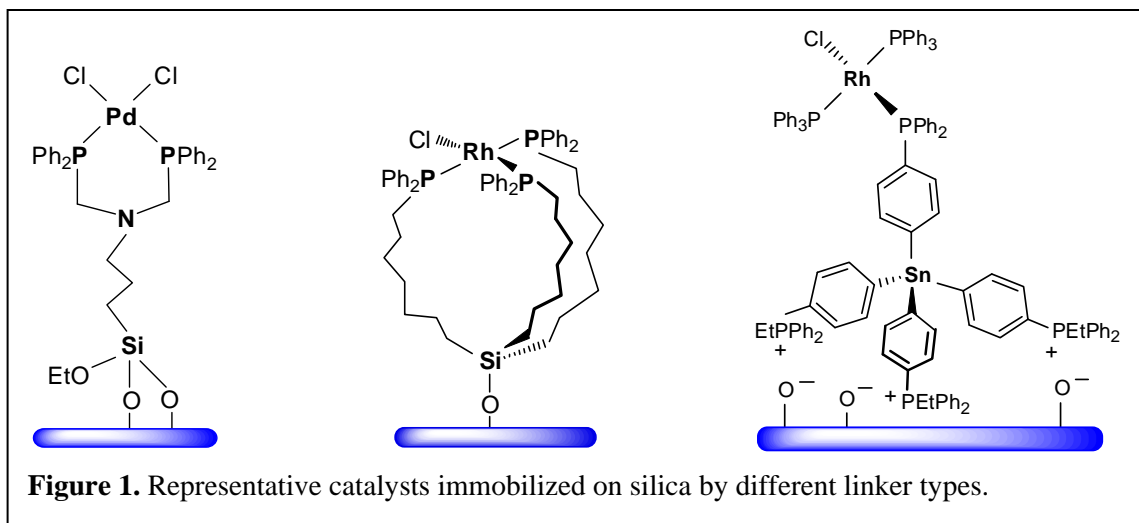
## Homogeneous Catalysts Immobilized on Silica by Optimized Linker Systems for Superior Lifetimes and Activities

J. Guenther, J. Pope, K. Cluff, J. Blüemel\*

Texas A&M University, Department of Chemistry, College Station, TX 77842  
e-mail: bluemel@tamu.edu

Molecular catalysts immobilized on oxide supports are easy to design and they are as selective and active as their homogeneous analogs. They can easily be separated from reaction mixtures and recycled many times.<sup>1</sup> Homogeneous catalysts can be bound to oxide supports, e.g. silica, by phosphine linkers.<sup>2-4</sup> For the analysis of the resulting amorphous solid materials we optimized classical solid-state NMR<sup>1,3</sup> (CP/MAS) and high-resolution (HRMAS) NMR spectroscopy of slurries.<sup>2,4</sup> Both methods can be employed for probing the nature and mobility of surface-bound species.

New insights concerning the synthesis, immobilization, characterization, activities, and lifetimes of Ni, Rh, and Pd/Cu catalysts<sup>1-4</sup> are presented. The most crucial element of immobilized catalysts is the linker, and therefore different types of chelate and monodentate linkers are compared (Figure 1). Especially exciting results are obtained with a new rigid linker scaffolds.<sup>3</sup> These rigid linkers finally solve two of the most persistent problems of immobilized catalysts, **(a)** decomposition of the catalyst by contact with the reactive support surface, and **(b)** deactivation by dimerization or agglomeration of neighboring catalyst molecules. For example, the rigid scaffold catalyst in Figure 1 can be recycled 30 times in a batchwise manner. Most interesting is a comparison with catalysts immobilized by chelate phosphine linkers with long alkyl chains.<sup>4</sup>



### References

1. J. Blüemel, *Coord. Chem. Rev.* **252**, 2410 (2008).
2. **(a)** T. Posset, J. Blüemel, *J. Am. Chem. Soc.* **128**, 8394 (2006); **(b)** T. Posset, J. Guenther, J. Pope, T. Oeser, J. Blüemel, *Chem. Commun.* **47**, 2059 (2011).
3. **(a)** Y. Yang, B. Beele, J. Blüemel, *J. Am. Chem. Soc.* **130**, 3771 (2008); **(b)** B. Beele, J. Guenther, M. Perera, M. Stach, T. Oeser, J. Blüemel, *New J. Chem.* **34**, 2729 (2010).
4. J. Guenther, J. Reibenspies, J. Blüemel, *Adv. Synth. Catal.* **353**, 443 (2011).

## Single-Molecule Fluorescence Imaging for Studying Organic, Organometallic, and Inorganic Reaction Mechanisms

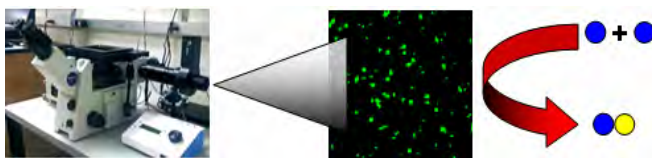
Postdoc: Eva Hensle  
Students: Alexander Fast  
Contacts: University of California, Irvine, Chemistry Department NSII 1102, Irvine, CA 92697-2025; [blums@uci.edu](mailto:blums@uci.edu)

### Goals and Objectives

Image individual steps in organic, organometallic, and inorganic reaction mechanisms using single-molecule fluorescence microscopy and use this increased understanding to develop new catalytic reactions. During the previous year: To develop methods to differentiate between homogeneous and heterogeneous catalysis by direct observation in multiple polymerization systems. The studies will answer important questions, such as: Is the active catalyst homogeneous or heterogeneous, given that both phases of species are often present under catalytic conditions? These goals and objectives for the previous year were achieved, as will be detailed below.

### DOE Interest

The reactive behavior of individual molecules is seldom observed, because we usually measure the average properties of billions of molecules. What we miss is important: The catalytic activity of less than 1% of the molecules under observation can dominate the outcome of a chemical reaction seen at a macroscopic level. Currently available techniques to examine reaction mechanisms (such as nuclear magnetic resonance spectroscopy and mass spectrometry) study molecules as an averaged ensemble. These ensemble techniques are unable to detect minor components (under ~1%) in mixtures or determine which components in the mixture are responsible for *reactivity* and *catalysis*. Ultimately, the development of single-molecule imaging technology could be a powerful tool to observe these “unobservable” intermediates and active catalysts (Figure 1). Single-molecule techniques have already transformed biology and the understanding of biochemical processes. This transformative imaging technique has broad, multidisciplinary impact with the potential to change the way the chemical community studies reaction mechanisms, especially in the core area of catalysis.



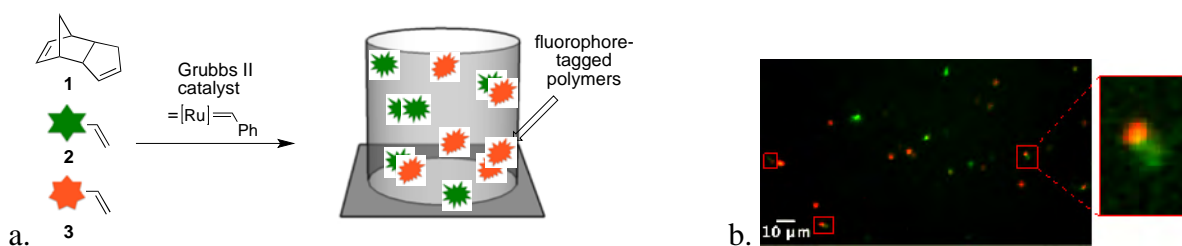
**Figure 1.** Project schematic: Fluorescent microscopy images chemical reactions at the single-molecule and single-particle level.

### Recent Progress

**Polymerization of polydicyclopentadiene:** Phase separation is a critical mechanistic hypothesis in the formation of polymers, since this phase-separation has been proposed to generate the specific bulk-properties suitable for application as membrane, ion exchanger, chromatography material or as solid-support for catalysts and reagents.<sup>1-2</sup> Therefore, the understanding of phase separation processes

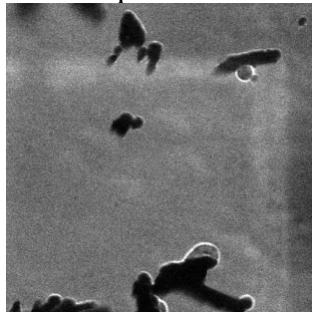
is an important goal/question and a lot of work has reported concerning this issue.<sup>2-3</sup> Previous reports use scanning electron microscopy (SEM) or transmission electron microscopy (TEM) measurements for morphology determination, techniques which require the quenching of the reaction or the removing of aliquots, processes that have the possibility of inducing artifacts.<sup>1,4</sup> To the best of our knowledge, a general in operando technique for imaging phase separation during polymerization reaction does not exist.

Phase separation of polydicyclopentadiene from both heptane solution and neat monomer has been characterized for the first time (Figure 2). Morphology of the precipitated polymers has been established for the first time to partially persist in the bulk polymer upon completion of the reaction. The fluorescence microscopy technique reveals the size of aggregated polymers and their change with respect to time. Two-fluorophore experiments reveal the origin and “timestamp” of polymer formation. The mechanism of polymerization at mid-reaction times is characterized as precipitation of polymers that are inactive toward further chain growth.



**Figure 2.** **a.** Schematic: in operando imaging of the phase separation polymerization of dicyclopentadiene. **b.** Data: polymer morphology results from coprecipitation of separately formed polymers (orange and green).

**Polymerization of ethylene oxide:** In heterogeneous catalysis, the number of active sites per particle often determines the efficiency and selectivity of the reaction, yet the determination of the number of catalytically active sites per particle remains a significant challenge.<sup>5</sup> A heterogeneous pathway for polymerization of ethylene oxide at the gas/solid (salph)Co surface interface was characterized by in operando optical microscopy. The single-crystal resolution of this technique revealed that only a small fraction of crystals showed high initial catalytic activity (Figure 3). In addition, each active particle displayed individual loci of reactivity rather than uniform reactivity distributed over the entire particle. Polymerization kinetics at an individual sites have been estimated show stepwise kinetics. This reactivity distribution data and single-site kinetic data would not be available through a traditional ensemble technique that examined bulk material properties.



**Figure 3.** Representative microscopy images ( $136 \times 136 \mu\text{m}^2$ ) showing single beads of clear PEO from individual active sites or localized clusters of active sites on dark catalyst after 4 hours. PPO present on less than 10% of all particles.

**Ongoing**

In the polydicyclopentadiene project: The persistence of polydicyclopentadiene morphologies formed at early reaction times to remain in the bulk polymer are being investigated. In the (saph)Co project: The kinetics of polymerization at individual sites of the (saph)Co catalyst is currently being explored.

## References

- (1) Della Martina, A.; Garamszegi, L.; Hilborn, J. G. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2036-2046; Della Martina, A.; Graf, R.; Hilborn, J. G. *J. App. Poly. Sci.* **2005**, *96*, 407-415. Kovačič, S.; Jeřábek, K.; Krajnc, P.; Slugovc, C. *Polym. Chem.* **2012**, *3*, 325-328.
- (2) Yu, Y.; Wang, M.; Gan, W.; Tao, Q.; Li, S. *J. Phys. Chem. B* **2004**, *108*, 6208-6215.
- (3) Toolan, D. T. W.; Howse, J. R. *J. Mater. Chem. C* **2013**, *1*, 603-616.
- (4) Wan, X.; Xu, J.; Xie, X.-M.; Guo, B.-H. *Colloid Polym. Sci.* **2011**, *289*, 1719-1728. Yoonessi, M.; Toghiani, H.; Kingery, W. L.; Pittman Jr., C. U. *Macromolecules* **2004**, *37*, 2511-2518. Knoke, S.; Korber, F.; Fink, G.; Tesche, B. *Macromol. Chem. Phys.* **2003**, *204*, 607-617. Amendt, M. A.; Chen, L.; Hillmyer, M. A. *Macromolecules* **2010**, *43*, 3924-3934. He, Y.; Yan, Y.; Zhang, L.; Zhu, S.; Zhang, Y. *Polymer-Plastics Technology and Engineering* **2011**, *50*, 1103-1108.
- (5) Buurmans, I. L. C.; Weckhuysen, B. M. *Nature Chem.* **2012**, *4*, 873-886.

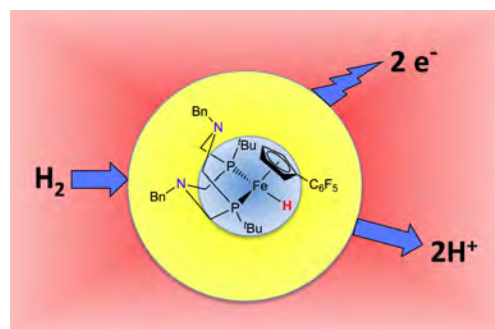
## Electrocatalytic Oxidation of Hydrogen by Iron Complexes

Lead PI: R. Morris Bullock  
 Co-PIs: Monte L. Helm and Daniel L. DuBois  
 Postdocs: Tianbiao (Leo) Liu and Elliott Hulley  
 Contact: Pacific Northwest National Laboratory, PO Box 999, MS K2-57  
 Richland, WA 99352; morris.bullock@pnl.gov

Solar and wind power are carbon-neutral, sustainable energy sources, but their intermittent nature requires a reliable method of storing energy. Catalysts that efficiently interconvert between electrical energy and chemical bonds (fuels) are needed for a sustainable and flexible energy supply in the future.  $\text{H}_2 \rightleftharpoons 2 \text{e}^- + 2 \text{H}^+$  Electro-catalysts based on inexpensive, earth-abundant metals are needed since most fuel cells are based on platinum, an expensive, precious metal.

The iron complex  $[\text{CpFe}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)(\text{H}_2)]^+$  ( $\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2 = 1, 5$ -diphenyl-3,7-dibenzyl-1,5-diaza-3,7-diphosphacyclooctane) catalyzes H/D exchange between  $\text{H}_2$  and  $\text{D}_2$  by a mechanism involving intramolecular heterolytic cleavage of  $\text{H}_2$  mediated by the pendant amine.<sup>1</sup> Similar complexes with no pendant amine under much slower reactions, indicating the key role of the pendant amine. This complex binds and heterolytically cleaves  $\text{H}_2$ , but is not an electrocatalyst for oxidation of  $\text{H}_2$  because of binding of an organic base to the metal. Our mononuclear  $\text{Fe}^{\text{II}}$  dihydrogen complexes containing pendant amines in the ligands mimic crucial features of the distal Fe site of the active site of the  $[\text{FeFe}]$ -hydrogenase required for H-H bond formation and cleavage. Requirements for heterolytic  $\text{H}_2$  cleavage at the active site of  $[\text{FeFe}]$ -hydrogenases and synthetic catalysts based on Fe are a ferrous ( $\text{Fe}^{\text{II}}$ ) center for binding of  $\text{H}_2$ , a properly positioned pendant amine in the ligand framework, and energy matching of the proton acceptor ability of the amine and the hydride acceptor ability of the metal, so that heterolytic cleavage of  $\text{H}_2$  is thermodynamically favored.

Rational modification of the steric and electronic parameters was carried out by installing an alkyl group with larger steric bulk on phosphorus, with the intent of preventing binding of the external amine base, while still enabling binding of  $\text{H}_2$  to the  $\text{Fe}^{\text{II}}$  center. An electron-withdrawing  $\text{C}_6\text{F}_5$  substituent was added to the Cp ligand, with the intent of increasing the acidity of the  $\text{Fe}(\text{H}_2)^+$  complex. The iron hydride complex  $[\text{Cp}^{\text{C}_6\text{F}_5}\text{Fe}(\text{P}^{\text{tBu}}_2\text{N}^{\text{Bn}}_2)\text{H}]$  is an electrocatalyst for oxidation of  $\text{H}_2$  (1 atmosphere) in fluorobenzene at 22 °C.<sup>2</sup>



## References

1. Liu, T.; Chen, S.; O'Hagan, M. J.; DuBois, M. R.; Bullock, R. M.; DuBois, D. L. "Synthesis, Characterization and Reactivity of Fe Complexes Containing Cyclic Diazadiphosphine Ligands: The Role of the Pendant Base in Heterolytic Cleavage of  $\text{H}_2$ " *J. Am. Chem. Soc.* **2012**, *134*, 6257-6272.
2. Liu, T.; DuBois, D. L.; Bullock, R. M. "An Iron Complex with Pendant Amines as a Molecular Electrocatalyst for Oxidation of Hydrogen," *Nature Chemistry*, **2013**, *5*, 228-233.

## Multifunctional solid-state catalysts for solar driven chemical conversion

Phillip Christopher

University of California, Riverside, Department of Chemical and Environmental  
Engineering, Riverside, CA 92521

Email: Christopher@engr.ucr.edu

Ever since the initial demonstration of photon-induced H<sub>2</sub> evolution from TiO<sub>2</sub> over 40 years ago, scientists and engineers have had high hopes for utilizing solar energy to drive chemical transformations. Viable solar-driven chemical conversion technologies have been slow to follow the initial discovery due to the stringent material design requirements necessary for achieving high rates of chemical conversions in low temperature photocatalytic processes. In this work, we discuss examples of how multiple energy stimuli can be combined with nanostructuring of solid-state materials to achieve high light utilization efficiencies and unique light absorption mechanisms that open new avenues for solar driven chemical conversions.

The first example is focused on the design of efficient Pt-based heterogeneous photocatalysts for oxidation reactions. Bulk metals exhibit very low efficiency for driving photocatalytic reactions based on the low energy of photon-induced electron excitations and fast charge carrier relaxation due to electron-electron scattering. Here we show that confining Pt to nanoscales (< 5nm particles) introduces new photon absorption mechanisms that allow for a unique and efficient pathway for photocatalytic transformations without needing a semiconductor absorber. We will show experimental signatures of nanoscale-induced photochemistry and discuss theoretical frameworks that capture salient qualitative characteristics of the process. In the second example, we discuss the design of a multifunctional system with two active sites co-localized on the same semiconducting support for efficient execution of artificial photosynthesis (CO<sub>2</sub> + 2H<sub>2</sub>O → CH<sub>4</sub> + 2O<sub>2</sub>). One active site is designed to perform photocatalytic endothermic water splitting and the other is designed to perform thermocatalytic exothermic CO<sub>2</sub> methanation thereby providing a unique pathway to execute artificial photosynthesis through a combined photocatalytic and thermocatalytic reaction pathway.



**Chemical Imaging of Single Metal Nanoparticle Catalysis**

Postdocs: Xiaochun Zhou, Neshia May Andoy, Kyu-Sung Han, Justin Sambur  
Students: Hao Shen, Eric Choudhary, Kaori Kubo, Ningmu Zou  
Contacts: Cornell University, Department of Chemistry and Chemical Biology,  
Ithaca, NY 14853; [pc252@cornell.edu](mailto:pc252@cornell.edu)

**Goal**

To develop and apply single-molecule fluorescence imaging methods to interrogate the catalytic properties of nanostructured catalysts in situ at sub-diffraction spatial resolution and single-reaction temporal resolution.

**DOE Interest**

Our experimental methods provide tools to make high spatial and temporal resolution measurements of catalytic reactions by nanostructured catalysts in real time under realistic reaction conditions. The results generate unprecedented insights into the structure-activity of nanocatalysts at varying length and time scales, which help efforts to improve current nanocatalysts and design new ones for maximum catalytic efficiencies for energy conversion processes.

**Recent Progress**

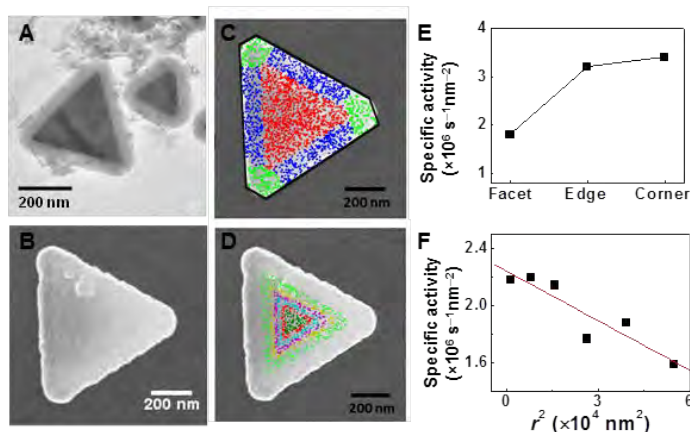
*Theoretical development in understanding single-turnover kinetics of nanoparticle catalysis (J. Chem. Phys. 2011, 135, 174509):* In collaboration with Prof. Roger Loring, we have developed a kinetic formalism to analyze the single-turnover kinetics of single nanoparticle catalysis. We proposed the use of constrained mean dwell times, defined as the mean dwell time in a state with the constraint that the immediately preceding dwell time in the other state is, for example, less than a variable time. These constrained mean dwell times for a kinetic model with dynamic disorder demonstrate that these quantities reveal correlations among dynamic fluctuations at different active sites on a multisite catalyst.

*Nanometer-resolution reactivity mapping and discovery of complex reactivity patterns on single 1D nanocrystal catalysts (Nature Nanotech. 2012, 7, 237-241):* We have used super-resolution fluorescence microscopy to quantify the catalysis of the nanorods at a temporal resolution of a single catalytic reaction and a spatial resolution of ~40 nm. We find that within the same surface facets on the sides of a single nanorod, the reactivity is not constant and exhibits a gradient from the center of the nanorod towards its two ends. Furthermore, the ratio of the reactivity at the ends of the nanorod to the reactivity at the sides varies significantly from nanorod to nanorod, even though they all have the same surface facets.

*Understanding of the catalytic behaviors of single Pt nanoparticles (~4.6 nm) in two different reactions (Nano Lett. 2012, 12, 1253-1259):* Using single-molecule microscopy of fluorogenic reactions we studied Pt nanoparticle catalysis at single particle, single-turnover resolution for two reactions: one an oxidative N-deacetylation and the other a reductive N-deoxygenation. These Pt nanoparticles show distinct catalytic kinetics in these two reactions: one following noncompetitive reactant adsorption and the other

following competitive reactant adsorption. In both reactions, single nanoparticles exhibit temporal activity fluctuations attributable to dominantly spontaneous surface restructuring. Depending on the reaction sequence, single Pt nanoparticles may or may not show activity correlations in catalyzing both reactions, reflecting the structure insensitivity of the N-deacetylation reaction and the structure sensitivity of the N-deoxygenation reaction.

*Most metal nanoparticles can catalyze a multitude of chemical transformations, for example Site-specific super-resolution activity mapping on single 2-D nanocatalysts (J. Am. Chem. Soc. 2013, 135, 1845-1852):* We have used single-molecule super-resolution imaging to directly visualize the site-specific catalytic reactions on single 2-D nanocrystal catalysts: Au nanoplates encapsulated in mesoporous SiO<sub>2</sub> shell (Figure 1A, B). We have directly quantified that the corners of the nanoplates are more active than the edges, which in turn are more active than the top facets (Figure 1C, E). Furthermore, we have discovered that within the top flat {111} facets, the catalytic activity is nonconstant, but rather shows a radial activity gradient from the center toward the edges (Figure 1D, F).



**Figure 1. Spatial reactivity patterns on single Au@mSiO<sub>2</sub> nanoplates.** (A) TEM image of two triangular Au@mSiO<sub>2</sub> nanoplates. (B) SEM image of a triangular Au@mSiO<sub>2</sub> nanoplate. (C) Locations of 2325 product molecules overlaid on top of the SEM image of the Au@mSiO<sub>2</sub> nanoplate in B. Each dot is the location of one product molecule. The locations are color-coded according to their respective regions on the nanoplate: flat facet (red), edges (blue) and corners (green). The solid black line outlines the outer contour of the mSiO<sub>2</sub> shell. The dashed black line outlines the perimeter of the Au nanoplate core. (D) Locations of 1055 product molecules overlaid on top of the SEM image of a Au@mSiO<sub>2</sub> nanoplate in B. The facets (i.e., top and bottom) are divided into radial segments from the center toward the periphery; the product locations in different segments are colored differently. The product molecules residing in the corner and edge regions are excluded here. (E) Specific activities of the different regions of the nanoplate from C. (F) Dependence of specific activities of radial segments on  $r^2$  for the nanoplate in D.  $r$  is the distance between the center of the nanoplate and the midpoint of the segment along the center-to-corner vector. Solid line is a linear fit.

*Massively scalable, parallel activity screening of nanocatalysts at the single-particle level (ACS Catalysis 2013, accepted):* We have demonstrated a single-molecule

fluorescence microscopy approach that can screen the activity quantitatively of a large number of catalyst particles in parallel at the single-particle level and sub-diffraction spatial resolution. It can identify directly high activity catalyst particles and resolve subpopulations in mixtures of catalysts. It is readily scalable and broadly applicable to heterogeneous catalysts. Using ensemble measurements to establish activity correlations between different reactions, we further show this approach can be extended to assess catalysts in reactions that do not involve fluorescent molecules. Coupled with high-throughput catalyst preparation and high-resolution structural/compositional analysis, this screening approach has promise in accelerating the development and discovery of new or better catalysts.

### Future Plans

*Single-molecule imaging of photo(electro)catalysis on single semiconductor nanocrystals:* We are extending our single-molecule super-resolution microscopy approach to study photo(electro)catalytic reactions on single semiconductor nanocrystals. We intend to map the photo-induced  $h^+$  and  $e^-$  reactivity on the surface of single catalyst particles under both photocatalytic and photoelectrocatalytic conditions. For photoelectrocatalysis, we will further correlate the catalytic activity with the photocurrent from a single particle. The objective here is to understand the correlation between surface reactivities of photogenerated  $h^+$  and/or  $e^-$  in a spatially resolved manner on single semiconductor nanostructures under photocatalytic and photoelectrocatalytic conditions, as well as the correlation among each nanostructure's  $h^+/e^-$  surface reactivities, photocurrent responses, and structure/morphology.

### Publications (2010-2013)

1. M. A. Ochoa-Daza, X. Zhou, P. Chen, R. F. Loring "Interpreting Single Turnover Catalysis Measurements with Constrained Mean Dwell Times" *Journal of Chemical Physics*, **2011**, *135*, 174509.
2. X. Zhou, N. M. Andoy, G. Liu, E. Choudhary, K.-S. Han, H. Shen, P. Chen "Quantitative Super-resolution Imaging Uncovers Reactivity Patterns on Single Nanocatalysts" *Nature Nanotechnology*, **2012**, *7*, 237–241.
3. K.-S. Han, G. Liu, X. Zhou, R. E. Medina, P. Chen "How does A Single Pt Nanocatalyst Behave in Two Different Reactions? A Single-Molecule Study" *Nano Letters*, **2012**, *12*, 1253-1259.
4. N. M. Andoy, X. Zhou, E. Choudary, H. Shen, P. Chen "Single-Molecule Catalysis Mapping Quantifies Site-specific Activity and Uncovers Radial Activity Gradient on Single 2D Nanocrystals" *Journal of the American Chemical Society*, **2013**, *135*, 1845-1852.
5. X. Zhou, E. Choudhary, N. M. Andoy, N. Zou, P. Chen "Scalable Parallel Screening of Catalyst Activity at the Single-Particle Level and Sub-diffraction Resolution" *ACS Catalysis* **2013**, accepted.

## Modeling of Late Transition Metal Catalysts for Energy Applications

UNT Postdoctorals: Dr. Claire L. McMullin; Dr. Jason A. McAfee  
 Graduate Students: Mr. (now Dr.) Travis M. Figg; Mr. (now Dr.) H. Emanuel Gonzalez; Mr. (now Dr.) Glenn R. Morello; Mr. Dale R. Pahls; Mr. Bruce Prince (PhD student, UNT)  
 Undergraduates: Ms. Brooke M. Otten  
 Collaborators: Dan Ess (BYU); Brent Gunnoe (UVa); Greg Hillhouse (Chicago); Pat Holland (Rochester); Pete Wolczanski (Cornell); Tim Warren (Georgetown)

### Goals

The major goals of DE-FG02-03ER15387 are to study the structure and reactivity of novel and emerging ligand systems in catalysis; to model novel catalysts for olefin hydroarylation; to identify mechanisms of group transfer by late transition metal complexes as a route to more efficient use of hydrocarbon feedstocks, and to integrate modern computational chemistry research with the work of leading experimental groups and fellow DOE-BES contractors to better understand mechanisms and intermediates of transition metal catalysis pertinent to the DOE research mission.

### DOE Interest

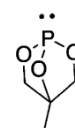
Potential Impact Areas of DE-FG02-03ER15387 include the more efficient and economical utilization of petroleum- and biomass-based feedstocks; the rational design of new and improved catalysts for hydrocarbon functionalization; the development of improved methods of modeling transition metal catalysts, and achieving the goals of “green” chemistry through catalysis. Alkyl arenes are produced on a large industrial scale from petroleum feedstocks. While alkyl-arenes have important uses ranging from solvents to pharmaceutical applications, and as starting materials for other valuable chemicals like styrene and phenol. Transition metal chemistry plays an important role in many technical areas within the energy sector. In all of these applications, chemists seek to leverage the ability of transition metals to stabilize a diverse array of different chemical states through judicious modification of metal, ligand and substituents on the supporting ligation. Modern computational chemistry plays an increasingly important role in terms of establishing structure-property relationships that are essential to rationally design new materials.

### Recent Progress

In 2012/13, significant progress was made in both research thrusts – arene functionalization by catalytic hydroarylation, and modeling of catalytic reactions by Earth-abundant, *3d* transition metals. Highlights of some of the most important research results of grant **DE-FG02-03ER15387** funded by BES through the Catalysis Science Program from the aforementioned time period are summarized below. Eleven (11) refereed scientific publications acknowledging DOE-BES support via **DE-FG02-03ER15387** were published in 2012 and thus far in 2013. Our DOE-BES supported research over the past year has described the work of 7 early career scientists (5 Ph.D. research students; 2 postdoctorals) at UNT.

### A. Modeling of Catalytic Production of Alkyl Arenes

Calculations were performed by Dr. Claire McMullin to understand the origin of  $\pi$ -acidity in a novel bicyclic phosphite, **A** (see figure to right), synthesized by Gunnoe and coworkers. The integration of our computational data with crystallography and cyclic voltammetry (CV) experiments indicate that the reduction in basicity in **A** results from smaller O–P–O angles in **A**, which decreases the energy of the low-energy unoccupied  $\sigma_{PO}^*$  orbitals and thus enhances  $\pi$ -acidity. Theory and CV demonstrate that this ligand  $\pi$ -acidity is transmitted to the metal and reflected in  $Ru^{III/II}$  reduction potentials. These properties were correlated with the activity of a  $TpRu(A)$ -based catalyst, delineating the impact of the steric and electronic profile of co-ligand **A** upon the rate-determining C–H activation barrier, turnover frequencies and olefin insertion rates.



The past year was one of exciting breakthroughs in our long standing research into olefin hydroarylation catalysis. We continued, in collaboration with Gunnoe, to study base metal replacements for the octahedral Ru<sup>II</sup> and square planar Pt<sup>II</sup> catalysts for which successful catalysis has been demonstrated. We enlisted the assistance of the Ess group (BYU) given their expertise in modeling “spin-flips” in catalysis. Formally spin-forbidden reactions were shown to be a key in Fe-catalyzed C—H bond activation through the integration of computational and experimental studies. Additionally, it is gratifying that the current joint theory-experiment success for Cp\*Fe<sup>II</sup> confirms modeling predictions made by former Cundari group member (now Dr.) Glenn Morello for related TpFe<sup>II</sup> models.

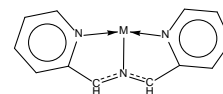
## B. Late Metal Catalysis for Hydrocarbon Functionalization

A major theme in our DOE-BES research has been predicated on the assumption that accessing very low-coordination metal complexes (*e.g.*, two- and three-coordination) will lead to enhanced reactivity. In conjunction with the Hillhouse group (U. Chicago), DFT calculations by former Ph.D. student (now Dr.) Glenn Morello were employed to delineate a novel mechanism of C—H bond activation in two-coordinate nickel-amido complexes involving oxidation (of the metal) followed by intramolecular deprotonation of a benzylic C—H bond. While the literature has focused on HAA (H-atom abstraction) routes to C—H bond activation by late 3d metal complexes, deprotonation routes are of interest as they favor selectivity for less substituted C—H bonds, which in many cases is the preferred regiochemistry for the functionalization of larger hydrocarbons such as propane and butane.

A DFT analysis of the reaction of bpyNiEt<sub>2</sub> with ArN<sub>3</sub> was performed for *para*-tolyl-azide (Ar = pTol), 3,5-dimethyl-phenyl-azide (Ar = mXy) and *ortho*-tolyl-azide (Ar = oTol), and mesityl-azide (MesN<sub>3</sub>) was performed by undergraduate Brooke Otten and Ph.D. student Travis Figg of UNT. Based on computed energetics, three reactions were proposed to compete: Ni—C bond homolysis, reductive elimination of butane, and nucleophilic attack (NA) by ArN<sub>3</sub>. NA and Ni—Et bond homolysis dominated at lower and higher temperatures, respectively. Calculated Ni—N and Ni—C bond dissociation free energies (BDFEs) suggested the role of radical pathways in discriminating bpyNiEt<sub>2</sub>/ArN<sub>3</sub> reactions. Calculations also highlighted the weak M<sub>3d</sub>—C bonds that favor radical pathways, which defines a major challenge in the design of catalyst using Earth-abundant 3d metals.

A key emphasis of our research program in the past grant period has been to delineate the critical ligand-based factors that differentiate base (3d) and precious (4d and 5d) metal catalysts. The greater propensity of the former for one-electron (radical) chemistry and their reduced ligand fields are two of the most important among these factors. The use of very high field ligands and non-innocent ligands (NILs) has been proposed as strategies to “en-noble” 3d metals. In the former, high field ligands may reduce what Wolczanski has termed the density of states (DOS) of the complex, which controls the manifold of accessible reaction pathways. For the latter strategy, NILs may be thought of as surrogates to provide the “extra” electron needed for two-electron transformations such as oxidative addition, reductive elimination, group transfer, *etc.* upon which many precious metal catalytic cycles are constructed.

In conjunction with the Wolczanski group, we have investigated the chemistry of a novel series of dipyriddyazaallyl (termed smif, one example is shown to the right) and related tridentate ligands. Through a combination of theory and experiment, the high crystal field strength of these ligands was demonstrated in the previous grant period. In the current grant period, their NIL behavior was the focus of our research.



In a recent joint theory-experiment study of Lewis base (B) “triggered” C—H bond activation by d<sup>2</sup> ML<sub>3</sub> complexes (L: π-donors like R<sub>3</sub>SiO<sup>-</sup> and NR<sup>2-</sup>) with our long time collaborators in the Wolczanski group (Cornell U.), several seminal conclusions were arrived at vis-à-vis C—H bond activation. Foremost among these was the proposal that the potency for C—H bond activation was related to the ability of the activating complex to access the dσ<sup>0</sup>dπ<sup>2</sup> electronic configuration of d<sup>2</sup>-ML<sub>3</sub>. The prerequisite for this nominally excited electronic configuration arises from the σ<sub>CH</sub><sup>0</sup>σ<sub>CH</sub><sup>\*0</sup> nature of the hydrocarbon C—H bond, *i.e.*, to most efficiently cleave a C—H bond, overlap considerations dictate that ML<sub>3</sub> must accept σ<sub>CH</sub> density (via its dσ orbital) and also be able to populate the σ<sub>CH</sub><sup>\*</sup> (via the dπ donor orbital).

## Future Plans

The square planar Pt<sup>II</sup> motif has proven to be a flexible workhorse in our studies of olefin hydroarylation catalysis. Current work (Bruce Prince, UNT) in Pt catalyzed hydroarylation focuses on leveraging these recent advances to better control linear:branched selectivity for  $\alpha$ -olefins.

Moving forward, we continue to emphasize the “reverse engineering” precious metal catalysts with Earth-abundant replacements. This research and other emerging data point to later metal imidyl (NR<sup>•</sup>) and oxyl (O<sup>•</sup>) moieties as having the right balance of high activity (for both C—H activation **and** C—E (E = O, N) functionalization steps) with plausible thermodynamic and kinetic accessibility with the right supporting ligands. Current research also focuses on how changes to late 3d metal catalysts impact their activity, focusing on hydrocarbon functionalization (*e.g.*, amination and oxidation) by late 3d metal dipyritylazaallyl complexes. Moreover, control of the “non-innocence” as well as stereoelectronic profile via modification of the ligand scaffold are of interest.

The ability to trigger C—H activation by coordination of a Lewis base to the Group 6 metal (W<sup>IV</sup>) is an exciting route to circumvent a major limiting factor with respect to C—H bond activation by the d<sup>0</sup>-ML<sub>3</sub> complexes we studied previously. It is obvious that the Lewis base triggering strategy is a steric and electronic “tightrope.” Hence, we continue to pursue modeling studies, closely grounded in experimental reality, to identify promising synthetic targets to exploit this novel strategy for C—H activation.

## Publications (2012-3)

- 227 - “DFT Study of Group 8 Catalysts for the Hydroarylation of Olefins: Influence of Ancillary Ligands and Metal Identity;” T. R. Cundari, G. R. Morello *JOMC* **2012**, 697, 15 - 22.
- 229 - “A Computational Comparison of Ni<sup>II</sup> and Pt<sup>II</sup> Hydrido-tris(pyrazolyl)borate Supported Hydroarylation Catalysis;” T. R. Cundari, H. E. Gonzalez *J. Mol. Cat. A* **2012**, 353 – 354, 1 - 6. (Editor’s Choice Article).
- 235 – “Coordination Chemistry of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2,2,1]heptane: Preparation and Characterization of Ru(II) Complexes;” E. E. Joslin, T. B. Gunnoe, M. Sabat, C. L. McMullin, T. R. Cundari, W. H. Myers *Inorg. Chem.* **2012**, 51, 4791 – 4801.
- 238 - “Bifunctional Reactivity of a Nickel-Imide in C-H Functionalization;” S. Wiese, J. McAfee, D. R. Pahls, C. L. McMullin, T. R. Cundari, T. H. Warren *JACS* **2012**, 134, 10114 – 10121.
- 246 – “Catalytic Hydroarylation of Olefins Using TpRu(L)(NCMe)Ph (L = 2,6,7-Trioxa-1-phosphabicyclo[2,2,1]heptane): Comparison to TpRu(L')(NCMe)Ph Systems [L' = CO, PMe<sub>3</sub>, P(pyr)<sub>3</sub> or P(OCH<sub>2</sub>)<sub>3</sub>CET];” E. E. Joslin, T. B. Gunnoe, M. Sabat, C. L. McMullin, T. R. Cundari, W. H. Myers *Organometallics* **2012**, 31, 6851 - 6860.
- 251 - “Single-Electron Oxidation of N-Heterocyclic Carbene-Supported Nickel Amides Yielding Benzylic C-H Activation;” C. A. Laskowski, G. R. Morello, C. T. Saouma, T. R. Cundari, G. L. Hillhouse *Chem. Sci.* (Edge Article) **2013**, 4, 170 - 174.
- 257 - “Selective Extraction of N<sub>2</sub> from Air by Diarylimine Iron Complexes;” E. R. Bartholomew, E. C. Volpe, P. T. Wolczanski, E. B. Lobkovsky, T. R. Cundari *JACS* **2013**, 135, 3511 - 3527.
- 259 - “Facile and Regioselective C–H Bond Activation of Aromatic Substrates by an Fe(II) Complex Involving a Spin-Forbidden Pathway;” S. E. Kalman, A. Petit, T. B. Gunnoe, D. H. Ess, T. R. Cundari, M. Sabat *Organometallics* **2013**, 32, 1797 – 1806.
- 261 - “Pt(II) Catalyzed Ethylene Hydrophenylation: Switching Selectivity between Alkyl and Vinyl Benzene Production;” B. A. McKeown, H. E. Gonzalez, M. R. Friedfeld, A. M. Brosnahan, T. B. Gunnoe, T. R. Cundari *Organometallics* – accepted.
- 263 - “Pt<sup>II</sup> Catalyzed Ethylene Hydrophenylation: Influence of Dipyrityl Chelate Ring Size on Catalyst Activity and Longevity;” B. A. McKeown, H. E. Gonzalez, T. B. Gunnoe, T. R. Cundari, M. Sabat *ACS Catalysis* – accepted.
- 264 - “Lewis Bases Trigger Intramolecular CH-Bond Activation: (silox)<sub>2</sub>W=N<sup>t</sup>Bu  $\leftrightarrow$  (silox)( $\kappa^2$ -O,C-OSi<sup>t</sup>Bu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)HW=N<sup>t</sup>Bu (silox = OSi<sup>t</sup>Bu<sub>3</sub>);” M. Marshak, D. C. Rosenfeld, W.D. Morris, P. T. Wolczanski, E. B. Lobkovsky, T. R. Cundari *Eur. J. Inorg. Chem.* – accepted.

## Natural Catalysts for Molten Cellulose Pyrolysis to Targeted Bio-Oils

Additional PIs: None  
Students: Alex Paulsen, Christoph Krumm  
Contacts: University of Massachusetts Amherst, 686 North Pleasant Street,  
Amherst, MA 01003; Dauenhauer@ecs.umass.edu

### Goal

Develop fundamental understanding of the role of inorganic catalysts naturally occurring within high temperature molten cellulose chemistry.

### DOE Interest

The chemistry of thermal degradation of cellulose and biomass biopolymers ultimately dictates the performance of numerous energy-related technologies including gasification, wood combustion, and fast pyrolysis of biomass. Development of kinetic models based on a fundamental understanding of molecular-level pyrolysis chemistry will ultimately lead to improved reactor design for energy applications. This research will specifically focus on the chemistry of the inorganic catalysts within biomass which significantly alter the products produced from cellulose pyrolysis.

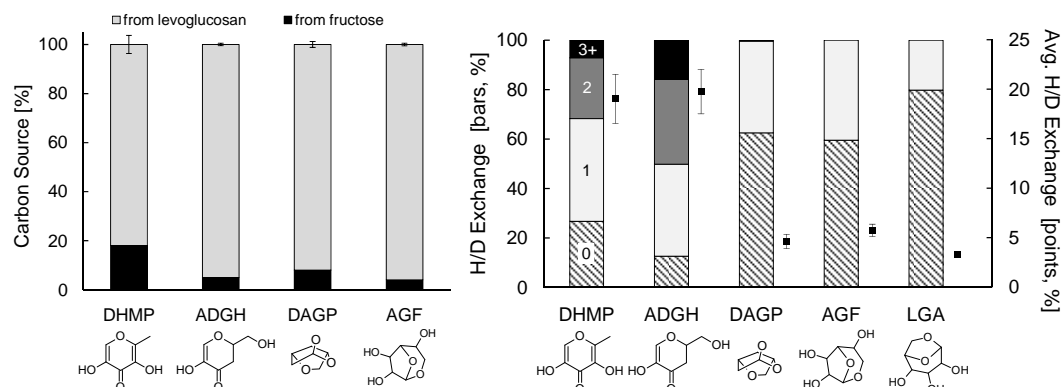
### Recent Progress

*Cellulose Chain Length Effect:* In an effort to provide fundamental descriptions of pyrolysis chemistries, we combined isothermal pyrolysis with first principles simulations to produce the first molecular-level insights into the formation of the five-membered furan ring and light oxygenates directly from cellulose [1]. Additionally, we have revealed the effect of chain length in cellulose pyrolysis [3], which exhibits strong influence on the distribution of pyrolysis products. Pyrolysis reactions are concluded to occur through two chemistries, intra-chain and chain end, which significantly differ in selectivity to anhydrosugar and furan products.

*Natural Catalysts and Isotopic Labeling of Pyrolysis Intermediates:* Secondary reactions within the intermediate liquid cellulose have been discovered using  $^{13}\text{C}$ -labeling to convert levoglucosan (the most abundant cellulose pyrolysis product) to pyrans and anhydrosugars [2]. As shown in Figure 1A, the major pyrolysis product classes of anhydrosugars and pyrans overwhelmingly are produced from the secondary reactions of levoglucosan. Furthermore, deuterium labeling of glucose (in a glucose/levoglucosan mixture) in Figure 1B reveals that dehydration-requiring reactions to form pyrans exhibit significant H/D exchange, indicating the potential impact of cellulose melt acid catalysis generated during reaction (i.e. lower pH).

*Transport Limitations in Pyrolysis Chemistry:* In our most recent work, we reveal insights into the formation and stability of the five-membered furan ring in cellulose pyrolysis with significant diffusion limitations [5]. We reveal the effect of transport limitations on product yields in cellulose pyrolysis where larger powder samples have different product yields (e.g., higher levoglucosan) compared to thin-films [6,7]. Additionally, we show the effect of reaction

temperature on product yields for thin-film pyrolysis and thereby construct a library of kinetically-limited, isothermal data for use in developing molecular-level kinetic models.



**Figure 1. Isotopic co-pyrolysis.** Co-pyrolysis experiments with powder mixtures of levoglucosan and  $^{13}\text{C}$ -labeled fructose (A), and levoglucosan and deuterated (all 12 positions) glucose (B). In (A), the percentage of each product (on a carbon basis) that originates from levoglucosan (gray) and  $^{13}\text{C}$ -labeled fructose (black) is shown. In (B), the percent of each product with 0, 1, 2, or 3+ hydrogens exchanged with deuterated glucose is shown. Points in (B) show the average percent hydrogens exchanged (average number of hydrogens exchanged divided by total number of hydrogens in the molecule) for each product. The reaction temperature was 500 °C. Error bars indicate 90% confidence intervals.

### Future Plans

*Impregnated Catalysis of  $\text{Ca}^{++}$ :* Understand the chemistry of homogeneous catalysis by naturally-occurring ions in cellulose pyrolysis.

*CaO Catalysis:* Develop an experimental method for studying CaO catalysis on cellulose melt chemistry.

### Publications (2011-2013)

- [1] M.S. Mettler, S.H. Mushrif, A.D. Paulsen, A.D. Javadekar, D.G. Vlachos, P.J. Dauenhauer, "Revealing pyrolysis chemistry for biofuels production: Conversion of cellulose to furans and small oxygenates," *Energy & Environmental Science* **2012**, 5, 5414.
- [2] M.S. Mettler, A.D. Paulsen, D.G. Vlachos, P.J. Dauenhauer, "Pyrolytic conversion of cellulose to fuels: Levoglucosan deoxygenation via elimination and cyclization within molten biomass," *Energy & Environmental Science* **2012**, 5, 7864-7868.
- [3] M.S. Mettler, A.D. Paulsen, D.G. Vlachos, P.J. Dauenhauer, "The chain length effect in pyrolysis: Bridging the gap between glucose and cellulose," *Green Chemistry* **2012**, 14, 1284-1288.
- [4] M.S. Mettler, D.G. Vlachos, P.J. Dauenhauer, "Top ten fundamental challenges of biomass pyrolysis for biofuels," *Energy & Environmental Science* **2012**, 5, 7797-7809.
- [5] V. Agarwal, P.J. Dauenhauer, G.W. Huber, S.M. Auerbach, "Ab initio dynamics of cellulose pyrolysis: Nascent decomposition pathways at 327 C and 600 C," *Journal of the American Chemical Society*, **2012**, 134(36), 14958-14972.
- [6] A.D. Paulsen, M.S. Mettler, P.J. Dauenhauer, "The role of sample dimension and temperature in cellulose pyrolysis," Accepted to *Energy & Fuels*.
- [7] A.D. Paulsen, M.S. Mettler, P.J. Dauenhauer, "Inert supports for catalyst-impregnated pyrolysis of cellulose," Submitted.



**Elemental Steps in Dehydration of Diols on TiO<sub>2</sub>(110)**

Lead PI: Johannes Lercher  
Additional PIs: Bruce D. Kay and Roger Rousseau  
Postdocs: Danda Acharya, Zhenjun Li, Xiao Lin, and Yeohoon Yoon  
Collaborators: Zhenrong Zhang (Baylor University)

Contact: Zdenek Dohnálek, Fundamental and Computational Sciences Directorate and Institute for Integrated Catalysis, Pacific Northwest National Laboratory, P.O. Box 999, MS K8-88, Richland, WA 99352; [Zdenek.Dohnalek@pnnl.gov](mailto:Zdenek.Dohnalek@pnnl.gov)

Simple diols (ethylene and propylene glycols) are employed as models for deoxygenation reactions of biomass. TiO<sub>2</sub>(110) is selected as a prototypical oxide catalyst to attain detailed mechanistic understanding of such reactions. In these studies atomically resolved imaging by scanning tunneling microscopy (STM) is combined with ensemble-averaging spectroscopic techniques such as temperature programmed desorption (TPD) and theoretical investigations via density functional theory (DFT). STM studies reveal that at low temperatures (140 K), diols adsorb on five-fold coordinated Ti<sup>4+</sup> sites. The molecules readily dissociate via O-H bond scission forming Ti-bound hydroxyalkoxy and bridging hydroxy (HO<sub>b</sub>) species. The reverse reaction leading to molecularly bound diols is also observed indicating the attainment of a dynamic equilibrium between these conjugate acid/base pairs. Above 250 K, diols readily diffuse to oxygen vacancies and irreversibly dissociate via O-H bond scission of one of the OH groups forming geminate pairs of hydroxyalkoxy and hydroxyl species, both anchored on bridging oxygen (O<sub>b</sub>) rows. The hydroxyalkoxy species rotate around their O<sub>b</sub> anchor, switching the position of their OH between the two adjacent Ti rows. The rotating species are also found to assist cross-O<sub>b</sub> row HO<sub>b</sub> hydrogen transfer. The OH group of the hydroxyalkoxy species is further observed to dissociate forming a dioxy species and an additional HO<sub>b</sub>. Annealing to ~450 K results in the formation of new dioxy intermediates that are centered on top of the O<sub>b</sub> rows. Alkenes as final products are observed to desorb between 600 and 700 K. For ethylene glycol, our coverage dependent TPD studies further show acetaldehyde as a second carbon containing product at high coverages. Detailed theoretical calculations yield a deep insight into the mechanism and energetics of the observed reaction steps.

This work is a part of Transition Metal Oxide BES/Catalysis Science program at PNNL. Research was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

**Supported-Nanoparticle Catalyst Formation in Contact With Solution: Kinetic,  
Mechanistic and Synthetic Fundamental Studies**

Postdoc: Prof. Saim Özkar  
Students: Patrick Kent; William Laxson  
Collaborator: Prof. Anatoly I. Frenkel, Yeshiva University, New York, NY  
Contacts: Department of Chemistry, Colorado State University,  
Ft. Collins, CO 80523 (970)-491-2541; [rfinke@lamar.colostate.edu](mailto:rfinke@lamar.colostate.edu)

**Goals**

A primary goal of our DOE-funded program is to establish the kinetics and mechanism(s) of the nucleation, growth and agglomerative formation of supported-nanoparticle heterogeneous catalysts. A second goal is to learn how to transfer the synthetic and mechanistic insights—that have been gained from the modern revolution in nanoparticle synthesis, characterization, and catalysis *in solution*—to the preparation of the next generation of improved, supported-nanoparticle heterogeneous catalysts.

**DOE Interest**

This research addresses key components of DOE's Grand Challenge for catalysis in the 21<sup>st</sup> century, specifically: (a) “nanocatalysis...the exciting possibility of building novel catalytic materials that combine the best features of homogeneous and heterogeneous catalysts”, (b) “catalysis design driven by fundamental research”, (c) “catalyst synthesis events, such as *nucleation and growth*”, (d) “greater control of self-assembly”, and the fact that (e) “nucleation and growth mechanisms are not yet sufficiently understood” to be able to exploit fully nanoparticle syntheses and their resultant catalysis. Overall, our research strives to fill a major hole in the scientifically and commercially important area of supported-nanoparticle heterogeneous catalysis—namely the issue of their kinetics and precise mechanism of formation—all while transferring solution-based nanoparticle kinetic, mechanistic and synthetic insights to the industrially more important area of supported-nanoparticle heterogeneous catalysts.

**Recent Progress**

We published 7 papers in the 2011 to early 2013 period; the titles of those publications are provided below. Significant to start is our 2012 review (publication #1 below; 38 pages and 294 references) which details what is, and is not, known about the kinetics and mechanisms of supported, “dirty/practical” heterogeneous catalysts—that is, industrially relevant heterogeneous catalysts. In publication #2 we were able to uncover the mechanism of formation of a supported-nanoparticle catalyst prepared in contact with solution. Follow-up publication #3 reveals that the key nanoparticle nucleation step is bimolecular, another important and previously unavailable insight, one relevant to controlling the size of the resultant nanoparticle catalyst.

Publications #4-7 below complete research began under our prior 3-year DOE grant, research that helps build the fundamental foundation of solution nanoparticle mechanisms of formation, catalysis and agglomeration. That work details (a) when nanoparticles are

the true heterogeneous (as opposed to homogeneous) catalyst (publication #4); (b) how the 2 agglomeration steps of our 4-step mechanism of nucleation, autocatalytic growth and 2 types of agglomeration applies to Au(0)<sub>n</sub> nanoparticles, mechanistic insights that replace a previous, mechanistically misleading, Avrami-type semi-empirical kinetic analysis (publication #5); and (c) how to perform and analyze nanoparticle 1,10-phenanthroline kinetic poisoning studies en route to learning more about the number of nanoparticle catalytically active sites (publication #6). In addition, we published (d) a collaborative studies with Professor Bruce Gates' group which employed our kinetic and poisoning methodologies en route to providing evidence for an atomically dispersed Ir true catalyst at 22 °C in that classic system (publication #7) In short, our DOE-supported research continues to be quite productive.

### Future Plans

Our plans follow closely our 2012 renewal proposal. Of immediate focus is to complete for publication Patrick Kent's work revealing that our solution 4-step mechanism of nanoparticle formation and agglomeration applies to the formation of supported Ir(0)<sub>~900</sub> nanoparticles on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> when beginning with (1,5-COD)IrCl/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in contact with solution. Next, we will focus on direct method, complimentary QXAFS and XRD/PDF monitoring of the (1,5-COD)IrCl/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to Ir(0)<sub>~900</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported-nanoparticle system—does that direct monitoring confirm, or refute and thereby refine in some fashion, our 2- and 4-step mechanisms of nanoparticle formation and agglomeration? Also in our plans are to complete a second, collaborative paper with Professor B. Gates on his interesting zeolite-supported iridium system in which our collaborative team was able to follow the sub-nanoparticle catalyst evolution and subsequent sintering.

### Publications (2011-2013)

1. J. E. Mondloch, E. Bayram, R. G. Finke, "A Review of the Kinetics and Mechanisms of Formation of Supported-Nanoparticle Heterogeneous Catalysts", *J. Mol. Catal. A.* **355** (2012) 1-38. ("Editor's Choice" selection).
2. J. E. Mondloch, R. G. Finke, "Supported-Nanoparticle Heterogeneous Catalyst Formation in Contact with Solution: Kinetics and Mechanism of the Conversion of Ir(1,5-COD)Cl/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to Ir(0)<sub>~900</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>", *J. Am. Chem. Soc.* **133** (2011) 7744-7756.
3. J. E. Mondloch, R. G. Finke, "Kinetic Evidence for Bimolecular Nucleation In Supported-Transition-Metal-Nanoparticle Catalyst Formation In Contact With Solution: The Prototype Ir(1,5-COD)Cl/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to Ir(0)<sub>~900</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> System", *ACS Catalysis* **2** (2012) 298-305.
4. E. Bayram, J. C. Linehan, J. L. Fulton, J. A. S. Roberts, N. K. Szymczak, T. D. Smurthwaite, S.Özkar, M. Balasubramanian, R. G. Finke, "Is It Homogeneous or Heterogeneous Catalysis Derived from [RhCp\*Cl<sub>2</sub>]<sub>2</sub>? In Operando XAFS, Kinetic and Crucial Kinetic Poisoning Evidence for Subnanometer Rh<sub>4</sub> Cluster-Based Benzene Hydrogenation Catalysis", *J. Am. Chem. Soc.* **133** (2011) 18889-18902.

5. S. Shields, W. E. Buhro, E. E. Finney, R. G. Finke, "Gold Nanocluster Agglomeration Kinetic Studies: Evidence for Parallel Bimolecular Plus Autocatalytic Agglomeration Pathways as a Mechanistic Alternative to an Avrami-Based Analysis", *Chemistry of Materials* **24** (2012) 1718-1725.

6. E. Bayram, R. G. Finke, "Quantitative 1,10-Phenanthroline Catalyst-Poisoning Kinetic Studies of Rh(0)<sub>n</sub> Nanoparticle and Rh<sub>4</sub> Cluster Benzene Hydrogenation Catalysts: Estimates of the Poison  $K_{\text{association}}$  Binding Constants, of the Equivalents of Poison Bound and of the Number of Catalytically Active Sites for Each Catalyst", *ACS Catalysis* **2** (2012) 1967-1975.

7. E. Bayram, J. Lu, C. Aydin, A. Uzun, N. D. Browning, B. C. Gates, Finke, R. G. "Mononuclear Zeolite-Supported Iridium: Kinetic, Spectroscopic, Electron Microscopic, and Size-Selective Poisoning Evidence for an Atomically Dispersed True Catalyst at 22 °C", *ACS Catalysis* **2** (2012) 1947-1957.

## Hydrogen-bonding Properties of Organic Silanols for Homogeneous Catalysis and Structural Models for Heterogeneous Catalysis

Annaliese K. Franz

Department of Chemistry, University of California, One Shields Avenue, Davis, CA 95616

email: [akfranz@ucdavis.edu](mailto:akfranz@ucdavis.edu)

Based on their hydrogen-bonding properties, organic silanols and silanediols provide a new mode of activation for catalyst design as well as a model to study surface reactivity of heterogeneous catalysts for organic transformations. We have synthesized new organic silanols and silanediols to study and evaluate as homogeneous hydrogen-bonding catalysts, with a specific focus on the cooperative hydrogen-bonding effects of silanediols and the synthesis of a new chiral bifunctional silanols. Applications of these catalysts for carbon-carbon bond-forming reactions and enantioselective synthesis will be presented, where we have demonstrated the importance of cooperative H-bonding effects and SiOH-acidification for silanediol catalysis. These studies also provide important insight for catalyst design, particularly for consideration of asymmetric catalysis, which must take into consideration the self-recognition properties of silanols. Our studies include NMR binding studies, diffusion-ordered NMR spectroscopy (DOSY), X-ray structural studies, and computational studies. NMR and X-ray structure analysis provide key insights regarding the self-association of silanediols as well as the strong binding with Lewis basic molecules. An update of our work with chiral scandium Lewis acid catalysts, and several activation strategies for asymmetric catalysis, will also be discussed.

### References:

Tran, N. T.; Min, T.; Franz, A. K. *Chem. Eur. J.* **2011**, *17*, 9897-9900.

Tran, N. T.; Wilson, S. O.; Franz, A. K. *Org. Lett.* **2012**, *14*, 186-189.

Wilson, S. O.; Tran, N. T.; Franz, A. K. *Organometallics*, **2012**, *31*, 6715-6718.

Min, T.; Fettingner, J. C.; Franz, A. K. *ACS Catalysis*. **2012**, *2*, 1661-1666.

## Activation of Carbohydrates for Applications in Biofuels and Biofeedstocks

Postdoc: Matthew McLaughlin  
Student: Laura Adduci, Trandon Bender  
Contact: Dept of Chemistry, UNC Chapel Hill, Chapel Hill NC, 27599-3290  
[mgagne@unc.edu](mailto:mgagne@unc.edu)

### Goal

To develop new methods for the activation of carbohydrate C-O bonds for the synthesis of value added compounds and biofuels. The focus of our current efforts is the development of systems for the catalytic activation of silanes to generate an available hydride equivalent and a Lewis acidic silyl cation, which together provide a means for glycosidic C-O activation.

### DOE Interest

Carbohydrates are plentiful and renewable C<sub>6</sub>-sources, but they are notoriously difficult to convert into useful chemical stuffs, partially because of their already high oxidation states. If new methods could be developed to convert these materials into valuable chemical substances, the value and utility of these feedstocks (starch, cellulose, sugar, etc.) would grow and thus enable a shifting of our reliance on petroleum or coal resources towards one that was renewable. To enable progress to this goal we are investigating the fundamental reactivity of carbohydrates towards catalysts that have previously been involved in a variety of C-O and C-X bond activation reactions.

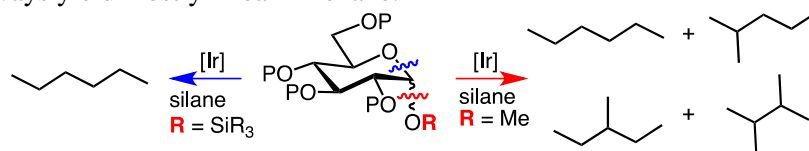
As part of our long-term goal of developing methodologies for the conversion of poly-saccharide feedstocks into value added materials, we have been investigating various methods for activating the key anomeric linkage in sugars. The guiding notion is that this bond not only links the sugars together, but is characterized by unique reactivity by virtue of its anomeric stabilization and the stereoelectronic effects that result. Learning to catalytically activate bonds at this center will provide the fundamental reactivity profiles that will eventually enable us to rationally design catalysts for their selective activation and subsequent conversion to modified, more useful structures. To this end, we have been investigating a number of approaches to their activation.

### Recent Progress

*Iridium catalysts for the conversion of glucose to hexanes.*

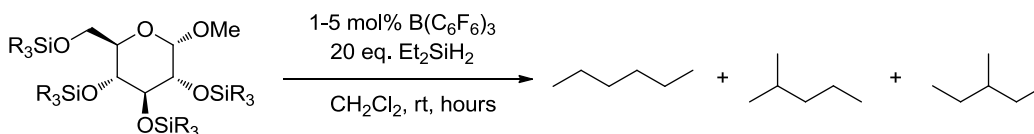
In light of diminishing petroleum feedstocks, there is significant interest in developing carbohydrate defunctionalization reactions. In this context we have examined the use of an iridium pincer catalyst originally reported by the Brookhart lab, (POCOP)IrH(L)<sup>+</sup>, for the hydrosilylative reduction of sugars. Utilizing the iridium-pincer catalyst, the sugar reacts with silane to generate a multitude of intermediates, which over time largely converge on hexane(s). Intriguingly, unlike most catalysts for sugar defunctionalization, this system operates at room temperature and is very selective for the reaction pathways that yield C<sub>6</sub> alkane products (up to 70% yield). This remarkable convergence to C<sub>6</sub> alkanes is possibly facilitated by the incredible kinetic hydricity of the transiently generated (POCOP)IrH<sub>2</sub>, which seems to suppress competition by dehydration, elimination, and other common reaction pathways. Analysis of the C<sub>6</sub> alkane product distribution from various sugar starting materials (e.g. C1-OMe glucose vs. C1-OSiR<sub>3</sub> glucose) has revealed dramatic variations in the relative amounts of n-hexane and alkyl-shifted hexane isomers. The source of this downstream product variation has been shown to result from

differences in the early chemistry of the reaction, which starts with either ring opening or deoxygenation at the anomeric position. Initial studies have indicated that the ring-closed intermediates yield greater amounts of alkyl-shifted products, whereas the open chain sugar reaction pathways yield mostly linear n-hexane.

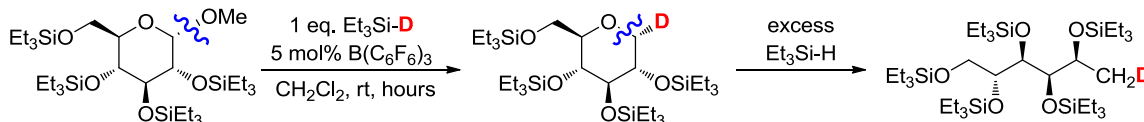


#### Boron catalysts for the deoxygenation of carbohydrates.

The success of our iridium-catalyzed hydrosilylative reduction of glucose to hexanes led us to investigate other Lewis acidic systems that have shown promising reactivity for alcohol reduction. In the presence of diethylsilane, one such Lewis acid, commercially available tris(pentafluorophenyl)borane or  $B(C_6F_5)_3$ , also performs a hydrosilylative reduction of glucose to a mixture of hexane isomers, at a rate that is even faster than that of the iridium-catalyzed reaction (hexanes observable within an hour vs. 1 day). However, different ratios of hexane isomers were observed, and we are still investigating whether the same mechanism governs the iridium- and  $B(C_6F_5)_3$ -catalyzed reactions. Under  $B(C_6F_5)_3$  catalysis, we were able to reduce a wide variety of monosaccharides, oligosaccharides, and polysaccharides, including methyl cellulose, to give deoxygenated products.

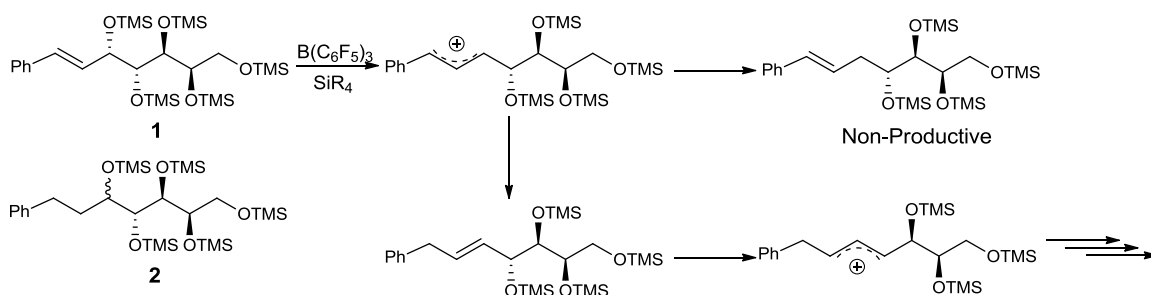


As the deoxygenation pathway is difficult to observe due to the fast rate and many simultaneous reactions taking place, we wondered whether bulkier silanes would be able to slow down the reaction or enhance selectivity, allowing us to gain some insight into the mechanism of the reaction. Treating silyl-protected C1-methoxy glucose with the bulkier triethylsilane in the presence of  $B(C_6F_5)_3$  led to a doubly deoxygenated species. While we were confident from earlier experiments that the first site on this carbohydrate to undergo reduction would be the C1 position, giving 1-deoxy glucose, we envisioned two likely sites for the second deoxygenation: the pyranose oxygen, giving either 1-deoxy glucitol or 5-deoxy glucitol, or the primary alcohol at C6, giving C1,C6-deoxy glucose. Deuterium labeling studies allowed us to identify this product as 1-deoxy glucitol, indicating that ring-opening on the C1 side is more favorable than either ring-opening on the C5 side or reduction of the primary C6 alcohol. We are particularly interested in this and other methods of obtaining partially deoxygenated products for use as biofeedstocks.



#### Mild hydrosilylative activation of allylic ethers with boron Lewis acids.

Activation of silane by a Lewis acid, such as tris(pentafluorophenyl)boron, has been utilized to perform hydrosilylative activation of primary and secondary silylethers. The suggested mechanism of this activation results in an oxonium ion that can be reduced with a hydride through an  $S_N1$ - or  $S_N2$ -like mechanism. If an  $S_N1$ -type mechanism were favored over  $S_N2$ , stabilization of the resulting carbocation would strongly influence the rate of activation. One way to increase stability of the carbocation is to introduce a stabilizing group, such as a phenyl or vinyl group. In particular, the addition of a vinyl group offers the intriguing possibility of the alkene propagating down an oxygen-rich backbone through an allyl carbocation, offering stabilization for each successive reduction:



With this in mind a styrene moiety was installed on galactose (**1**). Hydrogenation of this substrate yields a saturated species **2** with the same degree of oxygenation but without access to an allyl carbocation. Comparing the rate of starting material consumption for substrates **1** and **2** revealed that the presence of an allylic carbocation greatly influenced reactivity of the substrate. When reductions are carried out at reduced temperatures, below  $-50^\circ\text{C}$ , the allyl species proceed approximately nine times faster than the non-allyl species.

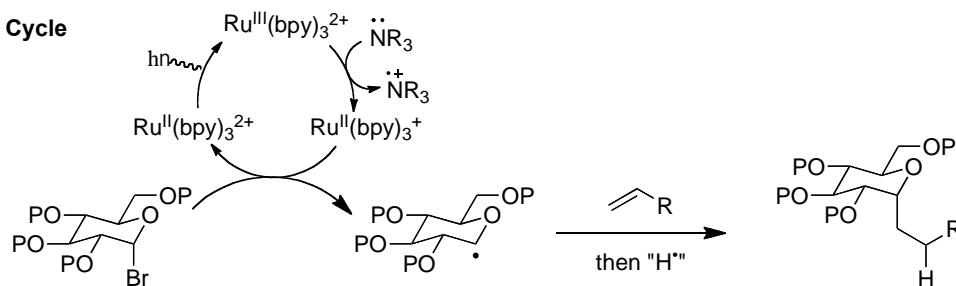
In contrast to  $SiEt_2H_2$ , the bulkier silane  $SiMe_2EtH$  did not offer complete deoxygenation of **1** below  $-50^\circ\text{C}$ . Surprisingly, under the same conditions, the addition of allyl benzene to the reaction mixture results in complete deoxygenation of **1**, suggesting a substantial rate increase. At this point the role of the allyl benzene and the mechanistic implications are still under investigation.

#### *Photoflow reactors for carbohydrate activation.*

The high yield and diastereoselectivity of our photomediated *C*-glycoside synthesis encouraged us to scale up this reaction, so that the *C1*-alkyl glycoside products could be used in a divergent synthesis of *C*-glycopeptides and *C*-glycolipids. In this system, a dicationic tris(bipyridine)ruthenium(II) catalyst is activated by visible light to generate a reductive photoredox equivalent, which is capable of converting a glycosyl halide to a *C1*-glycosyl radical. This glycosyl-based radical can be trapped with an electron-deficient alkene to generate the desired *C*-glycoside. While this reaction was efficient on small scales, attempts to increase the scale resulted in a dramatic decline in rate. This decrease can be attributed to Beer's law, which predicts that at our ideal catalyst concentration, 98% of the light is absorbed by the catalyst within 1 mm of the vessel wall, rendering the majority of the reaction volume dark and the majority of the catalyst unactivated.

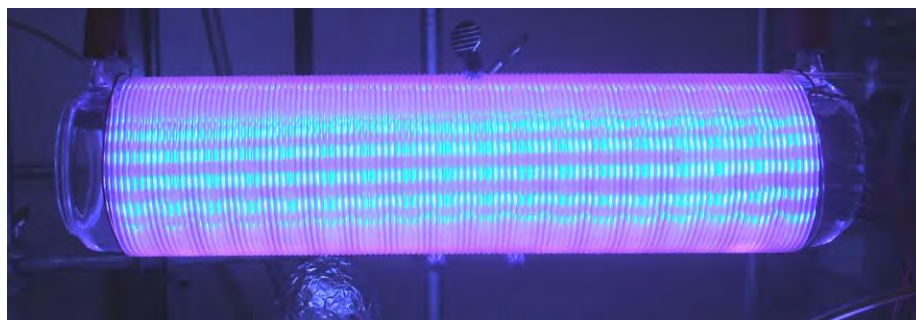


### Photoredox Cycle

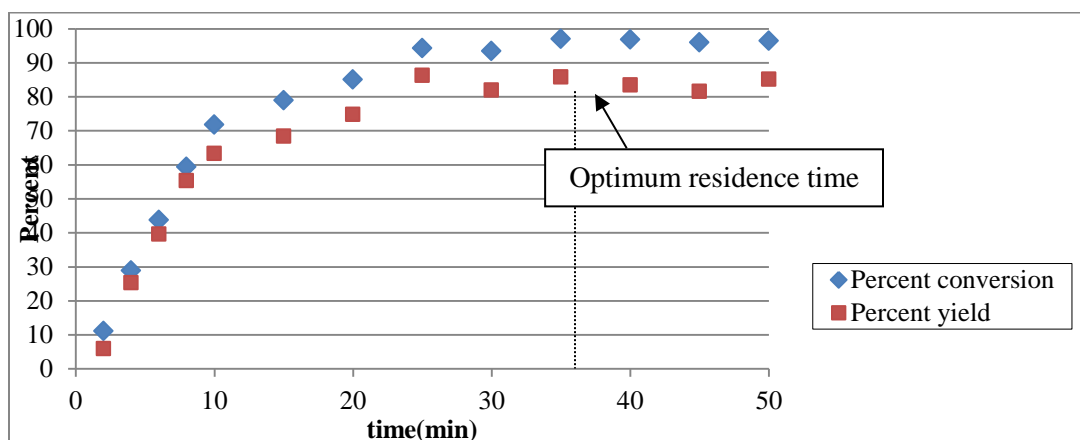


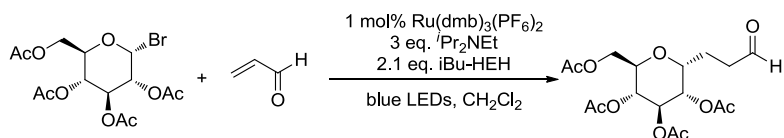
To circumvent this limitation, we assembled a photoflow reactor, in which transparent tubing with an inner diameter of 0.8 mm is coiled around strips of LED lights and the reaction mixture is irradiated as it flows through the tubing. This setup allowed us to recover the high efficiencies that we had observed on smaller scales. The reaction throughput was dramatically increased by rendering the reaction scale-independent, allowing us to generate multigram quantities of C-glycosides within a few hours.

### Photoflow reactor



To monitor the progress of reactions in the photoflow reactor, we perfected a method in which we first filled up the reactor with reaction mixture while the lights were off, and then turned on the lights, started the flow, and collected aliquots periodically from the reactor outlet. Each aliquot was analyzed for conversion and yield, allowing us to quickly pinpoint the optimum residence time for any particular reaction. Running a full-scale reaction using this residence time ensures that we are using the photoflow reactor with maximum efficiency.





## Future Plans

*Ir- and B-Catalysts for carbohydrate deoxygenation.* With protocols for active catalytic reductions in hand we plan to transition experiments to the deoxygenation of a broader collection of biomass materials, study mechanisms of deoxygenation, and seek to optimize partial deoxygenation protocols.

*Light Mediated Reductive Coupling.* Current work in this area focuses on characterizing photoflow reactors and improving catalysts efficiencies.

## Publications (2009-2013)

“Iridium-Catalyzed Hydrosilylative Reduction of Glucose to Hexane(s).” McLaughlin, M. P.; Adduci, L. L.; Becker, J. J.; Gagné, M. R. *J. Am. Chem. Soc.* **2013**, *135*, 1225-1227.

“A Photoflow Reactor for the Continuous Photoredox-Mediated Synthesis of C-Glycoamino Acids and C-Glycolipids.” Andrews, R. S.; Becker, J. J.; Gagné, M. R. *Angew. Chem. Int. Ed.* **2012**, *51*, 4140-4143.

“Investigating the Rate of Photoreductive Glucosyl Radical Generation.” Andrews, R. S.; Becker, J. J.; Gagné, M. R. *Org. Lett.* **2011**, *13*, 2406-2409.

“Oxidative Addition of Secondary C–X Bonds to Palladium(0): A Beneficial Anomeric Acceleration.” Munro-Leighton, C.; Adduci, L. L.; Becker, J. J.; Gagné, M. R. *Organometallics* **2011**, *30*, 2646-2649.

“Intermolecular Addition of Glycosyl Halides to Alkenes Mediated by Visible Light.” Andrews, R. S.; Becker, J. J.; Gagné, M. R. *Angew. Chem. Int. Ed.* **2010**, *49*, 7274-7276.

“Sn-Free Ni-Catalyzed Reductive Coupling of Glycosyl Bromides with Activated Alkenes.” Gong, H.; Andrews, R. S.; Zuccarello, J. L.; Lee, S. J.; Gagné, M. R. *Org. Lett.* **2009**, *11*, 879-882

“Oxidative Addition of Glycosylbromides to trans-Ir(PMe<sub>3</sub>)<sub>2</sub>(CO)Cl.” Pelczar, E. M.; Munro-Leighton, C.; Gagné, M. R. *Organometallics* **2009**, *28*, 663-665.

## Tuning Catalytic Properties of Molecular Metal Clusters on Supports

PIs: Ilke Arslan (Pacific Northwest National Laboratory), David Dixon (U. of Alabama), Bruce Gates (U. of California, Davis, UCD), Alexander Katz (U. of California, Berkeley, UCB)

Post-docs: Andrew Solovyov (UCB)

Graduate Students: Jing Lu (UCD), Joseph D. Kistler (UCD), Mingyang Chen (UA)

Collaborators: Nigel Browning (PNNL), C. Y. Chen (Chevron), Sonjong Hwang (Caltech), Tobin Marks (Northwestern), L. Wang (Southern Illinois)

### Goals

The analysis and control of catalytic properties of essentially molecular supported metals by choice of metal (e.g., Rh, Ir, Os); metal nuclearity (e.g., Ir, Ir<sub>4</sub>, Os, Os<sub>3</sub>, Os<sub>4</sub>, Os<sub>5</sub>, Os<sub>10</sub>), ligands, and support (also a ligand), including control of metal surface reactivity in a supported Ir<sub>4</sub> cluster catalyst is leading to a better understanding of catalytic properties and the design of new catalysts.

### DOE Interest

Molecular-scale structure-function relationships in catalysis and control of catalytic properties constitute a catalysis grand challenge that is central to DOE missions. This project focuses on harnessing the power of synthesis, self assembly, spectroscopy, atomic-resolution microscopy, theory, and catalyst performance testing to understand well-defined, essentially molecular metal clusters as catalysts on support surfaces. Our intent is that this project be at the forefront in the synthesis, characterization, and imaging of metal cluster catalysts consisting of well-defined sites for catalysis, encompassing fundamental understanding of catalysts and discovery of active sites with new selective properties.

### Recent Progress

Essentially molecular metal complexes and clusters have been synthesized on supports from organometallic precursors such as Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(acac) and Os<sub>3</sub>(CO)<sub>12</sub>. The structures have been determined precisely by IR and EXAFS spectroscopies, and atomic-resolution TEM, and further characterized by density functional theory calculations. The supports include those that are crystalline, which allow precise characterization of the metal-support interface. The properties of the supported clusters have been varied systematically by incorporation of ligands, which influence the catalytic properties by electronic and steric effects. Zeolites are especially valuable supports for the determination of the metal-support interface structure and for visualization of individual metal atoms as they aggregate to form clusters. Vacant binding sites have been created on supported Ir<sub>4</sub> clusters by controlled removal of initially present CO ligands by simple dissociation in flowing gas or, alternatively, a new method consisting of reactive decarbonylation with the bulky oxidant trimethylamine-N-oxide. Both syntheses lead to metal sites that are accessible to CO. Accessibility of reactants to catalytic sites in zeolites is increased by delamination, and the delamination process has been elucidated by tomographic methods in TEM.

The chemistry of supported site-isolated cobalt, rhodium, and iridium complexes was investigated with DFT and the results compared with experimentally determined spectra. The data characterize ligand exchange reactions and catalytic reactions of adsorbed ligands, including

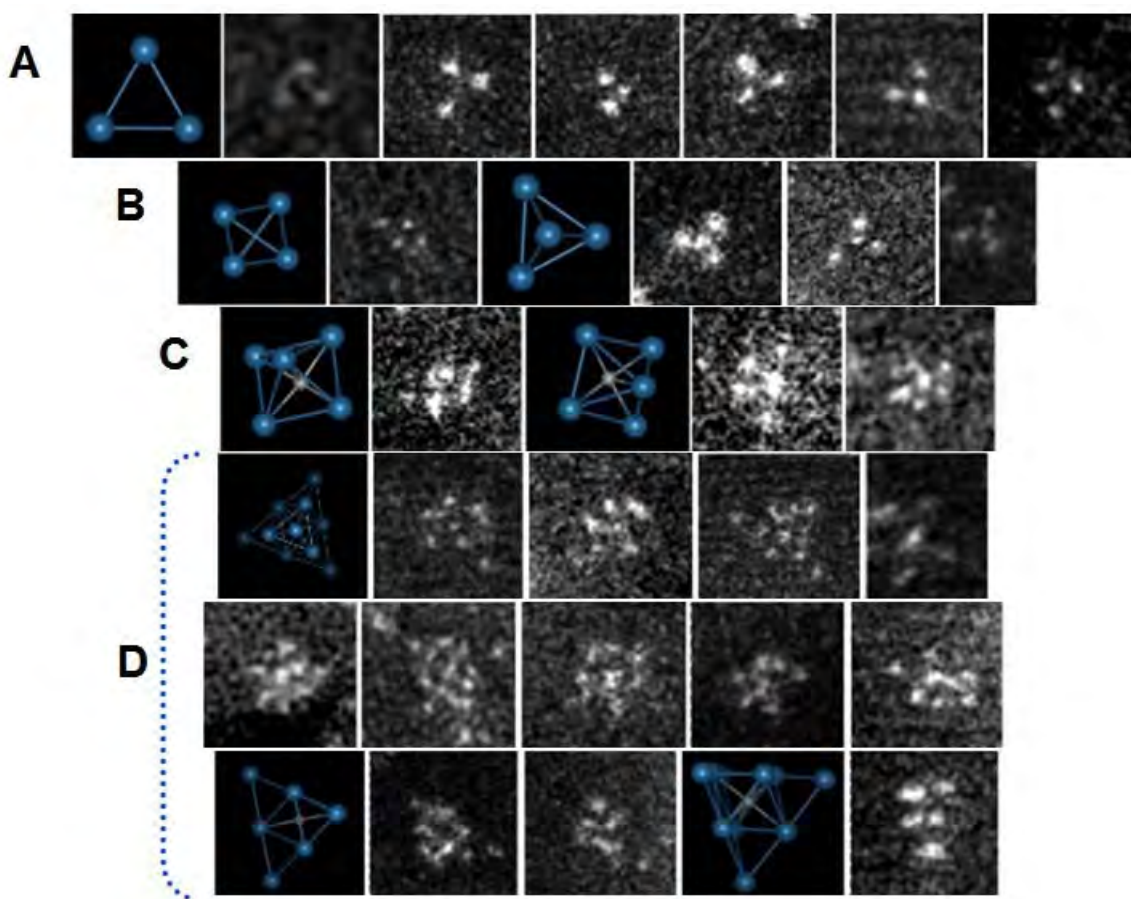
olefin hydrogenation and acetylene cyclotrimerization. Several molecular models were used to characterize various binding sites of the metal complexes in the zeolites. The calculated structures and energies indicate a metal–oxygen (M(I)–O) coordination number of two for most of the supported complexes but a value of three when the ligands include  $C_2H_5$  or H. The results characterizing various isomers of supported metal complexes incorporating hydrocarbon ligands indicate that some carbene and carbyne ligands could form. A set of ligand bond dissociation energies was determined to explain reactivity trends, as were calculated potential energy surfaces for ethylene hydrogenation. These complexes can be converted into supported metal clusters, exemplified by  $Ir_4$ , and similar calculations are being done to characterize them. Agreement between theory and experiment is good, and the use of a simple acid site model was validated by use of a much larger model. The most reliable calculations of the structures and energetics of  $Ir_n$  ( $n = 2-8$ ) clusters were calculated using CCSD(T) and MRCI ( $n = 2, 3$ ). The inclusion of spin orbit corrections (neglected in all previous work) is critical to obtaining good estimates of cluster binding energies and further heightens the need to include such corrections for third-row transition metal calculations. A method was developed for the calculation of the energetics of CO addition to form  $Ir_n(CO)_m$  clusters. For example, the results provided an energetic rationalization of the observed equilibrium between  $Ir_4(CO)_{12}$  and  $Ir_6(CO)_{16}$  as a function of temperature and CO partial pressure.

Imaging by HAADF-STEM has been used to characterize individual Ir atoms in zeolite HSSZ-53-supported iridium complexes, and the first steps of cluster formation were observed as the Ir atoms moved under the influence of the electron beam in the one-dimensional pores of the zeolite.  $Ir_6$  clusters were formed in zeolite NaY and imaged with atomic resolution, determining the locations of the clusters in zeolite supercages. Images of the zeolite UCB-1 were determined at various stages of delamination, with the results providing evidence of the nature of the delamination process.

A family of osmium clusters was prepared on MgO, and the two-dimensional STEM images determined the three-dimensional structures of Os,  $Os_3$ ,  $Os_4$ ,  $Os_5$ , and  $Os_{10}$  frames (Fig. 1); this work foretells the use of HAADF-STEM to determine the structures of individual metal clusters in supported industrial catalysts. STEM images of iridium clusters forming from atomically dispersed iridium complexes on MgO showed that cluster growth occurred until the clusters became about 1 nm in diameter, and the clusters merely bounced off each other, being stabilized at this critical size, which had been predicted by theory—this is a “smart” sinter-resistant catalyst—iridium may be unique in allow the formation of such stabilized clusters, independent of the support.

Silica-supported  $Ir_4$  clusters ligated with bulky calixarene-containing phosphine ligands were treated to form the various types of open “coordinatively unsaturated” clusters shown in Fig. 2. A crucial enabling discovery in line with previously proposed mechanical models of stability of such open clusters is the role of the sterically bulky calixarene ligand (shown schematically on the top panel of Fig. 2). Open clusters with this ligand are stable whereas they are not with the sterically less demanding and smaller  $PPh_2Me$  ligand (this was verified using dynamic light scattering). We investigated the kinetic consequences of open sites synthesized using two different methods: (a) simple CO dissociation via gas flow and (b) reactive decarbonylation using TMAO (Fig. 2). We characterized ethylene hydrogenation reaction kinetics when using

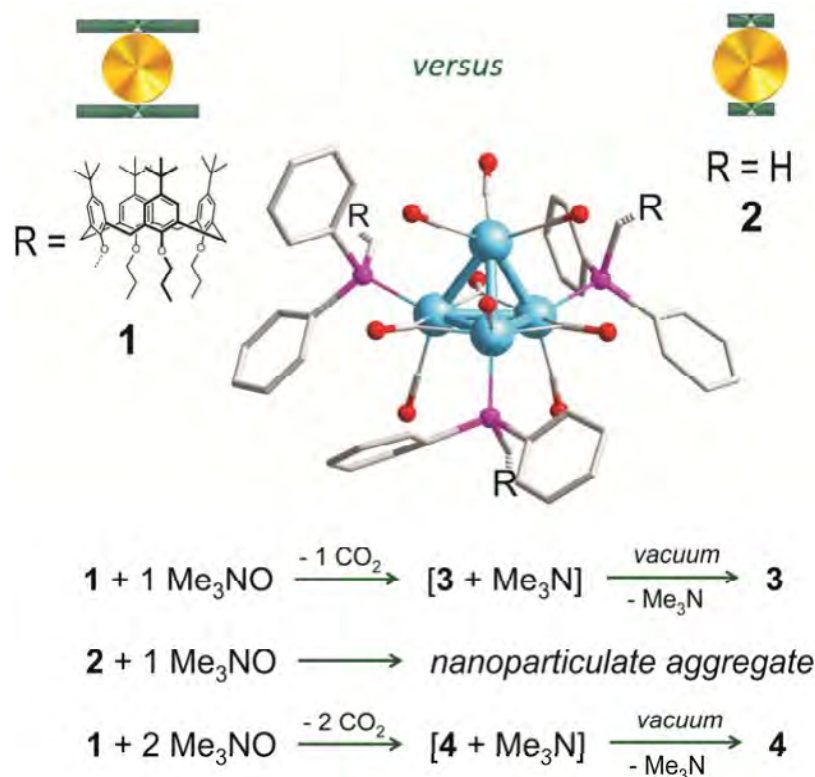
both types of open sites (i.e., those derived from both methods), in the form of supported clusters on silica. The initial activity of the supported closed cluster (1) catalyst was nearly zero, and this remained so even after open sites were created on this cluster as a result of CO dissociation in flowing gas (*vide infra*). In sharp contrast, both supported open clusters synthesized via reactive decarbonylation with TMAO exhibited significant initial activities, and remained much more active than the supported closed catalyst, even after a significant time ( $> 24$  h) on stream. By this time on stream, the supported closed catalyst had lost more than 70% of its initial carbonyl ligands. There was no direct correlation between catalytic activity and the number of CO ligands removed on a metal cluster catalyst—instead the sites created by reactive decarbonylation with TMAO were active for ethylene hydrogenation, whereas those created by simple desorption of CO during gas-flow treatment were not. Thus, the data demonstrate selectivity associated with subtle control of catalysis depending on how vacancies are synthesized on the metal surface.



**Fig. 1.** Crystallographic models of osmium clusters and corresponding images of MgO-supported osmium clusters. (A)  $\text{Os}_3$  framework in  $[\text{Os}_3(\text{CO})_{11}]^{2-}$  and images of  $\text{Os}_3$  clusters, (B)  $\text{Os}_4$  framework in  $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$  and images of  $\text{Os}_4$  clusters, (C)  $\text{Os}_5$  framework in  $[\text{Os}_5\text{C}(\text{CO})_{14}]^{2-}$  and images of  $\text{Os}_5$  clusters, (D)  $\text{Os}_{10}$  framework in  $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$  and images of  $\text{Os}_{10}$  clusters. Images are of sample treated in flowing helium at 548 K and 1 bar for 2 h followed by flowing CO at 548 K and 1 bar for 4 h.

### Future Plans

A deeper understanding of how to control reactivity of CO vacancies and catalytic properties of metal clusters is a major goal of the future work; we will address how to control and characterize the local environment surrounding vacancies on the clusters, using spectroscopy, microscopy, and theory. We will extend the investigation to other clusters such as hexanuclear rhodium and iridium carbonyls.



**Fig. 2.** Schematic representation of  $\text{Ir}_4(\text{CO})_9(\text{phosphine})_3$  clusters consisting of calixarene phosphine **1** and  $\text{PPH}_2\text{Me}$  in **2**. Bottom panel represents the method of synthesizing a vacancy by reactive decarbonylation using TMAO. This procedure is used to synthesize stable calixarene-bound open clusters **3** and **4**.

### Publications (2011–2013)

"Prototype Supported Metal Cluster Catalysts:  $\text{Ir}_4$  and  $\text{Ir}_6$ ," A. Uzun, D. A. Dixon, and B. C. Gates, *ChemCatChem*, **3**, 95 (2011).

" $\text{Ir}_6$  Clusters Compartmentalized in the Supercages of Zeolite NaY: Direct Imaging of a Catalyst with Aberration-Corrected Scanning Transmission Electron Microscopy," C. Aydin, J. Lu, M. Shirai, N. D. Browning, and B. C. Gates, *ACS Catal.*, **1**, 1613 (2011).

"Tracking Iridium Atoms with Electron Microscopy: First Steps of Metal Nanocluster Formation in One-Dimensional Zeolite Channels," C. Aydin, J. Lu, A. J. Liang, C.-Y. Chen, N. D. Browning, and B. C. Gates, *Nano Lett.*, **11**, 5537 (2011).

"Hydrogen Activation and Metal Hydride Formation Trigger Cluster Formation from Supported Iridium Complexes," J. Lu, C. Aydin, N. D. Browning, and B. C. Gates, *J. Am. Chem. Soc.*, **134**, 5022 (2012).

"Electron Tomography: Seeing Atoms in Three Dimensions," I. Arslan and E. A. Stach, *Nat. Mats.*, **11**, 911 (2012).

"A Smart Catalyst: Sinter-resistant Supported Iridium Clusters Visualized with Electron Microscopy," C. Aydin, J. Lu, N. D. Browning, and B. C. Gates, *Angew. Chem., Int. Ed.*, **51**, 5929 (2012).

"Structures and Stability of  $\text{Ir}_n(\text{CO})_m$ ," M. Y. Chen, J. E. Dyer, B. C. Gates, A. Katz, and D. A. Dixon, *Mol. Phys.*, **110**, 1977 (2012).

"Defragmenting Catalysis" (editorial), B. C. Gates and T. J. Marks, *Angew. Chem., Int. Ed.*, **51**, 11644 (2012).

"Gold nanoparticle-catalyzed reduction in a model system: Quantitative determination of reactive heterogeneity of a supported nanoparticle surface," M. M. Nigra, I. Arslan, and A. Katz, *J. Catal.*, 115–121 (2012).

"Sinter-Resistant Catalysts: Supported Iridium Nanoclusters with Intrinsically Limited Sizes," J. Lu, C. Aydin, N. D. Browning, L. Wang, and B. C. Gates, *Catal. Lett.*, **142**, 1445 (2012).

"Computational Study of the Low-lying Electronic States of  $\text{Ir}_n$  Clusters with  $n = 2 - 8$  at the DFT, CASSCF, and CCSD(T) Levels," M. Chen and D. A. Dixon *J. Phys. Chem. A*, **117**, 3676 (2013).

## From Hydrodesulfurization to Hydrodeoxygenation: What are the similarities at the atomic-scale?

B. Baek, S. Kasiraju, L. C. Grabow\*

University of Houston, Department of Chemical and Biomolecular Engineering  
4800 Calhoun Rd., Houston, TX 77204-4004  
e-mail: grabow@uh.edu

Fast pyrolysis of biomass is a promising low-cost technology that produces bio-oil suitable for use as transportation fuel after an appropriate upgrade step. The upgrade is necessary to increase the heating value, lower the viscosity and improve the long-term stability, and can be achieved by reducing the oxygen content through hydrotreatment over heterogeneous catalysts. While hydrodeoxygenation (HDO) of bio-oil is an emerging technology, hydrotreating for the removal of sulfur from petroleum products (HDS) has matured over decades and detailed knowledge regarding the catalyst structure, active sites and reaction mechanism are available. Both hydrotreating processes show similarities on the macroscopic scale and the identification of atomic-scale catalytic reactivity descriptors may speed up the discovery of novel HDO catalysts from existing knowledge of HDS chemistry.

We have investigated the HDO mechanism of acetaldehyde, a surrogate molecule for the over 400 different oxygenated species in biomass-derived pyrolysis oil, on the Ru(0001) RuO<sub>2</sub>(110) and the RuO<sub>2</sub>/TiO<sub>2</sub>(110) overlayer surfaces using Density Functional Theory (DFT) calculations. Future efforts will focus on HDO of furan to make a direct comparison with results of similar studies of thiophene HDS on CoMoS.<sup>1,2</sup> The surface structure of metal-sulfides and metal-oxides under reaction conditions and the role of surface vacancies as active sites during both, HDS and HDO, are discussed. DFT results indicate that acetaldehyde can be selectively deoxygenated on vacancy sites of RuO<sub>2</sub>(110), but metallic Ru favors C-C bond over C-O bond scission, which leads to the unwanted decarboxylation reaction and the formation of carbon deposits.

Given the higher C-O bond scission selectivity on the metal-oxide, we intend to screen more metal-oxides for their HDO activity and selectivity. Therefore, we are developing a simplified model for the description of the surface free energy of rutile(110) surfaces that will allow the prediction of surface phase diagrams and equilibrium O-vacancy concentrations by calculating just a few parameters. In combination with a more detailed understanding of the HDO mechanism on metal-oxide catalysts and by drawing parallels to the related and well-studied HDS catalysis, new and efficient materials for HDO can be developed faster and ultimately lead to an increased utilization of biofuels.

### References

- (1) Moses, P. G.; Hinnemann, B.; Topsøe, H.; Nørskov, J. K. *Journal of Catalysis* **2009**, *268*, 201–208.
- (2) Moses, P. G.; Hinnemann, B.; Topsøe, H.; Nørskov, J. K. *Journal of Catalysis* **2007**, *248*, 188–203.



## Controlling Heterogeneous Catalyst Selectivity Using Grafted Metallocalixarene Active Sites

Students: Ying-Jen Wanglee (U. of California at Berkeley, UCB), Partha Nandi UCB), Andrew Solovyov (UCB)

Collaborators: Vitaly I. Kalchenko (Ukrainian Academy of Sciences, Ukraine), Matthew Neurock (University of Virginia), Sonjong Hwang (Caltech), Jeffrey Reimer (UCB).

### Goal:

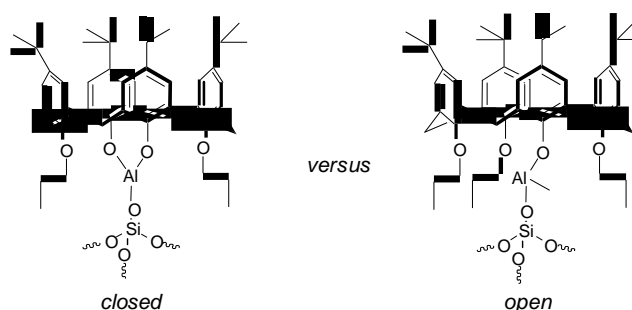
The design and synthesis of supported molecular active sites consisting of grafted metals within open/closed coordination geometries on solid surfaces, for the control of selective catalysis.

### DOE Interest:

There is a mounting body of evidence (glucose isomerization, MPV reduction, and Baeyer-Villiger oxidation with Sn-Beta, olefin epoxidation with TS-1, etc) that suggests control of open versus closed coordination geometries of grafted cations on surfaces can play a significant role in catalysis. This is yet another example of molecular structure of grafted surface-bound species and catalytic function, which is a subset of a greater grand challenge related to molecular structure-function correlations in catalysis on surfaces.

### Recent Progress:

Control of Open and Closed Coordination Geometries in Metal Complexes

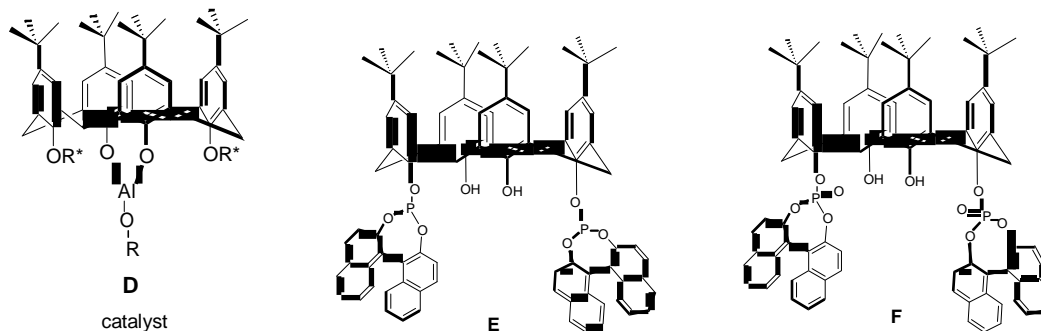


We have successfully demonstrated a new approach for the control and understanding of heterogeneous catalysts, with the synthesis by design of open and closed variants of a grafted Lewis acid active site shown above. These sites are characterized and used to elucidate details of reaction mechanism and active site connectivity requirements, which have proven difficult to achieve using other means. The calixarene acts as a molecular template that enforces an either open or closed coordination geometry surrounding the metal center due to its lower-rim substituents as well as site isolation by virtue of its steric bulk.  $^{27}\text{Al}$  NMR spectroscopy of Al(III)-calixarene molecular precursors and  $^{27}\text{Al}$  MAS NMR spectroscopy of the closed variant of the grafted Lewis acid site material exhibit resonances consistent with a pseudo-tetrahedral, coordinatively unsaturated aluminum center. Elemental and thermogravimetric analyses show a calixarene to Al ratio of unity – as required for a molecular active site. Control of open versus closed

configurations of the grafted Lewis acid site is demonstrated by the complete lack of observed activity of the closed site for MPV reduction, which is known to require open sites for synthesizing bound alkoxide within the reaction mechanism. The open variant of this catalyst has an MPV reduction activity that is virtually identical to previously reported Al(III)-calixarene homogeneous catalysts. For olefin epoxidation using organic *tert*-butyl-hydroperoxide as oxidant, the open and closed catalysts exhibit similar activity. This observation sheds light on a longstanding question within olefin epoxidation catalysis when using hydroperoxide as oxidant: covalent binding of hydroperoxide may not be required and instead dative coordination to the Lewis acid center may be sufficient for catalytic oxo transfer. The latter result is confirmed via DFT calculations of the transition state barrier for olefin epoxidation using analogs of the open and closed materials as catalysts.

#### Chiral MPV Catalysis Using Al(III)-Calixarene Active Sites

We have recently synthesized enantioselective catalysts for the MPV reaction based on an Al(III) complex. Our approach is based on the design of symmetric calixarene ligands of type **D** previously reported. We have specifically already found ligand **E**, when used in conjunction with Al(III) isopropoxide, to be a highly enantioselective MPV catalyst – capable of catalyzing this reaction in excess of 99% ee.



#### Future Plans:

We are interested in generalizing our understanding of open/closed site requirements for epoxidation catalysis to other metals including grafted Ti(IV) on silica and grafted Ta(V) on silica. Our approach leverages on synthesizing the first open/closed variants of a grafted metal catalytic site above, to investigate the kinetic consequences of site requirements for these new metals. Previously, we have described a closed grafted Ti(IV)-calixarene catalyst on silica (Notestein et al., *J. Am. Chem. Soc.* 2004). Using solid-state NMR spectroscopy and labeling strategies to ensure that metal coordination geometry remains unchanged during catalysis, which can be verified by lack of removal of lower-rim substituents via intramolecular Lewis-acid catalyzed ether cleavage, we plan to investigate similar site requirements for open variants of the Ti(IV)-calixarene grafted on silica site. In addition, we plan to use similar approaches for investigating open/closed grafted Ta(V)-calixarene complexes on silica. Finally, we are in the process of understanding more fully attributes that lead to enantioselectivity in MPV reductions, when using the calixarene ligands described above.

**Publications 2011 - 2013:**

*MPV Reduction Using Al(III)-Calix[4]arene Lewis Acid Catalysts: Molecular-Level Insight Into Effect of Ketone Binding* by P. Nandi, Y.I. Matvieiev, V. I. Boyko, K. A. Durkin, V. I. Kalchenko, and A. Katz, *Journal of Catalysis* **2011**, 284, 42 – 49.

*Catalytic consequences of open and closed grafted Al(III)-calix[4]arene complexes for hydride and oxo transfer reactions* by P. Nandi, W. Tang, A. Okrut, X. Kong, S.-J. Hwang, M. Neurock, A. Katz, *Proceedings of the National Academy of Sciences USA*, **2013**, in press, [www.pnas.org/cgi/doi/10.1073/pnas.1211158110](http://www.pnas.org/cgi/doi/10.1073/pnas.1211158110)

**DOE Early Career Award and Institute for Atom-efficient Chemical Transformations** Jeffrey P. Greeley

## **Interfacial Electrocatalytic Processes and Heterogeneous Catalysis of Biomass from First Principles**

Early career: PI

IACT: co-PI

Current postdocs: Zhenhua Zeng

Xiangkui Gu

Collaborators: Nenad Markovic (Argonne), Maria Chan (Argonne), IACT co-PI's

Contacts: Purdue University, 480 Stadium Mall Dr., West Lafayette, IN 47907;

[jgreeley@purdue.edu](mailto:jgreeley@purdue.edu)

### **Goals**

Develop first principles-based models of electrochemical processes at liquid-metal interfaces. Develop efficient methods of treating complex biomassic reaction networks on transition metal catalyst surfaces.

### **DOE interest**

Chemical processes occurring at electrified liquid-solid interfaces are central to phenomena ranging from fuel cell electrocatalysis to solid electrolyte interphase formation in lithium ion batteries. However, these processes remain poorly understood at a molecular level, and first principles calculations are well-positioned to provide the insight that is needed to ultimately develop the next generation of electrochemical devices. In a similar manner, heterogeneous catalytic processes that convert biomassic feedstocks to fuels generally occur at aqueous-solid interfaces, and the reaction networks involved in these conversions are often so complex as to defy facile experimental characterization. First principles-based methods, combined with efficient bond order-based techniques, are beginning to provide insights into these complex chemistries.

### **Recent progress**

*Activity and selectivity trends in direct hydrogen peroxide synthesis at aqueous-metal interfaces:* We have combined periodic Density Functional Theory (DFT) calculations with microkinetic analyses to understand trends in both the activity and selectivity of transition metals and alloys for the production of hydrogen peroxide from hydrogen and oxygen. The resulting multidimensional

volcano plot rationalizes experimental intuition about this reaction and suggests targets for future catalyst design efforts.

*Inverse electrocatalysts:* Alkaline fuel cells have the potential to catalyze key electrochemical reactions without relying exclusively on costly platinum-based electrodes. We are exploring a novel class of bifunctional inverse electrocatalysts, suitable for operation in alkaline environments, that facilitates rapid bond-breaking at three-phase interfaces of base-metal hydroxyoxides on noble metal substrates. We have developed ab-initio phase diagrams of one and two monolayer films of nickel, cobalt, and manganese hydroxyoxides on Pt(111) substrates and have quantified the change in oxidation state of these films as a function of electrode potential. We have further shown, in conjunction with our experimental collaborators at Argonne National Laboratory, that edges and three-phase interfaces of these films impact the dissociation barriers for key reaction steps in the hydrogen evolution reaction, a critical chemistry in the production of hydrogen in chlor-alkali electrolyzers. By further developing detailed models of alkaline hydrogen evolution and hydrogen oxidation on well-defined surfaces of gold and platinum, and by comparing these results to our analyses at the three-phase interfaces, we have shown that the latter catalysts can exhibit significantly reduced activation barriers for key elementary reaction steps in these alkaline chemistries.

*Ab-initio molecular dynamics at water-metal interfaces:* To move beyond static models of water bilayers at water-metal interfaces, we are exploiting leadership computing resources at Argonne to run extended (>20 ps) ab-initio molecular dynamics simulations of liquid water on flat and stepped metal surfaces. We have established benchmarks for the statistical quality of the MD simulations and have observed spontaneous self-assembly of well-ordered water bilayers near the interfaces. We are currently exploring the effect of thermal fluctuations in these spontaneously formed bilayer structures on the energetics of reaction intermediates for the oxygen reduction reaction and for electrochemical reduction of NO<sub>x</sub>-containing species.

*Reaction networks of complex biomassic intermediates at metal surfaces:* the combinatorial complexity of reaction networks involving biomass-derived species, including alcohols and polyols, is such that full DFT calculations are computationally prohibitive. We have developed an approach that combines DFT calculations with bond order conservation-based methods to significantly accelerate the determination of the energetics of these reaction networks, without significant loss of accuracy. We have applied this method to determine trends in activity and selectivity of glycerol decomposition on a series of transition metal surfaces.

## **Future plans**

*Inverse electrocatalysts:* we will continue development of our models of three-phase interfaces, incorporating explicit water layers into the models and extending the considered classes of

reactions to CO electrooxidation and oxygen reduction. We ultimately hope to propose novel base metal/precious metal pairs with superior electrocatalytic properties.

*Reaction networks and solvated charges near metal surfaces:* building upon our AIMD work at water-metal interfaces, we will determine the impact of these dynamical ensembles on elementary bond-breaking barriers and will extend the models to incorporate solvated charges near the metal surfaces. These charges will constitute preliminary models of electrochemical double layers.

*Microkinetic treatment of biomass reactivity on metal surfaces:* we will extend our treatments of glycerol decomposition trends to metal alloys, including both reduced and partially oxidized (bifunctional inverse catalyst) alloys. We will combine our DFT results with microkinetic modeling to produce quantitative reaction rate estimates for these chemistries.

### Selected publications from the current grant period

- 1) "The road from animal electricity to green energy: combining experiment and theory in electrocatalysis." J. Greeley and N. Markovic, *Energy and Environmental Science* **5** (2012) 9246.
- 2) "Trends in Selective Hydrogen Peroxide Production on Transition Metal Surfaces from First Principles." R. Rankin and J. Greeley, *ACS Catalysis* **2** (2012) 2664.
- 3) "Rational Development of Ternary Alloy Electrocatalysts." C. Wang, D. Li, M. Chi, J. Pearson, R. Rankin, J. Greeley, Z. Duan, G. Wang, D. van der Vliet, K. More, N. Markovic, and V. Stamenkovic. *J. Phys. Chem. Letters* **3** (2012) 1668.
- 4) "Designing 3d-M(Ni,Co,Fe,Mn)-hydr(oxy)oxide catalysts for the water electrolyzer reactions by tuning OH<sup>-</sup>-Mn<sup>+</sup> energetics." R. Subbaraman, D. Tripkovic, K. Chang, D. Strmcnik, A. Paulikas, P. Hirunsit, M. Chan, J. Greeley, V. Stamenkovic, and N. Markovic. *Nature Materials* **11** (2012) 550.
- 5) "Unique electrochemical adsorption properties of Pt-skin surfaces." D. F. van der Vliet, C. Wang, D. Li, A. P. Paulikas, J. Greeley, R. Rankin, D. Strmcnik, D. Tripkovic, N. Markovic, and V. Stamenkovic, *Angewandte Chemie International Edition* **51** (2012) 3139.
- 6) "Periodic Trends in Adsorption and Activation Energies for Heterometallic Diffusion on (100) Transition Metal Surfaces." H. Yildirim, S. Sankaranarayanan, and J. Greeley, *J. Phys. Chem. C* **116** (2012) 22469.
- 7) "Compositional Tuning of Structural Stability of Lithiated Cubic Titania via Vacancy Filling Mechanism Under High Pressure." H. Xiong, H. Yildirim, P. Podsiadlo, J. Zhang, V. Prakapenka, J. Greeley, E. Shevchenko, K. Zhuvavlev, S. Tkachev, S. Sankaranarayanan, and T. Rajh, *Physical Review Letters* **110** (2013) 078304.
- 8) G. A. Ferguson, F. Mehmood, R. Rankin, J. Greeley, S. Vajda, and L. A. Curtiss, *Topics in Catalysis* **55** (2012) 353 – invited issue.
- 9) "Trends in methanol decomposition on transition metal alloy clusters from scaling and Brønsted-Evans-Polanyi relationships." F. Mehmood, R. B. Rankin, J. Greeley\*, and L. A. Curtiss, *Physical Chemistry Chemical Physics* **14** (2012) 8644. \*corresponding author
- 10) "Investigation of Catalytic Finite-Size-Effects of Platinum Metal Clusters." L. Li, A. H. Larsen, N. A. Romero, V. Morozov, C. Glinsvad, F. Abild-Pedersen, J. Greeley, K. W. Jacobsen, and J. K. Norskov, *J. Phys. Chem. Letters* **4** (2013) 222.
- 11) "A Density Functional Theory Analysis of Trends in Glycerol Decomposition on Close-Packed Transition Metal Surfaces", *Phys. Chem. Chem. Phys.* **15** (2013) 6745-6785.
- 12) "Decomposition Pathways of Glycerol via C-H, O-H, and C-C Bond Scission on Pt(111): A Density Functional Theory Study." B. Liu and J. Greeley. *J. Phys. Chem. C* **115** (2011) 19702.
- 13) "Density Functional Theory Study of C-O Bond Scission and Selectivity Considerations in Glycerol Decomposition on Pt(111)." B. Liu and J. Greeley, *Topics in Catalysis* **55** (2012) 280 – invited issue.

## Development of Transition Metal Catalysts for the Functionalization of Carbon-Hydrogen Bonds: Fundamental Studies of Catalytic Hydroarylation of Olefins

Postdocs: N/A  
 Students: Bradley McKeown, Evan Joslin, Steve Kalman, Max Friedfeld, Anna Brosnahan, Benjamin Vaughn  
 Collaborators: Thomas R. Cundari (U. of North Texas), Daniel H. Ess (Brigham Young University), Brian Trewyn (Colorado School of Mines),  
 Contact: Department of Chemistry, University of Virginia, Charlottesville, VA 22904; tbg7h@virginia.edu

### Goal

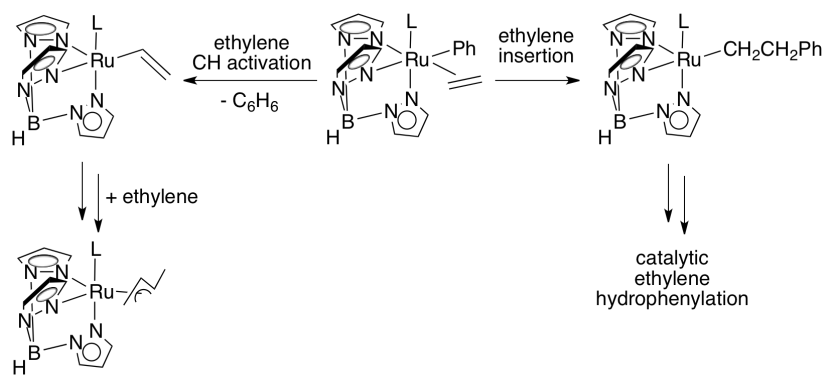
The goal of this project is to increase understanding of fundamental aspects surrounding homogeneous catalysts for the addition of carbon-hydrogen bonds across carbon-carbon multiple bonds. These studies will facilitate the rational design of future catalysts for the hydroarylation or hydroalkylation of carbon-carbon multiple bonds.

### DOE Interest

Arenes and olefins are primary chemical building blocks for the chemical industry. Upgrading these hydrocarbons to higher value materials generally involves either heterofunctionalization (e.g., oxidation) or C–C bond forming reactions, and many of the processes currently practiced involve forcing conditions (high temperatures and/or high pressures). This project is focused on the development of new molecular catalysts for C–H functionalization chemistry, especially the conversion of aromatic and olefin substrates to alkyl or vinyl arenes via olefin hydroarylation or oxidative olefin hydroarylation. Emphasis is placed on mechanistic studies and development of new understanding of how catalyst structure (e.g., ligand donor ability, ligand steric profile, metal oxidation state, metal identity) influences the dynamics of reactions within the desired catalytic cycle as well as likely, and undesirable, side reactions.

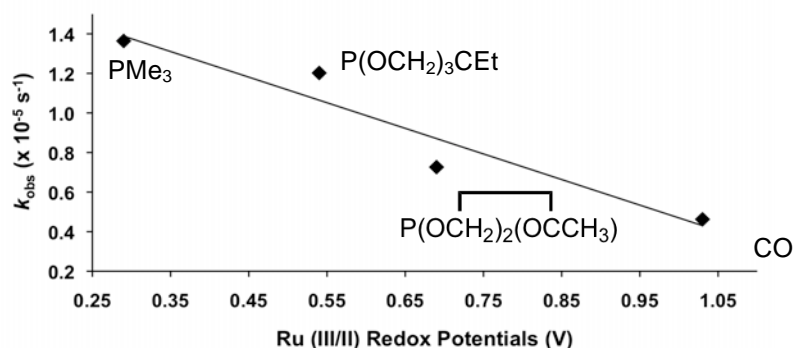
### Recent Progress

**Ruthenium Catalysts.** For catalytic olefin hydroarylation, we have previously reported on the influence of ancillary ligand "L" for Ru(II) catalysts of the type TpRu(L)(NCMe)Ph (L = CO, P(pyr)<sub>3</sub> (pyr = N-pyrrolyl), P(OCH<sub>2</sub>)<sub>3</sub>CEt and PMe<sub>3</sub>). We have extended this series to include the



phosphabicyclo[2,2,1]heptane [P(OCH<sub>2</sub>)<sub>2</sub>(OCCH<sub>3</sub>)]. These studies revealed that the overall rate of C<sub>6</sub>D<sub>6</sub> C–D activation by TpRu(L)(NCMe)Ph increases as the donor ability of L increases, but overall efficiency for catalytic hydrophenylation of ethylene decreases with increasing donor

ability. The primary route for catalyst deactivation with strongly donating ligands is competitive ethylene C–H activation, which ultimately leads to the formation of stable  $\eta^3$ -allyl complexes.



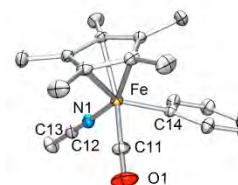
**Figure.** Plot of  $k_{obs}$  ( $\times 10^{-5}, s^{-1}$ ) values vs. Ru(III/II) potentials (vs. NHE, V) for the C–D activation of  $C_6D_6$  by  $TpRu(L)(NCMe)Ph$  at 60 °C with 0.065 mmol of added NCMe.

**Table.** Comparison of TON and TOF for ethylbenzene production from catalytic hydrophenylation of ethylene by  $TpRu(L)(NCMe)Ph$  complexes.

L	TON	Time	TOF ( $s^{-1}$ ) <sup>b</sup>	Relative TOF	$E_{1/2}$ (V vs. NHE)
CO	415	40 h	$6.7 \times 10^{-3}$	14	1.03
P(OCH <sub>2</sub> ) <sub>2</sub> (OCCH <sub>3</sub> )	90 <sup>a</sup>	50 h	$1.5 \times 10^{-3}$	3	0.69
P(OCH <sub>2</sub> ) <sub>3</sub> CEt	20 <sup>a</sup>	24 h	$4.8 \times 10^{-4}$	1	0.54
PMe <sub>3</sub>	0 <sup>a</sup>	---	---	---	0.29

<sup>a</sup> Catalyst deactivation occurs by formation of  $TpRu(L)(\eta^3-C_3H_4Me)$ . <sup>b</sup> Calculated after 4 h at 90 °C with 15 psi ethylene and 0.025 mol % of catalyst.

**Iron Catalysts.** Using  $Cp^*Fe(CO)(NCMe)Ph$  ( $Cp^*$  = pentamethylcyclopentadienyl) we have demonstrated that Fe(II) is capable of regioselective aromatic C–H activation at temperatures  $\leq 50$  °C. Kinetic studies, regioselectivities, isotopic labeling and computational studies are consistent with an Fe-mediated C–H activation without the formation of free radicals. The ability of this complex to insert ethylene into the Fe–Ph bond has also been demonstrated. Efforts to extend these studies to Fe-catalyzed olefin hydroarylation are ongoing.



**Platinum Catalysts.** We have placed substantial effort toward the study of Pt(II) catalysts for olefin hydroarylation. A detailed mechanistic study using  $[(^t\text{bpy})Pt(Ph)(L)]^+$  ( $^t\text{bpy}$  = 4,4'-di-tert-butyl-2,2'-bipyridyl; L = THF,  $NC_5F_5$ , or NCMe) complexes has been completed. Recently, we have demonstrated that selectivity for vinyl arene versus alkyl arene production can be controlled by the donor ability of 4/4'-substituents for  $[(^x\text{bpy})Pt(Ph)(L)]^+$  ( $^x\text{bpy}$  = 4,4'-X-2,2'-bipyridyl) catalysts for which the 4/4' "X" substituents are varied among <sup>t</sup>Bu, H, OMe,  $NO_2$ , Br and  $CO_2Et$ . Efforts to exploit this discovery for efficient catalytic synthesis of vinyl arene are ongoing. We have also demonstrated that substituting the 2,2'-bipyridyl ligand with 2,2'-dipyridylmethane results in a substantial increase in catalyst efficiency.

## Future Plans

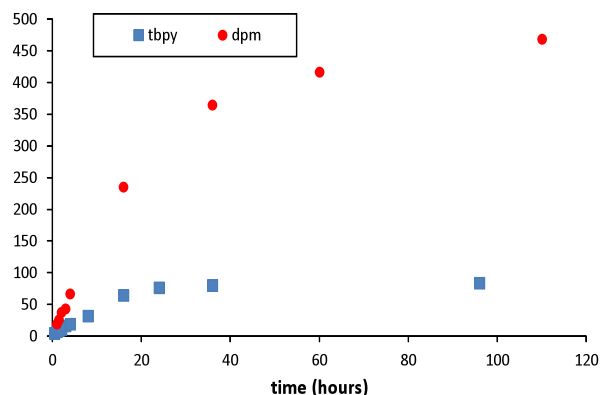
**Objective 1.** Study catalytic olefin hydroarylation using  $Ru^{II}$  catalysts supported by poly(pyrazolyl) ligands with similar or reduced electron density relative to  $TpRu(CO)(NCMe)Ph$ .



**Objective 2.** Extend chemistry of  $(^x\text{bpy})\text{Pt}^{\text{II}}$  to  $\text{Pd}^{\text{II}}$  and  $\text{Rh}^{\text{I}}$  catalysts. Preliminary calculations suggest that  $\text{Rh}^{\text{I}}$  catalysts should have lower overall activation barriers (compared with analogous  $\text{Pt}^{\text{II}}$  catalysts) for olefin hydroarylation, and we believe that  $\text{Pd}^{\text{II}}$  catalysts will be advantageous for the development of  $\tau_0$  oxidative olefin hydroarylation.

**Objective 3.** Continue to pursue catalysts for olefin hydroarylation based on first-row transition metals.

**Objective 4.** Develop single-site catalysts supported on mesoporous silica nanoparticles (MSNs) using the molecular catalysts based on Ru, Pt, Pd and Fe.



**Figure.** Comparison of TO versus time for ethylene hydrophenylation (100 °C) catalyzed by  $[(\text{N}\sim\text{N})\text{Pt}(\text{Ph})(\text{THF})]^+$  ( $\text{N}\sim\text{N}$ ) = 'bpy or dpm. 0.01 mol % Pt in  $\text{C}_6\text{H}_6$  with 0.1 MPa  $\text{C}_2\text{H}_4$ .

### Publications (2010 – 2013)

- " $\text{Pt}^{\text{II}}$  Catalyzed Ethylene Hydrophenylation: Influence of Dipyridyl Chelate Ring Size on Catalyst Activity and Longevity" McKeown, B. A., Gonzalez, H. E., Gunnoe, T. B.\*, Cundari, T. R.\*, Sabat, M. Manuscript accepted *ACS Catalysis*.
- " $\text{Pt}^{\text{II}}$  Catalyzed Ethylene Hydrophenylation: Switching Selectivity between Alkyl and Vinyl Benzene Production" McKeown, B. A., Gonzalez, H. E., Friedfeld, M. R., Brosnahan, A. M., Gunnoe, T. B.\*, Cundari, T. R.\*, Sabat, M. *Organometallics* ASAP.
- "Facile and Regioselective C–H Bond Activation of Aromatic Substrates by an Fe(II) Complex Involving a Spin-Forbidden Pathway" Kalman, S. E., Petit, A., Gunnoe, T. B.\*, Ess, D. H.\*, Cundari, T. R.\*, Sabat, M. *Organometallics* **2013**, *32*, 1797-1806.
- "2,2,2-Tris(pyrazolyl)ethoxide ( $\text{Ep}^{\text{ox}}$ ) Ruthenium (II) Complexes, ( $\text{Ep}^{\text{ox}}$ ) $\text{RuCl}(\text{L})(\text{L}')$ : Synthesis, Structure and Reactivity" Quillian, B., Joslin, E. E., Gunnoe, T. B.\*, Sabat, M. Manuscript *Inorg. Chem.* **2013**, *52*, 1113-1121.
- "Catalytic Hydroarylation of Ethylene using  $\text{TpRu}(\text{L})(\text{NCMe})\text{Ph}$  ( $\text{L}$  = 2,6,7-Trioxa-1-phosphabicyclo[2,2,1]heptane): Comparison to  $\text{TpRu}(\text{L}')(\text{NCMe})\text{Ph}$  Systems ( $\text{L}'$  = CO,  $\text{PMe}_3$  or  $\text{P}(\text{OCH}_2)_3\text{CEt}$ )" Joslin, E. E., McMullin, C. L., Gunnoe, T. B.\*, Cundari, T. R.\*, Sabat, M., Myers, W. H. *Organometallics* **2012**, *31*, 6851-6860.
- "Coordination Chemistry of 4-Methyl-2,6,7-Trioxa-1-phosphabicyclo[2,2,1]heptane: Preparation and Characterization of Ru(II) Complexes" Joslin, E. E., McMullin, C. L., Gunnoe, T. B.\*, Cundari, T. R.\*, Sabat, M. *Inorg. Chem.* **2012**, *51*, 4791-4801.
- "DFT Study of Group 8 Catalysts for the Hydrophenylation of Ethylene: Influence of Ancillary Ligands and Metal Identity" Morello, G. R., Cundari, T. R.\*, Gunnoe, T. B.\* *J. Organomet. Chem.* **2012**, *697*, 15-22.
- "Mechanistic Studies of Ethylene Hydrophenylation Catalyzed by Bipyridyl Pt(II) Complexes" McKeown, B. A., Gonzalez, H. E., Friedfeld, M. R., Gunnoe, T. B.\*, Cundari, T. R.\*, Sabat, M. *J. Am. Chem. Soc.* **2011**, *133*, 19131-19152.
- "Transition Metal Catalyzed Hydroarylation of Olefins using Unactivated Substrates: Recent Developments and Challenges" Andreatta, J. R., McKeown, B. A., Gunnoe, T. B.\* *J. Organomet. Chem.* **2011**, *696*, 305-315 (invited review).

## Highly Selective Bimetallic Hydrodeoxygenation Catalysts

Jason C. Hicks\*, Dallas J. Rensel  
University of Notre Dame, Department of Chemical and Biomolecular Engineering,  
Notre Dame, IN 46556  
e-mail: [jhicks3@nd.edu](mailto:jhicks3@nd.edu)

A key challenge in the design of catalysts for biomass conversions is control over product selectivity due to the abundance of reactive functionalities present in the feedstocks. To produce fuels from lignocellulosic biomass, highly selective catalysts are needed which deoxygenate biomass without hydrogenating the valuable aromatic compounds present in bio-oils or lignin.[1] A non-sulfided, unsupported bimetallic FeMoP material was synthesized and studied as a catalyst for C-O bond cleavage reactions involving aryl ethers and alkyl ethers.[2] Using the deoxygenation of phenol as one model reaction, the FeMoP catalyst exhibited selectivities as high as ~ 96 % benzene, 3 % cyclohexene, and 1 % cyclohexane at 400 °C and 2.1 MPa H<sub>2</sub> at near complete conversion (> 99%). A significant increase in deoxygenation selectivities was observed with Fe-rich catalysts compared to Mo-rich catalysts. Detailed x-ray diffraction, temperature programmed reduction, and transmission electron microscopy experiments indicated that formation of these FeMoP orthorhombic crystals is both time and temperature dependent. Furthermore, to achieve high deoxygenation selectivities, an optimum in catalyst preparation temperature is noticed. Mechanistic deuterium studies, oxidative stability, and recyclability of these materials are also discussed.

### References

1. J. C. Hicks, *J. Phys. Chem. Lett.*, **2011**, 2, 2280-2287.
2. D. J. Rensel, S. Rouvimov, M. Gin, J. C. Hicks, *J. Catal.*, in revision.

## New Single-atom Catalysts for Activation and Selective Reaction of Small Molecules, Including Alkanes

Main PI: Emilio E. Bunel  
Additional PIs: Elizabeth Mader, Marc Johnson, SonBinh T. Nguyen, Peter C. Stair, Adam S. Hock, Jeff Miller  
Postdocs: Steve Kraft, Kristine Tanabe, Erin M. Broderick (former), Neil Schweitzer (former), Bo Hu (IIT graduate student)  
Collaborators: Marek Pruski, Larry Curtiss, Jeffrey Greeley, Hack-Sung Kim  
Contacts: E. Mader, CSE Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439; [mader@anl.gov](mailto:mader@anl.gov)  
M. Johnson, CSE Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439; [mjohnson@anl.gov](mailto:mjohnson@anl.gov)  
S. Nguyen, Dept. Of Chemistry, Northwestern University, Evanston, IL 60208; [stn@northwestern.edu](mailto:stn@northwestern.edu)  
P. Stair, Dept. Of Chemistry, Northwestern University, Evanston, IL 60208; [pstair@northwestern.edu](mailto:pstair@northwestern.edu)  
A. Hock, Dept. Of Chemical and Biological Sciences, Illinois Institute of Technology, Chicago, IL 60616; [ahock@iit.edu](mailto:ahock@iit.edu)  
J. Miller, CSE Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439; [millerjt@anl.gov](mailto:millerjt@anl.gov)

### Goal

The objective of this research is to develop a new class of thermally stable single-atom heterogeneous catalysts that combine the best properties of heterogeneous and homogeneous catalysts. One goal is to demonstrate that single atom catalysts offer the design control and structural uniformity of homogeneous catalysts, and the thermal stability and robustness of heterogeneous catalysts. We utilize both traditional hard supports as well as a new class of tailorable porous organic polymers (POPs) to produce well-defined metal binding sites. A second goal is to show that these catalysts perform new chemistry, by activating small molecules by different mechanisms and reaction pathways than supported nano-particles. The project combines a precise application of organometallic grafting and atomic layer deposition to prepare and stabilize the single atom sites; state-of-the-art characterization of the active sites at reaction conditions; and quantum mechanical modeling to provide insight into the mechanisms of molecular activation and reaction pathways. The catalyst targets selected are those which offer the potential to activate C-H bonds which may lead to new selective catalyst systems for the conversion of light alkanes to liquid fuels.

### DOE Interest

Combining the tunability options of homogeneous catalyst architectures with the robust nature of heterogeneous catalysts remains an unsolved problem. Furthermore, understanding and controlling the site or ensemble of sites at the molecular level is a “grand challenge” of catalysis science. We are studying thermodynamically limited reactions and their low-temperature microscopic reverse reactions to understand the key steps in C-H, C-C, and other bond activations relevant to the conversion of light alkanes to liquid fuels.

## Recent Progress

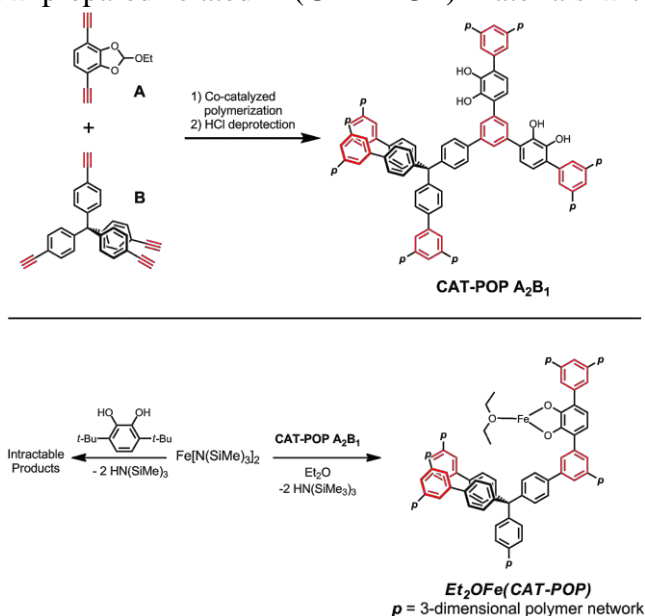
Our efforts fall into highly integrated categories:

- 1) Synthesis of new materials and advancing the art of preparing single-atom catalysts with novel structure and reactivity. Importantly, the target single-atom sites are to be thermally stable to maintain their unique structure and reactivity.
- 2) Catalysis and mechanistic studies to elucidate the mechanisms of our reactions and compare them between hard and soft-supported catalysts.
- 3) Advanced *in situ* characterization, including under reaction conditions by Raman, infrared, and x-ray absorption spectroscopy to determine the metal's coordination geometry, oxidation state, electronic properties, and reaction intermediates.
- 4) Theoretically analyze potential reaction mechanisms, deactivation pathways, and predict spectroscopic observables.

- Synthesis of new materials and catalysts.

We have prepared a library of single, isolated atom catalysts upon traditional supports such as high-surface area oxides and amorphous, porous organic polymers (POPs) that contain metal binding units such as catechols. We have leveraged our experience in organometallic synthesis to prepare low-coordinate species that are unstable in solution. For example, we recently described an iron catecholate immobilized in a POP, Fe(CAT-POP), with no freely homogeneous analogue (Fig. 1). We have now prepared related M(CAT-POP) materials with Ta, Co, Mn, Cr, V, and other metals. Furthermore, we have new capabilities in atomic layer deposition (ALD) to prepare small clusters and single atoms protected by overcoating.

We have also prepared a number of low-coordinate species on oxide supports and characterized them by x-ray absorption spectroscopy (XAS), catalytic measurements, infrared and Raman measurements, and theoretical calculations. These materials, when properly synthesized, also give rise to very low-coordinate metal centers capable of catalytic selectivities that resemble homogeneous systems.



- Catalysis and mechanistic studies.

Both classes of single-atom catalysts are catalytically active for a variety of reactions. They also display reactivities and selectivities indicative of the combination of homogeneous and heterogeneous catalysis features. These include selective propane *dehydrogenation* (to propylene and hydrogen) and *room temperature* hydrosilylation, low-temperature arene hydrogenation (e.g. toluene, benzonitrile, benzaldehyde), and functional group hydrogenation



- Determination of new reaction pathways: We are exploring new reactions based on the understanding of the new reaction pathways we are developing.

### Publications 2011-2013:

1. Sildake, N.A.; Tanabe, K.K; Broderick, E.M., Kobayashi, T.; Goldston, J.F.; Pruski, M.; Johnson, M.J.A.; Nguyen, S.T.; Mader, E.A.; “Stabilizing Species Inaccessible in Solution: The Synthesis and Characterization of a Tantalum-Amide containing Porous Organic Polymer” **2013**, *In preparation*.
2. Hu, B., Schweitzer, N. M., Lanci, M., Miller, J. T., and Hock, A. S. “A Comparison of Catalysis by Supported Iron Metal Nanoparticles and Single Site Fe(II)” **2013**, *to be submitted*
3. Hu, B., Schweitzer, N. M., Das, U., Kim, H. K., Stair, P. C., Curtiss, L., Hock, A. S., and Miller, J. T. “Heterogeneous Lewis Acid Co(II)/SiO<sub>2</sub> Catalyst for C-H Activation: Propane Dehydrogenation” **2013**, *to be submitted*
4. Kraft, S. J., Hu, B., Zhang, G., Miller, J. T., Hock, A. S, “In Situ X-Ray Absorption Spectroscopy and Non-classical Catalytic Hydrogenation Catalysis by an Iron(II)Catecholate Immobilized in a Porous Organic Polymer” *submitted*, **2013**
5. Kraft, S. J.; Sánchez, R. H.; Hock, A. S., A Remarkably Active Iron Catecholate Catalyst Immobilized in a Porous Organic Polymer. *ACS Catalysis* **2013**, 826-830.
6. Schweitzer, N. M.; Hu, B.; Miller, J. T.; Hock, A. S. “Selective Alkane Activation with Single Site Atoms on Amorphous Supports” *patent application filed*, **2013**
7. Schweitzer, N. M.; Hu, B.; Das, U.; Kim, H.; Lu, J.; Stair, P. T.; Curtiss, L.; Miller, J. T.; Hock, A. S., “Propylene Hydrogenation and Propane Dehydrogenation on Heterogeneous, Single-Site Catalytic Sites” *submitted* **2013**
8. Maria, S.; Poli, R.; Gallagher, K. J.; Johnson, M. J. A.; Hock, A. S., “Ether Complexes Of Molybdenum(III) And (IV) Chloride.” *Inorg. Synth.* **2013**, *Submitted*.
9. Broderick, E. M.; Browne, S. C.; Johnson, M. J. A., “NaW<sub>2</sub>Cl<sub>7</sub>(THF)<sub>5</sub> and hexa-alkoxide complexes that contain the M<sub>2</sub> (M = Mo, W) triply bonded unit.” *Inorg. Synth.* **2013**, *Submitted*.
10. Tanabe, K. K.; Siladke, N. A.; Broderick, E. M.; Kobayashi, T.; Goldston, J. F.; Weston, M. H.; Farha, O. K.; Hupp, J. T.; Pruski, M.; Mader, E. A.; Johnson, M. J. A.; Nguyen, S. T., Stabilizing unstable species through single-site isolation: a catalytically active TaV trialkyl in a porous organic polymer. *Chemical Science* **2013**, *Advance Article*. DOI: 10.1039/C3SC22268C
11. R.C. Nelson and J.T. Miller, “An Introduction to X-ray Absorption Spectroscopy and Its In Situ Application to Organometallic Compounds and Homogeneous Catalysts,” *Catalysis*

- Science and Technology, 2, 461-470 (2012). Lu, J., Fu, B., Kung, M.C., Xiao, G., Elam, J.W., Kung, H.H., Stair, P.C., Coking and Sintering Resistant Palladium Catalysts Achieved through Atomic Layer Deposition. *Science* **2012**, 335, 1205.
12. Lu, J., Liu, B., Greeley, J.P., Feng, Z., Libera, J.A., Lei, Y., Bedzyk, M.J., Stair, P.C., Elam, J.W., Porous Alumina Protective Coatings on Palladium Nanoparticles by Self-Poisoned Atomic Layer Deposition, *Chemistry of Materials* **2012**, 24, 2047.
  13. Mehmood, F., Rankin, R.B., Greeley, J.P., and Curtiss, L.A., Trends in Methanol Decomposition on Transition Metal Alloy Clusters from Scaling and Bronsted-Evans-Polyani Relationships, *Physical Chemistry Chemical Physics* **2012**, 14, 8644.
  14. Wiedner, E. S.; Gallagher, K. J.; Johnson, M. J. A.; Kampf, J. W., "Synthesis of Molybdenum Nitrido Complexes for Triple-Bond Metathesis of Alkynes and Nitriles." *Inorg. Chem.* **2011**, 50, 5936-5945.
  15. Feng, H., J.A. Libera, P.C. Stair, J.T. Miller, and J.W. Elam, *Sub-nanometer Palladium Clusters Synthesized by Atomic Layer Deposition*. ACS Catalysis, 2011. **1**(6): p. 665-673.
  16. Feng, H., J.L. Lu, P.C. Stair, and J.W. Elam, *Alumina Over-coating on Pd Nanoparticle Catalysts by Atomic Layer Deposition: Enhanced Stability and Reactivity*. Catalysis Letters, 2011. **141**(4): p. 512-517.
  17. Stair, P.C., *Where the action is*. Nat. Chem., 2011. **3**(5): p. 345-346.
  18. Enterkin, J.A., W. Setthapun, J.W. Elam, S.T. Christensen, F.A. Rabuffetti, L.D. Marks, P.C. Stair, K.R. Poeppelmeier, and C.L. Marshall, *Propane Oxidation over Pt/SrTiO<sub>3</sub> Nanocuboids*. ACS Catal., 2011. **1**(6): p. 629-635.
  19. J. Kugai, J.T. Miller, N. Guo, C. Song, *Oxygen-Enhanced Water Gas Shift on Ceria-supported Pd-Cu and Pt-Cu Bimetallic Catalysts*, J. Catal., 277, 46-53 (2011).
  20. Lei, Y., Jelic, J., Nitche, L., Meyer, R.J., Miller, J.T., *The Effect of Particle Size and Adsorbates on L<sub>3</sub>, L<sub>2</sub> and L<sub>1</sub> X-Ray Absorption Near-Edge Spectra of Supported Pt Nanoparticles*" Top Catal. 54, 334-248 (2011).
  21. Kugai, J., Miller, J.T., Guo, N., Song, C., *Role of Metal Components in Pd-Cu Bimetallic Catalysts Supported on CeO<sub>2</sub> for the Oxygen-Enhanced Water Gas Shift*. Appl. Catal. B: Environ., 105, 306-316 (2011).
  22. J. Guo, C. Xie, K. Lee, N. Guo, J.T. Miller, M.J. Janik, C. Song, *Improving the Carbon Resistance of Ni-based Steam Reforming Catalyst by Alloying with Rh. A Computational Study Coupled with Reforming Experiments and EXAFS Characterization*, ACS Catalysis, 1, 574-582 (2011).



## Catalyst Design for Hydrodeoxygenation of Biomass: Towards a Molecular Level Understanding

George W. Huber

Chemical and Biological Engineering, University of Wisconsin, Madison, WI

Email:huber@engr.wisc.edu

Hydrodeoxygenation (HDO) is a platform technology for conversion of biomass feedstocks into a range of fuels and chemicals including C1-C6 alkanes; C1-C6 mono-alcohols, polyols, and cyclic ethers. The challenge with HDO is to selectively produce targeted products while minimizing hydrogen consumption. The hydrothermal conditions in HDO cause permanent deactivation to standard catalytic materials. Understanding the complicated reaction networks in HDO has aided in the design of more efficient catalysts.

The reaction pathways that occur for HDO can be demonstrated using sorbitol as a model compound. During this reaction a complex network of chemical reactions occurs that can be grouped into five classes of reactions: 1) C-O bond cleavage (dehydration); 2) C-C bond cleavage (decarbonylation and retro-aldol condensation); 3) hydrogenation; 4) isomerization; and 5) C-O-C bond hydrogenolysis. These reactions occur on metal sites, acid sites and bifunctional metal-acid sites.

The catalyst selectivity for aqueous phase dehydration reactions is a function of the Brønsted to Lewis acid ratio of the catalyst for both heterogeneous and homogeneous catalysts. Lewis acid catalyst sites catalyze isomerization and humin formation reactions. Brønsted acid sites catalyze dehydration and hydration reactions. We measured the initial reaction rates on a per site basis for aqueous-phase hydrogenation of different oxygenated compounds over various alumina-supported monometallic catalysts (Pd, Pt, Ru, Rh, Ni, and Co) in a high-throughput reactor. Ru is the most active monometallic catalyst for aqueous phase hydrogenation of acetic acid, acetaldehyde, propanal, acetone, and xylose. Pd is the most active monometallic catalyst we have tested for aqueous phase hydrogenation of furfural and furfuryl alcohol.

We have used two general classes of bifunctional catalysts for HDO of sorbitol that contain both acid and metal sites. These catalysts include catalysts that have metal-acid sites that are in atomic level contact (Pt-ReO<sub>x</sub>/C) and catalysts that have metal acid sites that are atomically separate (Pt/Zr-P). The Pt-ReO<sub>x</sub>/C has higher rates of isomerization, and decarbonylation reactions than Pt/Zr-P leading to a difference in product selectivity. The reaction rate on a Pt basis for Pt-ReO<sub>x</sub>/C was determined to be almost 32 times that of Pt/Zr-P. However, both catalysts had comparable activity based on the Pt surface sites as measured after reaction.

Future advances in developing a molecular understanding of the HDO process combined with identification of structure-function relationships of the key fundamental reactions will allow the development of more efficient processes for the production of fuels and chemicals from biomass.



**Atomically Precise Metal Nanoclusters for Catalytic Application**

Postdoc: Gao Li  
Student: Santosh Kumar (partial)  
Collaborators: Dr. Qingjie Ge (Dalian Institute of Chemical Physics), Dr. De-en Jiang (ORNL)  
Contact: Carnegie Mellon University, Department of Chemistry, Pittsburgh, PA 15213;  
Email: [rongchao@andrew.cmu.edu](mailto:rongchao@andrew.cmu.edu)

**Goal**

Develop atomically precise metal nanoclusters ranging from tens to hundreds of atoms in size for catalytic application

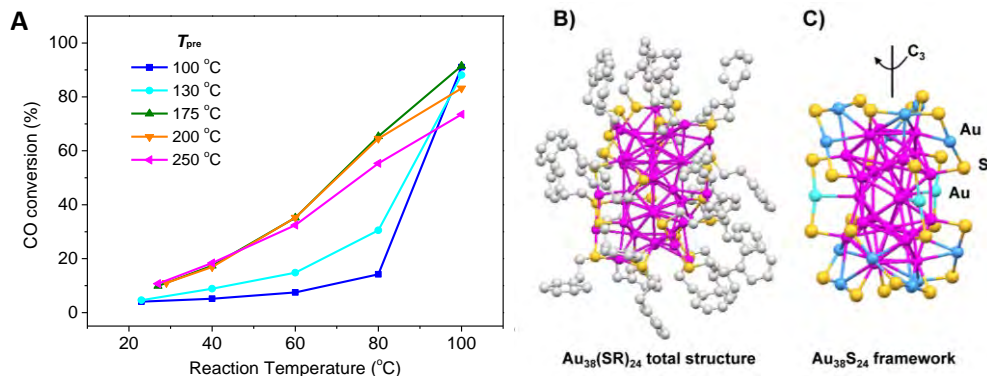
**DOE Interest**

Atomically precise metal nanoclusters provide some exciting opportunities for fundamental catalysis research, such as the tuning of catalytic activity/selectivity at the single-atom level through controlled doping of nanoclusters, the study of structure-reactivity relationships of nanoclusters in solution or supported on solids, as well as the identification of catalytic sites at the atomic level. The crystallographic characterization reveals the atomic structure of nanoclusters, which permits the identification of the molecular adsorption geometry and elementary steps of catalytic reaction mechanisms through a combination of experiment and theory. Such information is important for fundamental understanding of catalytic processes and rational catalyst design.

**Recent Progress**

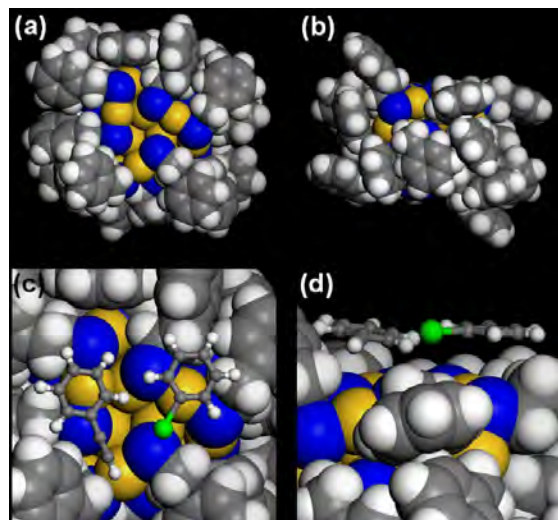
*Nanocluster synthesis and structure:* The synthesis and structural characterization of gold nanoclusters has been achieved. We have successfully prepared several robust gold nanoclusters protected by thiolates, such as  $\text{Au}_{25}(\text{SR})_{18}$ ,  $\text{Au}_{38}(\text{SR})_{24}$ , and  $\text{Au}_{144}(\text{SR})_{60}$ . These ultrasmall nanoclusters (all below 2 nm diameter) exhibit *discrete* electronic structures due to quantum size effect, as opposed to *quasi-continuous* band structure of conventional metal nanoparticles or bulk metals. Among the gold nanoclusters,  $\text{Au}_{25}(\text{SR})_{18}$  and  $\text{Au}_{38}(\text{SR})_{24}$  have been crystallographically characterized, and their total structures (metal core plus surface ligands) serve as the basis for structure-property correlations. We have investigated the CO oxidation and  $\text{C}\equiv\text{C}$  bond activation/Sonogashira cross-coupling reactions by such nanoclusters.

*CO oxidation:*  $\text{CeO}_2$ -supported and  $\text{Au}_{38}(\text{SR})_{24}$  nanocluster catalyst was prepared by deposition. Interestingly, a mild thermal treatment of the catalyst in  $\text{O}_2$  without removing ligands was found to largely enhance the catalytic activity (Fig 1). The activity of ligand-on and -off catalysts was compared.



**Fig 1.** A) Effect of pretreatment temperature ( $T_{pre}$ ) on CO conversion over  $Au_{38}(SR)_{24}/CeO_2$ . Pretreatment: in  $O_2$  for 2 h and  $T_{pre}$  is as labeled. Reaction conditions: GHSV= 15,000 mL  $g^{-1} h^{-1}$ , 0.05 g supported catalyst (net  $Au_{38}(SCH_2CH_2Ph)_{24} = 0.5$  mg). B) total structure of  $Au_{38}(SR)_{24}$ . C) the  $Au_{38}S_{24}$  framework (metal core size:  $1 \times 1.1$  nm).

***C≡C bond activation and reaction:*** We prepared  $CeO_2$ -supported  $Au_{25}(SR)_{18}$  nanocluster catalyst and investigated  $C \equiv C$  bond activation. We chose Sonogashira cross-coupling as a probe reaction to investigate how the activated  $C \equiv C$  substrates (e.g. phenylacetylene) reacts with iodobenzene (or *p*-iodoanisole for the convenience of NMR analysis). We demonstrate that  $Au_{25}(SR)_{18}$  nanoclusters supported on oxides (i.e.  $CeO_2$ ,  $TiO_2$ , and  $SiO_2$ ) can catalyze Sonogashira cross-coupling between phenylacetylene and *p*-iodoanisole with high conversion of *p*-iodoanisole (up to 96.1%) and excellent selectivity (up to 88.1%). The well-defined structure of  $Au_{25}(SR)_{18}$  provides an important clue as to the catalytically active sites (Fig 2). The sterically unhindered facets on the cluster surface allow easy reactant access; each facet comprises three surface gold atoms from three separate “staple”-like  $-S(R)-Au-S(R)-Au-S(R)-$  protecting motifs. DFT theory modeling shows that both reactants prefer to adsorb on the open facet with the phenyl ring facing a surface gold atom. Each reactant has an adsorption energy of -0.40 to -0.48 eV. When they co-adsorb on the catalyst, the two reactants are well positioned to couple with their  $Ph-C \equiv CH$  and  $Ph-I$  groups pointing towards the third gold atom of the open facet. These results suggest a great potential to correlate the atomic structure and the catalytic performance of an atomically precise nanocluster.



**Fig 2.** (a) Top view of one of the two open facets of  $Au_{25}(CH_2CH_2Ph)_{18}$  clusters where three external gold atoms are exposed; the other facet is on the back side. (b) Side view of the two facets which are at top and bottom. (c) Top view and (d) side view of the co-adsorption of phenylacetylene and iodobenzene on the surface of the  $Au_{25}(SCH_2CH_2Ph)_{18}$  clusters. Au, yellow; S, blue; C, gray; H, white; I, green.

### **Future Plans**

Detailed mechanism of O<sub>2</sub> activation on ligand-on and -off nanocluster catalysts. More investigations will be carried out to obtain details of the thermal O<sub>2</sub> pretreatment step and the generated active oxygen species.

Effect of heteroatom doping of nanoclusters on the catalytic effect. Pt, Pd, Ag, and Cu-doped Au<sub>25</sub>(SR)<sub>18</sub> nanoclusters will be investigated.

Selective hydrogenation of C≡C and C=C substrates, as well as selective oxidation reactions (such as epoxidation).

### **Publications (September 2012-present)**

1. Nie, X.; Zeng, C.; Ma, X.; Qian, H.; Ge, Q.; Xu, H.; Jin, R. "CeO<sub>2</sub>-supported Au<sub>38</sub>(SR)<sub>24</sub> nanocluster catalyst for CO oxidation: A comparison of ligands-on and -off catalysts", *Nanoscale* 2013, DOI: 10.1039/C3NR00970J.
2. Li, G. and Jin, R. "Atomically Precise Gold Nanoclusters as New Model Catalysts", *Acc. Chem. Res.* 2013, <http://dx.doi.org/10.1021/ar300213z>.

## Proton-Coupled Electron Transfer Activation in Organic Synthesis

Robert Knowles, Department of Chemistry, Princeton University

Proton-coupled electron transfer is a key mechanism of substrate activation in biological redox catalysis. However, its applications in organic synthesis remain largely unexplored. Herein, we report the development of new catalytic protocols for ketyl-olefin and enantioselective ketyl-hydrazone couplings and present evidence to support concerted proton-coupled electron transfer being the operative mechanism of ketyl formation. Notably, reaction outcomes could be correctly predicted by a simple thermodynamic formalism relating the oxidation potentials and pKa values of specific Brønsted acid/reductant combinations to their capacity to act jointly as a formal hydrogen atom donor.

## Multifunctional Catalysts to Synthesize and Utilize Energy Carriers

Additional PIs: A. Appel, T. Autrey, M. Bullock, D. Camaioni, H. Cho, D. Dixon (Univ of AL), Z. Dohnalek, F. Gao, V. Glezakou, M. Henderson, J. Hu, E. Iglesia (Univ of CA), A. Karkamkar, B. Kay, G. Kimmel, J. Linehan, J. Liu, I. Lyubinetsky, D. Mei, C. Peden, R. Rousseau, G. Schenter, W. Shaw, J. Szanyi, Y. Wang, Z. Wang, R. Weber.

**Contact:** Johannes Lercher, P.O. Box 999, MS: K2-12, Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, Washington; johannes.lercher@pnnl.gov

### Background

The central role and critical importance of catalysis in a future based on sustainability, together with the insight that developments have to be knowledge-based have motivated significant efforts to better understand catalyzed processes and to develop new catalytic routes from this knowledge. The progress on describing elementary steps and predicting the behavior of catalytically active substances has been achieved by combining advanced physicochemical methods, kinetic analysis and computational approaches describing the interaction and conversion of reactants with molecular catalysts as well as catalytically active surfaces and nanoparticles. This progress has been paralleled, however, by an even more pronounced specialization into areas, such as heterogeneous and organometallic catalysis or organocatalysis, with limited cross-fertilization at best. The magnitude and complexity of the problem, however, mandate the use of transdisciplinary knowledge about breaking and making C-O, O-H and H-H bonds to devise new routes for better utilization of energy and material resources.

To act on this challenge, Pacific Northwest National Laboratory established the Institute for Integrated Catalysis (IIC) to foster collaboration and cross-fertilization of ideas across catalysis fields and between fundamental and applied research. Over the last year we have made strong efforts towards developing a common language to address the underlying fundamental physical and chemical principles that guide catalysis ranging from molecular complexes to solid surfaces and particles. While maintaining strong roots in disciplines, we are using common motifs of catalyst sites and common principles of catalytic transformations to realize the target reactions. This strategy is expected to generate knowledge eventually leading to step-up progress and radical changes in the way catalysts and catalytic processes are developed.

Overall, three main energy carriers are used worldwide, carbon (and hydrocarbons), hydrogen, and electrons. The use of hydrogen and electrons in transportation has been limited by their low volumetric energy density in storage systems, making hydrocarbon-based fuels the preferred high-density energy carrier for stationary and transportation applications. Conventionally, the stored energy is accessed by oxidizing carbon and hydrogen, forming O-H and C-O bonds and performing work with the produced heat or electricity. Conversely, to synthesize energy carriers sustainably, it is consequently required to reverse the direction, i.e., to break C-O and O-H bonds and form C-C, C-H and H-H bonds.

### Structure of the program

The program addresses, therefore, the fundamental aspects of breaking C-O and OH bonds forming C-H bonds to generate carbon-based energy-carriers as well as to generate hydrogen in stepwise processes. The reduction equivalents will be provided by hydrogen and electrons; the required energy input will be provided by heat and (electrical) potential. Hydrogen is, therefore,

Conversion of biogenic molecules with and without water	Reduction of CO <sub>2</sub> to energy carriers	Generation and conversion of H <sub>2</sub>
Multifunctional solid catalysts for lignin to hydrocarbons – Understanding and controlling scalable catalytic routes in aqueous phase (ST 1.1) Well-defined metal oxide catalysts – Understanding fundamental chemical transformations and the role of water for catalyzed reactions (ST1.2)	Multifunctional catalyst for CO <sub>2</sub> reduction (ST2.1) An energy-based approach to bifunctional molecular catalysis for CO <sub>2</sub> reduction and fuel utilization (ST 2.2)	Fundamental studies of photocatalysis (ST3.1) Activation of small molecules with bi-functional ambiphilic catalyst complexes (ST 3.2) H <sub>2</sub> activation and conversion catalyzed by ambiphilic surfaces (ST3.3)

**Figure 1** Overview of thrusts and project clusters for understanding principles of multifunctional catalysis to synthesize and utilize energy

both a target and the reactant in this approach. The proposed program comprises three thrust areas with subtasks (Figure 1), focusing on direct and indirect CO<sub>2</sub> reduction and on elementary studies aimed at generating and using H<sub>2</sub>. The bifunctionality, i.e., the simultaneous interaction of more than

one catalytically active site with the substrate is the key to achieving the atom and energy efficiency in individual steps. The combination of several types of these sites with carefully selected energetics and rate constants is used to generate complex catalysts able to enhance the rates of multistep processes.

**Thrust Area 1: Conversion of biogenic molecules in the presence and absence of water** addresses the multi-step conversion of polar molecules on multifunctional surfaces. The aim is to develop a better understanding of the role the metal as well as the acid-base functions on oxide surfaces as they interact with increasingly complex polar biogenic molecules. The surfaces are well-defined and allow bridging between single crystals and dispersed materials. The role of increasing concentrations of water will be explored via structural characterization and mechanistic analysis. Hydrodeoxygenation and hydroalkylation will be the reactions we will use to exemplify potential routes from lignocellulosic biomass to alkane energy carriers requiring several catalytic functions acting sequentially. Since most reactions will either involve water or will occur in the presence of water, we will explore its role on catalytic transformations. While competing for reaction sites, water influences the adsorbed state of reactants and products as well as of the structure and dynamics of transition states. We hypothesize that competition and relative stabilization of reactants and intermediates by water will drastically influence the rates and selectivities of the observed reactions.

**Thrust Area 2: Conversion of CO<sub>2</sub> to energy carriers** is focused on mechanistic understanding of the catalytic reduction of CO<sub>2</sub> to energy carriers (e.g. methane, methanol, formaldehyde, and formic acid, as well as C<sub>2</sub> and higher fuels). The bifunctional sites for CO<sub>2</sub> reduction in enzymes motivate us to design and test potential heterogeneous and homogeneous catalysts with bifunctional motifs. Both forward (CO<sub>2</sub> → energy carrier) and reverse (energy carrier → CO<sub>2</sub>) reaction pathways are being explored to unravel the details of underlying reaction mechanisms. Our primary goal is to compare and contrast various mechanistic aspects of the observed chemistries, gain a molecular level understanding of the fundamental reaction steps, identify the reaction intermediates and their stability, and determine the role that reaction conditions can have on the energetics and kinetics. Theoretical simulations will parallel the experimental work and will serve to underpin the program to help extract fundamental principles, and identify key thermodynamic/kinetic quantities, which can be used to postulate design principles for catalysts.

**Thrust 3: Generation and conversion of H<sub>2</sub>** assumes as its central hypothesis that efficient production and utilization of molecular hydrogen is key to sustainable synthesis of energy carriers; i.e., for storing energy chemically. The three tasks described in this thrust address

formation and activation of molecular hydrogen by multifunctional catalysts. All of the tasks focus on the fundamental understanding of properties and chemistry at polar interfaces; i.e., the hydrogen formation from water notably in the absence of bulk water, as well as the activation by sterically well-defined Lewis acid - base pairs (frustrated Lewis pairs, or FLPs) and the subsequent utilization of  $H^-$  and  $H^+$  for hydrogenation reactions. It has been observed that this polar environment leads to the heterolytic activation hydrogen at ambient temperature and pressure, and the program is focused on understanding and utilizing this reaction pathway.

## **Results from subtasks**

### **Subtask 1.1.: From lignin to hydrocarbon energy carriers – understanding and controlling scalable catalytic routes in aqueous phase**

The conversion of lignin to hydrocarbon energy carriers requires a cascade of reactions. While lignin is the most intractable component of lignocellulose, its conversion to useful products is particularly important, because the carbon in lignin is the most reduced one in lignocellulose. In the present phase we have focused efforts on understanding the catalytic chemistry of lignin fragments in an aqueous environment. In particular, we explored ether hydrogenolysis and hydrolysis, the hydrodeoxygenation of alcohols and the alkylation of (substituted) phenols in aqueous phase using supported noble and base metals as well as zeolites combining experiments with theoretical studies.

The presence of water exerts a pronounced effect on reactants, transition states and products, as water molecules not only compete with the reactants for active sites, they also stabilize or destabilize specific states along the reaction pathway. Water also modifies the surface of catalyst components leading potentially to surface reorganization or even corrosion/destruction of the catalyst. The latter impact of water was explored, e.g., by following the state of Pd and Ni catalysts under reaction conditions using X-ray absorption spectroscopy. It showed that both metals were not oxidized and interacted only weakly with  $H_2O$  in presence of 30 bar  $H_2$ . Under typical operating conditions ( $T \leq 250^\circ C$ ,  $p(H_2) = 30$  bar) the metal surfaces were in equilibrium with  $H_2$ . In consequence, hydrogenation, hydrogenolysis and even hydrolysis were effectively catalyzed by supported Pd and Ni catalysts, allowing for higher reaction rates on these metal particles than observed previously by molecular catalysts.

Zeolites on the other hand were shown to be uniquely effective to cleave C-O bonds (dehydration had 100x higher activity per proton than mineral acids) and to form C-C bonds (alkylation of phenol is only possible in sufficiently large zeolite pores). Using in situ  $^{13}C$  MAS NMR spectroscopy cyclohexanol dehydration was shown to be reversible and protonation/deprotonation of cyclohexene to be fast compared to the addition of water. A combination of spectroscopies and transmission electron microscopy showed that water affected zeolites the more negatively the higher the concentration of structural defect sites was.

### **Subtask 1.2: Well-defined metal oxide catalysts - understanding fundamental chemical transformations and the role of water for catalyzed reactions**

Catalytic materials for upgrading biomass-derived molecules to fuels include metals dispersed on oxide- and carbon-support materials, and oxide materials themselves (including zeolites) that are essential as catalysts for acid/base and redox reactions. Among these materials, oxides have been the subject of far fewer fundamental studies aimed at developing structure/function relationships. Current oxide-based heterogeneous catalysts are structurally and chemically complex and their experimental assessment can seldom be interpreted with atomic-level precision. We seek to reduce the complexity to levels addressable and controllable at the atomistic level – structurally and mechanistically – while maintaining rigorous connections with the conditions and materials

relevant to catalysis. We are employing an integrated experimental/theoretical approach to advance our current ability to understand, design, and control the catalytic and surface chemistry of transition metal oxides, specifically for heterogeneous reduction-oxidation and acid-base chemistries. The approach combines novel solid-state inorganic synthesis, surface science, experimental and theoretical/computational chemical physics, and mechanistic organic chemistry and is highlighted below.

**Regioselectivity in alcohol dehydration.** The origin in the variations of trans-/cis-2-butene product selectivity ratios in 2-butanol dehydration over solid acid catalysts were investigated using a combined experimental-theory approach. Reactivity measurements over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, AlO<sub>x</sub>/SBA-15, and H-form zeolites with widely varying Si/Al ratios and pore structures showed over two orders of magnitude change in the trans-/cis-2-butene product ratio. Activation energy barriers calculated for the concerted C-O and  $\beta$ -C-H bond breakings of adsorbed butoxy intermediates by dispersion-corrected DFT calculations correctly predicted the trans-/cis-2-butene product ratio observed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The very low trans-2-butene selectivity on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can now be understood by the formation of a late transition state with high energy barrier caused by the strong van der Waals interaction between the  $\gamma$ -H atoms and the flat catalyst surface. Trans-/cis-2-butene selectivity ratios much higher than that dictated by thermodynamic equilibrium can be achieved by introducing additional geometric constraints around the active catalytic site (e.g., varying the 3D environment around the active center in zeolites).

**Alcohol rotation on oxide surfaces.** The rotational motion of adsorbates on oxide surfaces remains mostly unexplored. In our STM study we showed detailed analysis of the rotational motion of alkoxy species on TiO<sub>2</sub>(110). Alkoxy species bound on the O<sub>b</sub> rows can be prepared via alcohol dissociation at V<sub>O</sub>'s. STM images after exposure to 1-, 2-, 3-octanol at 300 K show bright "X" shaped features centered above the original position of V<sub>O</sub> with four lobes stretched onto the neighboring Ti<sup>4+</sup> rows. These "X" shaped features were interpreted as being due to alkyl chain rotation among equivalent local energy minima with a rate that is faster than the STM acquisition time and thus represent a time-average of the conformers. For 4-octanol, an "I" shaped feature perpendicular to the O<sub>b</sub> rows is observed suggesting the presence of only two conformers. In all cases the alkyl chains are located on Ti<sub>5c</sub> rows and minimize their overlap with the O<sub>b</sub> rows allowing increased vdW interaction of the hydrocarbon chains with Ti<sup>4+</sup> cations over O<sup>2-</sup> anions. Direct evidence for the rotation of the octoxy species was further obtained by imaging at 150 K. Full torsional potentials for the alkoxy species in the presence and absence of neighboring OH<sub>b</sub> species were calculated to understand the energetics of the rotational motion. For isolated 3-octoxy and 3-octoxy-OH<sub>b</sub> pair, the cross-O<sub>b</sub> row barriers were calculated to be 0.67 and 0.75 eV in good agreement with the experimentally estimated values.

### **Subtask 2.1: Multifunctional catalysts for CO<sub>2</sub> reduction to fuels.**

Experimental and theory capabilities are combined to investigate in quantitative detail the mechanistic chemistry of catalytic CO<sub>2</sub> conversion to value added fuels (CH<sub>4</sub>, CH<sub>3</sub>OH, and C<sub>2</sub> oxygenated hydrocarbons) by well characterized multifunctional catalysts in a wide range of media including vapor phase, liquid phase and ionic liquid environments. The subtask is divided into 4 experimental thrusts and a cross cutting theory activity. In thrust 1 high surface area model multifunctional model catalysts are synthesized, characterized and their reaction kinetics measured. It has been found that atomically dispersed Pd and Ru supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are able to activate CO<sub>2</sub> and produce CO with high selectivity, whereas, the primary product of CO<sub>2</sub> reduction over larger nanoparticles is CH<sub>4</sub>. Our work has substantiated the critical role of Lewis acidic oxides in the CO<sub>2</sub> reduction process: atomically dispersed Pd supported on carbon nanotubes is completely inactive, however, doping with La<sub>2</sub>O<sub>3</sub> results in a catalyst with activity and selectivity comparable atomically dispersed Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. In thrust 2 we investigate atomically



resolved and ensemble averaged surface science techniques to synthesize and study well-defined planar model of mono- and bifunctional catalytic structures for CO<sub>2</sub>. Our work to date focused on the detailed understanding of CO<sub>2</sub> adsorption, diffusion, binding and dissociation on reduced and oxidized TiO<sub>2</sub>(110) surfaces. In thrust 3 PolyOligoSiloSquioxane (POSS) **clusters are investigated as an intermediate class of materials** between traditional homogeneous and heterogeneous catalysts. A series of Ru supported POSS catalysts have been synthesized that can be deployed in either homogeneous solution or supported on surfaces to function as heterogeneous catalysts. First it has been demonstrated that homogeneous catalysts can be tethered to POSS without loss of reactivity. Moreover catalyst where Ru is directly integrated into the POSS framework have also shown an ability to reduce CO<sub>2</sub> to formate in solution as well and CO<sub>2</sub> to CO when supported on alumina. Indeed the reactivity of the Ru supported POSS sites is found to be identical to the atomically dispersed Ru sites of thrust 1. As a final thrust we combine a CO<sub>2</sub> capture function a switchable ionic liquid with conversion by catalytically reducing CO<sub>2</sub> directly in that medium. Recently we have found that CO<sub>2</sub> reduction to formate can be readily achieved at temperatures as low as 25-65°C using both Ru and Co based homogeneous catalysts as well as heterogeneous catalysts including Ru/carbon and Pd/Al<sub>2</sub>O<sub>3</sub>.

### **Subtask 2.2: An energy-based approach to bifunctional molecular catalysis for CO<sub>2</sub> reduction and fuel utilization**

This subtask is focused on the developing an understanding of how to rationally design molecular catalysts for the reduction of CO<sub>2</sub> as well as the corresponding fuel utilization reactions, with the overall goal of storing carbon-neutral energy in the form of chemical bonds. The interconversion of these carbon-based species can occur using either electrocatalysis or thermal catalysis, and both are utilized in this subtask. For the design of molecular catalysts for C<sub>1</sub> transformations, two approaches are used. The first is the consideration of reaction energetics for each step of a catalytic transformation, and the second is the use of multiple catalyst-substrate interactions, as is ubiquitously observed in the active sites of enzymes. The resulting bifunctional catalysts have been shown to be more active than their monofunctional analogs, and therefore, the extension of this feature to new catalytic transformations is expected to be beneficial.

The effort on this subtask is divided into the specific steps in the overall reduction of CO<sub>2</sub> to CH<sub>3</sub>OH, starting with the electrocatalytic reduction of CO<sub>2</sub> to CO and the hydrogenation of CO<sub>2</sub> to formic acid, and the subsequent reduction of these two products, as well as the reduction of formaldehyde to CH<sub>3</sub>OH. Fuel utilization reactions are also studied, including the electrocatalytic oxidation of formate or alcohol. In addition to developing catalysts for these specific transformations, we strive to develop dynamic control of catalyst properties, from relatively simplistic functions, such as recovery of homogeneous catalysts, to the more elegant control over reactivity exerted in enzymatic systems.

### **Subtask 3.1: Fundamental studies of water splitting on model TiO<sub>2</sub>, RuO<sub>2</sub> and mixed TiO<sub>2</sub>-RuO<sub>2</sub> catalysts.**

The objective of this project is to provide fundamental insight into catalytic and photocatalytic water splitting reactions using model TiO<sub>2</sub>, RuO<sub>2</sub> and mixed TiO<sub>2</sub>-RuO<sub>2</sub> materials. While TiO<sub>2</sub> has been a standard research material for expanding fundamental knowledge of heterogeneous catalysis and photocatalysis, its photocatalytic applicability is limited by its poor match to the solar spectrum and by its poor catalytic activity for H<sub>2</sub> and O<sub>2</sub> formation. Researchers have explored overcoming the latter limitation through use of co-catalysts supported on TiO<sub>2</sub>. In this renewal effort, we will concentrate on obtaining a better fundamental understanding of the role of supported RuO<sub>2</sub> as a co-catalyst in the photocatalytic splitting of water to H<sub>2</sub> and O<sub>2</sub>. Co-catalysts are widely employed in many TiO<sub>2</sub> photocatalytic applications to enhance catalytic performance or increase functionality. RuO<sub>2</sub> has emerged as an important material in assisting H-

H and O-O bond formation reactions in water splitting. However, the details of how RuO<sub>2</sub> functions in these capacities are poorly understood. We will employ simple probe photochemical and chemical reactions to examine how RuO<sub>2</sub> films, nanoparticles and clusters enhance the catalytic and photocatalytic properties of TiO<sub>2</sub>. We will also examine the chemical and photochemical production of H<sub>2</sub> (and O<sub>2</sub>) from water on RuO<sub>2</sub> alone, RuO<sub>2</sub> supported on TiO<sub>2</sub> and mixed phases of RuO<sub>2</sub>-TiO<sub>2</sub>. The outcome of this research will be a better understanding specifically of RuO<sub>2</sub> as a co-catalyst in water splitting on TiO<sub>2</sub>, and in general of the properties of co-catalysts in heterogeneous catalytic and photocatalytic processes.

**Subtask 3.2: Activation of small molecules with bi-functional amphiphilic catalyst complexes.**

*Fundamental insight into the properties of amphiphilic centers to activate small molecules* is a timely challenge, requiring novel theoretical and experimental approaches, with critical relevance to fundamental understanding in catalysis. We are interested in quantum effects in H-bonding and H<sub>2</sub> activation reactions, the role of large amplitude motions in strained molecular complexes, and how weak interactions, e.g., van der Waals and electrostatic interactions affect the structure and dynamics in the ionic salts of Lewis acid Lewis base pair complexes. We have been developing reaction calorimetry techniques to provide a direct measure of kinetics and thermodynamics simultaneously. This work has resulted in providing the first experimental insight into the energy landscape describing the catalytic reduction of polar substrates by Frustrated Lewis pairs (FLP). These new techniques under development are not specific to FLP chemistry and will be beneficial to understanding catalytic reactions in general. Our combined experimental and computational study is designed to provide insight into the tunable chemical & physical parameters in Lewis acid/base pairs that will lead a fundamental understanding of the kinetics and thermodynamics of molecular catalytic hydrogen reactions.

Progress this year has demonstrated a novel experimental approach to measure both the kinetics and thermodynamics of catalytic reaction pathways. With this new methodology we have been able to gain insight into the reaction mechanism, i.e., a termolecular reaction pathway for intermolecular FLPs, the first measure of the activation barrier and driving force for the hydrogen activation step. The technique can be used to measure both absolute rates for the individual steps in the catalytic reaction cycle and a measure of the TOF for the full catalytic cycle. Our computational results suggest that the H<sub>2</sub> activation step is asynchronous with a side on Lewis acid and head on Lewis base interaction leading to heterolytic scission of hydrogen. And finally, we have begun the development of computational methods to investigate the role of solvent viscosity and polarity on the catalytic reduction of polar substrates using Frustrated Lewis pairs.

**Subtask 3.3: H<sub>2</sub> activation and conversion catalyzed by amphiphilic surfaces.**

We are creating and characterizing frustrated, surface-supported donor-acceptor complexes and modeling the kinetics of the reactions they catalyze, particularly hydrogen activation. The frustration promises to afford heterolytic activation of the reactants that migrate into the gap between the electron-donating and electron-accepting poles. To achieve the frustration we are exploring two types of catalyst precursors: 1) a family in which an acid-base pair is formed from a strong supported Lewis acid and a sterically hindered base and 2) a family created using photo-activation of a ligand-to-metal-charge-transfer band of a transition metal chromophore.

## Publications (2011-2013)

### Subtask 1.1.: From lignin to hydrocarbon energy carriers – understanding and controlling scalable catalytic routes in aqueous phase

Zhao, C., D. M. Camaioni and J. A. Lercher (2012). "Selective catalytic hydroalkylation and deoxygenation of substituted phenols to bicycloalkanes." *Journal of Catalysis* **288**: 92-103.

Hu, M. Y.; Feng, J.; Camaioni, D. M.; Turcu, R. V. F.; Peden, C. H. F.; Lercher, J. A.; Hu, J. Z. (2012). "In-situ MAS-NMR investigations on catalytic conversion of biogenic molecules in the presence of aqueous water." *Prepr. Pap.-Am. Chem. Soc., Div. Energy Fuels Chem.*, **57**: 215.

Shi, H., O. Y. Gutierrez, G. L. Haller, D. H. Mei, R. Rousseau and J. A. Lercher (2013). "Structure sensitivity of hydrogenolytic cleavage of endocyclic and exocyclic C-C bonds in methylcyclohexane over supported iridium particles." *Journal of Catalysis* **297**: 70-78.

Chase, Z.; Fulton, J. L.; Pham, V.-T.; Camaioni, D. M.; Balasubramanian, M.; Mei, D.; Weber, R.; Zhao, C.; Lercher, J. A. (2013) "X-ray absorption spectroscopy of supported palladium catalysts during hydrodeoxygenation of phenol in water." *Prepr. Pap.-Am. Chem. Soc., Div. Energy Fuels Preprints*, **58**:1066.

### Subtask 1.2: Well-defined metal oxide catalysts - understanding fundamental chemical transformations and the role of water for catalyzed reactions

Grant, D. J., T.-H. Wang, M. Vasiliu, D. A. Dixon and K. O. Christe (2011). "F<sup>+</sup> and F<sup>-</sup> Affinities of Simple N<sub>x</sub>F<sub>y</sub> and O<sub>x</sub>F<sub>y</sub> Compounds." *Inorganic Chemistry* **50**(5): 1914-1925.

Carr, RC; M Neurock, and E Iglesia (2011). "Catalytic Consequences of Acid Strength in the Conversion of Methanol to Dimethyl Ether." *J. Catal.* **278**: 78-93.

Feller, D; KA Peterson, and DA Dixon (2011). "Ab Initio Coupled Cluster Determination of the Heats of Formation of C<sub>2</sub>H<sub>2</sub>F<sub>2</sub>, C<sub>2</sub>F<sub>2</sub> and C<sub>2</sub>F<sub>4</sub>." *J. Phys. Chem. A* **115**: 1440-1451.

Zhai, HJ; XH Zhang, WJ Chen, X Huang, and LS Wang (2011). "Stoichiometric and Oxygen-Rich M<sub>2</sub>O<sub>n</sub><sup>-</sup> and M<sub>2</sub>O<sub>n</sub> (M = Nb, Ta; n = 5-7) Clusters: Molecular Models for Oxygen Radicals, Diradicals, and Superoxides." *J. Am. Chem. Soc.* **133**: 3085-3094.

Wang, X; H-G Cho, L Andrews, M Chen, DA Dixon, H-S Hu, and J Li (2011). "Matrix Infrared Spectroscopic and Computational Investigations of the Lanthanide Metal Atom-Methylene Fluoride Activation Products CH<sub>2</sub>LnF<sub>2</sub>." *J. Phys. Chem. A* **115**: 1913-1921.

Kwak, JH; D Mei, J Szanyi, Y Wang, CHF Peden, and RJ Rousseau (2011). "The (100) Facets of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: the Active Surfaces for Alcohol Dehydration Reactions." *Catal. Lett.* **141**: 649-655.

Li, S; CL Guenther, MS Kelley, and DA Dixon (2011). "Molecular Structures, Acid-Base Properties, and Formations of Group VIB Transition Metal Hydroxides." *J. Phys. Chem. C* **115**: 8072-8103.

Li, K; L Zhang, DA Dixon, and TM Klein (2011). "Undulating Topography for HfO<sub>2</sub> Thin Films Deposited in a Meso-Scale Reactor using Hafnium (IV) tert butoxide." *AIChE Journal* **57**: 2989-2996.

Li, Z; Z Zhang, YK Kim, RS Smith, F Netzer, BD Kay, R Rousseau, and Z Dohnálek (2011). "Growth of Ordered Ultra-thin Tungsten Oxide Films on Pt(111)." *J. Phys. Chem. C* **115**: 5773-5783.

Stott, AC; PB Abel, C DellaCorte, SV Pepper, and DA Dixon (2011). "Computational Studies of the NiTi Alloy System: Bulk, Supercell, and Surface Calculations." *MRS Proceedings* **1295**: 15-20.

Li, Z; Z Zhang, BD Kay, and Z Dohnálek (2011). "Polymerization of Formaldehyde and Acetaldehyde on Ordered (WO<sub>3</sub>)<sub>3</sub> Films on Pt(111)." *J. Phys. Chem. C* **115**: 9692-9700.

Sun, J.; K Zhu, F Gao, CM Wang, J Liu, CHF Peden, and Y Wang (2011). "High Yield Bio-Ethanol Conversion to Isobutene: Zn<sub>x</sub>Zr<sub>y</sub>O<sub>z</sub> Mixed Oxides for a Novel and Highly Selective Process to Value-Added Products from Biomass." *J. Am. Chem. Soc.* **133**: 11096-11099.

- Li, Z; RS Smith, BD Kay, and Z Dohnálek (2011). "Determination of Absolute Coverages for Small Aliphatic Alcohols on TiO<sub>2</sub>(110)." *J. Phys. Chem. C* **115**: 22534–22539.
- Li S and DA Dixon (2011). "Structural and Electronic Near Degeneracy of M<sub>3</sub>O<sub>9</sub><sup>-</sup> (M = Cr, Mo, W)." *J. Phys. Chem. C* **115**: 19190–19196.
- Zhu, K.; J Sun, J Liu, L Wang, H Wan, J Hu, Y Wang, CHF Peden, Z Nie (2011). "Solvent Evaporation Assisted Preparation of Oriented Nanocrystalline Mesoporous MFI Zeolites." *ACS Catal.* **1**: 682-690.
- Vasiliu, M; K. Guynn, and DA Dixon (2011). "Prediction of the Thermodynamic Properties of Key Products and Intermediates from Biomass." *J. Phys. Chem. C* **115**: 15686–15702.
- Govind, N; K Lopata, R Rousseau, A Andersen, and K Kowalski (2011). "Visible Light Absorption of N-Doped TiO<sub>2</sub>-Rutile Using (LR/RT)-TDDFT and Active Space EOMCCSD Calculations." *J. Phys. Chem. Letters.* **2**: 2696-2701.
- Kwak, JH; CHF Peden, and J Szanyi (2011). "Using a Surface Sensitive Chemical Probe and a Bulk Structure Technique to Monitor the  $\gamma$ - to  $\theta$ -Al<sub>2</sub>O<sub>3</sub> Phase Transformation." *J. Phys. Chem. C* **115**: 12575-12579.
- Wang, TH; Z Fang, NW Gist, S Li, DA Dixon, and J L Gole (2011). "Computational Study of the Hydrolysis Reactions of the Ground and First Excited Triplet States of Small TiO<sub>2</sub> Nanoclusters." *J. Phys. Chem. C* **115**: 9344-9360.
- Zhao, YF; Y Yang, CA Mims, CHF Peden, J Li, D Mei (2011). "Insight Into Methanol Synthesis from CO<sub>2</sub> Hydrogenation on Cu(111): Complex Reaction Network and the Effects of H<sub>2</sub>O." *J. Catal.* **281**: 199-211.
- Wagner, M; S Surnev, MG Ramsey, G Barcaro, L Sementa, FR Negreiros, A Fortunelli, Z Dohnalek, FP Netzer (2011). "Structure and Bonding of Tungsten Oxide Clusters on Nanostructured Cu-O Surfaces." *J. Phys. Chem. C* **115**: 23480–23487.
- Hu, JZ; JH Kwak, Y Wang, and CHF Peden (2011). "Characterizing Surface Acid Sites of Dispersed Tungsten Oxide Catalysts on Mesoporous Silica Using Solid State <sup>15</sup>N NMR." *J. Phys. Chem. C* **115**: 23354-23362.
- Deskins, NA; R Rousseau, M Dupuis (2011). "The Distribution of Ti<sup>3+</sup>-Surface Sites in Reduced TiO<sub>2</sub>." *J. Phys. Chem C* **115**: 7562-7572.
- Li, K; S Li, N Li, TM Klein, and DA Dixon (2011). "Tetrakis(ethylmethylamido) Hafnium Adsorption and Reaction on Hydrogen-Terminated Si(100) Surfaces," *J. Phys. Chem. C* **115**: 18560–18571.
- Kwak, J.H.; R Rousseau, D Mei, CHF Peden, and J Szanyi (2011) "The Origin of Regioselectivity in 2-Butanol Dehydration on Solid Acid Catalysts." *Chem. Cat. Chem.* **3**: 1557-1561.
- Vasiliu, M; S Li, AJ Arduengo, and DA Dixon (2012). "Bond Energies in Models of the Schrock Metathesis Catalyst." *J. Phys. Chem. C* **115**: 12106-12120.
- Li, SC; Z Li, Z Zhang, BD Kay, R Rousseau, and Z Dohnálek (2012). "Preparation, Characterization, and Catalytic Properties of Tungsten Trioxide Cyclic Trimers on FeO(111)/Pt(111)." *J. Phys. Chem. C* **116**: 908-916.
- Simonetti, DA; RT Carr, E Iglesia (2012). "Acid Strength and Solvation Effects on Methylation, Hydride Transfer, and Isomerization Rates During Catalytic Homologation of C-1 Species," *J. Catal.*, **285**: 19-30.
- Hu, JZ; JA Sears, HS Mehta, JJ Ford, JH Kwak, K; Zhu, Y Wang, J Liu, DW Hoyt, and CHF Peden (2012) "A Large Volume Magic Angle Spinning Nuclear Magnetic Resonance Probe for *In Situ* Investigations with Constant Flow of Reactants." *Phys. Chem. Chem. Phys.* **14**: 2105-2532.

Flaherty, DW; NT Hahn, RA May, SP Berglund, Y-M Lin, KJ Stevenson, Z Dohnalek, BD Kay, and CB Mullins (2012) "Reactive Ballistic Deposition of Nanostructured Model Materials for Electrochemistry." *Acc. Chem. Res.* **45**: 434–443.

Szanyi, J; M Daturi, G Clet, DR Baer, and CHF Peden (2012) "Well-Studied Cu-BTC Still Serves Surprises: Evidence for Facile  $\text{Cu}^{2+}/\text{Cu}^+$  Interchange." *Phys. Chem. Chem. Phys.* **14**: 4383–4390.

Li, S; H-J Zhai, L-S Wang, and D.A Dixon (2012) "Structural and Electronic Properties of Reduced Transition Metal Oxide Clusters,  $\text{M}_4\text{O}_{10}$  and  $\text{M}_4\text{O}_{10}^-$  ( $\text{M} = \text{Cr}, \text{W}$ ), from Photoelectron Spectroscopy and Quantum Chemical Calculations," *J. Phys. Chem. A* **116**: 5256-5271.

Jeong, SY; HJ Kim, J-H Bae, DH; Kim, CHF Peden, Y-K Park, and JK Jeon (2012) "Synthesis of butenes through 2-butanol dehydration over mesoporous materials produced from ferrierite." *Catal. Today* **185**: 191-197.

Kim, B.; Z Li, BD Kay, Z Dohnálek, and YK Kim (2012) "Unexpected Nondissociative Binding of  $\text{N}_2\text{O}$  on Oxygen Vacancies on a Rutile  $\text{TiO}_2(110)-1\times 1$ ." *J. Phys. Chem. C* **116**: 1145-1150.

Peterson KA; D Feller, and DA Dixon (2012) "Chemical accuracy in ab initio thermochemistry and spectroscopy: Current strategies and future challenges." *Theor. Chem. Acc.* **131**: 1079 (20 pages), DOI 10.1007/s00214-011-1079-5.

Gounder, R; A Jones, RT Carr, and E Iglesia (2012) "Solvation and Acid Strength Effects on Catalysis by Faujasite Zeolites." *J. Catal.* **286**: 214-223.

Haiges, R; M Rahm, DA Dixon, EB Garner, III, and KO Christe (2012) "Binary Group 15 Polyazides. Structural Characterization of  $[\text{Bi}(\text{N}_3)_4]^-$ ,  $[\text{Bi}(\text{N}_3)_5]^{2-}$ ,  $[\text{bipy}\cdot\text{Bi}(\text{N}_3)_5]^{2-}$ ,  $[\text{Bi}(\text{N}_3)_6]^{3-}$ ,  $\text{bipy}\cdot\text{As}(\text{N}_3)_3$ ,  $\text{bipy}\cdot\text{Sb}(\text{N}_3)_3$  and  $[(\text{bipy})_2\cdot\text{Bi}(\text{N}_3)_3]_2$ , and the Free Pair Activation of Valence Electrons." *Inorg. Chem.* **51**: 1127-1141.

She, X; JH Kwak, J Sun, J Hu, MY Hu, CM Wang, CHF Peden, and Y Wang (2012) "A Comparative Study of SBA-15 Mesoporous Silica Supported Tungsten Oxide and Rhenium Oxide Catalysts for 2-Butanol Dehydration." *ACS Catal.* **2**: 1020-1026.

Vasiliu, M; DJ Grant, DA Dixon, and D Feller (2012) "Heats of Formation of  $\text{MH}_x\text{Cl}_y$  ( $\text{M} = \text{P}, \text{Si}, \text{As}, \text{Sb}$ ) Compounds and Main Group Fluorides from High Level Electronic Structure Calculations." *J. Phys. Chem. A* **116**: 3717-3727.

Fang, Z; M Outlaw, K Smith, N Gist, S Li, DA Dixon, and JL Gole (2012) "Computational Study of the Hydrolysis Reactions of Small  $\text{MO}_2$  ( $\text{M} = \text{Zr}$  and  $\text{Hf}$ ) Nanoclusters with Water." *J. Phys. Chem. C* **116**: 8475-8492.

Kim, B; ZJ Li, BD Kay, Z Dohnálek, and YK Kim (2012) "The effect of oxygen vacancies on the binding interactions of  $\text{NH}_3$  with rutile  $\text{TiO}_2(110)-1\times 1$ ." *PCCP* **14**: 15060-15065.

Stott, AC; TP Vaid, EJ Bylaska, and DA Dixon (2012) "Tuning Band Gap Energies in  $\text{Pb}_3(\text{C}_6\text{X}_6)$  Extended Solid-State Structures." *J. Phys. Chem. C* **116**: 8370-8492.

Feller, D; KA Peterson, and DA Dixon (2012) "Further benchmarks of a composite, convergent, statistically-calibrated coupled cluster-based approach for thermochemical and spectroscopic studies." *Mol. Phys.* **110**: 2381-2399.

Li, ZJ; B Smid, YK Kim, V Matolin, BD Kay, R Rousseau, and Z Dohnálek (2012) "Alcohol dehydration on monooxo  $\text{W}=\text{O}$  and dioxo  $\text{O}=\text{W}=\text{O}$  species." *J. Phys. Chem. Lett.* **3**: 2168-2172.

Dixon, DA; D Feller, and KA Peterson, "A Practical Guide to Reliable First Principles Computational Thermochemistry Predictions Across the Periodic Table." In *Annual Reports in Computational Chemistry*, Vol. 8, ed. R. A. Wheeler, Section Ed. G. S. Tschumper, Elsevier, Amsterdam, 2012, Chapt. 1, pp. 1-28.

Lin, X; Y Yoon, NG Petrik, ZJ Li, ZT Wang, VA Glezakou, BD Kay, I Lyubinetsky, GA Kimmel, R Rousseau, and Z Dohnálek (2012) "Structure and dynamics of  $\text{CO}_2$  on rutile  $\text{TiO}_2(110)-1\times 1$ ." *J. Phys. Chem. C* **116**: 26322-26334.

- Mikulas, T; Z Fang, JL Gole, MG White, and DA Dixon (2012) “The Presence of Ti(II) Centers in Doped Nanoscale TiO<sub>2</sub> and TiO<sub>2-x</sub>N<sub>x</sub>.” *Chem. Phys. Lett.* **539-540**: 58-63.
- Wu, L; Y Liu, C Zhang, S Li, DA Dixon, and D-S Yang (2012) “Mass-analyzed threshold ionization of an excited state of lanthanum dioxide.” *J. Chem. Phys.* **137**: 034307 (8 pages).
- Shen, M; DP Acharya, Z Dohnálek, and MA Henderson (2012) “Importance of diffusion in methanol photochemistry on TiO<sub>2</sub>(110).” *J. Phys. Chem. C* **116**: 25465-25469.
- Gong, Y; L Andrews, CA Bauschlicher, Jr., KS Thanthiriwatte, and DA Dixon (2012) “Infrared Spectroscopic and Theoretical Studies of the OTiF<sub>2</sub>, OZrF<sub>2</sub> and OHfF<sub>2</sub> Molecules with Terminal Oxo Ligands.” *Dalton Trans.* **41**: 11706-11715.
- Zhao YF; R Rousseau, J Li, and D Mei (2012) “Theoretical study of syngas hydrogenation to methanol on the polar Zn-terminated ZnO(0001) surface.” *J. Phys. Chem. C* **116**: 15952-15961.
- Vasiliu, M; A Jones, K Guynn, and DA Dixon (2012) “Prediction of the Thermodynamic Properties of Key Products and Intermediates from Biomass – II.” *J. Phys. Chem. C* **116**: 20738-20754.
- Smid, B; ZJ Li, A Dohnalkova, BW Arey, RS Smith, V Matolin, BD Kay, and Z Dohnálek (2012) “Characterization of nanoporous WO<sub>3</sub> films grown via ballistic deposition.” *J. Phys. Chem. C* **116**: 10649-10655.
- Thanthiriwatte, KS; M Vasiliu, DA Dixon, and KO Christe (2012) “Structural and Energetic Properties of Closed Shell XF<sub>n</sub> (X = Cl, Br and I; n = 1–7) and XO<sub>n</sub>F<sub>m</sub> (X = Cl, Br and I; n = 1-3; m = 0 – 6) Molecules and Ions Leading to Stability Predictions for Yet Unknown Compounds.” *Inorg. Chem.* **51**: 10966-10982.
- Kimmel GA; MD Baer, NG Petrik, J VandeVondele, R Rousseau, and CJ Mundy (2012) “Polarization- and Azimuth-Resolved Infrared Spectroscopy of Water on TiO<sub>2</sub>(110): Anisotropy and the Hydrogen-Bonding Network.” *J. Phys. Chem. Lett.* **3**: 778-784.
- Peterson, KA; DA Dixon, and H Stoll (2012) “The Use of Explicitly Correlated Methods on XeF<sub>6</sub> Predicts a C<sub>3v</sub> Minimum with a Sterically Active, Free Valence Electron Pair on Xe.” *J. Phys. Chem. A* **116**: 9777-9782.
- Zhang, ZR; Y Yoon, X Lin, D Acharya, BD Kay, R Rousseau, and Z Dohnálek (2012) “OH group dynamics of 1,3-propanediol on TiO<sub>2</sub>(110).” *J. Phys. Chem. Lett.* **3**: 3257-3263.
- Chen, M; R Craciun, N Hoffman, and DA Dixon (2012) “Ligand Bond Energies in *cis*- and *trans*- [L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> Complexes: Benchmarking Density Functional Theory vs. CCSD(T).” *Inorg. Chem.* **51**: 13195-13203.
- Kovarik, L; A Genc, CM Wang, A Qiu, CHF Peden, J Szanyi, and JH Kwak (2013) “Tomography and High Resolution Electron Microscopy Study of Surfaces and Porosity in a Plate-like  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.” *J. Phys. Chem. C* **117**: 179-186.
- Shi H; OY Gutierrez, GL Haller, D Mei, R Rousseau, and JA Lercher (2013) “Structure sensitivity of hydrogenolytic cleavage of endocyclic and exocyclic C-C bonds in methylcyclohexane over supported iridium particles.” *J. Catal.* **297**: 70-78.
- Yang, Y; CA Mims, DH Mei, CHF Peden, and CT Campbell (2013) “Mechanistic Studies of Methanol Synthesis over Cu from CO/CO<sub>2</sub>/H<sub>2</sub>/H<sub>2</sub>O Mixtures: the Source of C in Methanol and the Role of Water.” *J. Catal.* **298**: 10-17.
- Lin, X; Z-T Wang, I Lyubinsky, BD Kay, and Z Dohnálek (2013) “Interaction of CO<sub>2</sub> with oxygen adatoms on rutile TiO<sub>2</sub>(110).” *PCCP* **15**: 6190-6195.
- Li, Y; Z Wei, J Sun, F Gao, CHF Peden, and Y Wang (2013) “Effect of Sodium on the Catalytic Properties of VO<sub>x</sub>/CeO<sub>2</sub> Catalysts for Oxidative Dehydrogenation of Methanol.” *J. Phys. Chem. C* **117**: 5722-5729.

Clayton, DA; TE McPherson, S Pan, M Chen, DA Dixon, and D Hu (2013) "Spatial and Temporal Variation of Surface-Enhanced Raman Scattering at Ag Nanowires in Aqueous Solution." *PCCP* **15**: 850-859.

Appel, A.M.; AB Bocarsly, JE Bercaw, H Dobbek, M Dupuis, DL DuBois, JG Ferry, E Fujita, R Hille, PJA Kenis, CA Kerfeld, RH Morris, CHF Peden, A Portis, S Ragsdale, TB Rauchfuss, JNH Reek, LC Seefeldt, M Spitler, RJ Stack, RK Thauer, and GL Waldrop, "Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO<sub>2</sub>." *Chemical Reviews* (2013) in press

Li, S and DA Dixon, "Structural and Electronic Properties of Group 6 Transition Metal Oxide Clusters." Invited Chapter in *Catalysis by Nanoparticles*, Ed. S. Suib, Elsevier, in press, 2013.

Li, W-Z; L Kovarik, DH Mei, J Liu, Y Wang, and Peden, C.H.F. "Anti-sintering Pt nanoparticles stabilized by MgAl<sub>2</sub>O<sub>4</sub> spinel {111} facets." *Nature Communications* (2013) in press.

Fang, Z and DA Dixon, "Computational Study of H<sub>2</sub> and O<sub>2</sub> Production from Water Splitting by using Small MO<sub>2</sub> Nanoclusters (M = Ti, Zr, Hf)." *J. Phys. Chem. A*, WEB ASAP, April 2013.

### **Subtask 2.1: Multifunctional catalysts for CO<sub>2</sub> reduction to fuels**

Mudiyanselage, K; JF Weaver, and J Szanyi. "Catalytic Decomposition of Ba(NO<sub>3</sub>)<sub>2</sub> on Pt(111)." *Journal of Physical Chemistry C*, 115(13) (2011) 5903-5909

Du Y.; Kim D. J.; Varga T.; et al. "Formation of single-phase BaO nanoclusters" *Thin Solid Films* 519(16) (2011) 5335-5338

Kwak J.H.; Mei D.; Peden C.H. F., Rousseau R., Szanyi J., "(100) facets of gamma-Al<sub>2</sub>O<sub>3</sub>: The Active Surfaces for Alcohol Dehydration Reactions" *Catalysis Letters*, 141(5) (2011) 649-655.

Kwak J.H.; Peden C.H. F.; Szanyi J. "Using a Surface-Sensitive Chemical Probe and a Bulk Structure Technique to Monitor the gamma- to theta-Al<sub>2</sub>O<sub>3</sub> Phase Transformation" *The Journal of Physical Chemistry*, 225(25) (2011) 12575-12579.

Kwak J. H.; Rousseau R.; Mei D., Peden C.H.F., Szanyi J, The Origin of Regioselectivity in 2-Butanol Dehydration on Solid Acid Catalysts', *ChemCatChem* 3(10) (2011) 1557-1561

Szanyi J, Daturi M.; Clet G., Baer D, Peden C.H.F "Well-studied Cu-BTC still serves surprises: evidence for facile Cu<sup>2+</sup>/Cu<sup>+</sup> interchange" *Physical Chemistry Chemical Physics*, 14(13) (2012) 4383-4390.

Mudiyanselage K.; Szanyi J, "NO<sub>2</sub> uptake under practically relevant conditions on BaO/Pt(1 1 1)" *Catalysis Today* 181(1) (2012) 116-123

Size-Dependent Catalytic Performance of CuO on gamma-Al<sub>2</sub>O<sub>3</sub>: NO Reduction versus NH<sub>3</sub> Oxidation, Kwak, Ja Hun; Tonkyn, Russell; Tran, Diana; Peden, Charles HF, Szanyi, János; ACS Catal. 2 1432-1440 (2012)

Tomography and High-Resolution Electron Microscopy Study of Surfaces and Porosity in a Plate-like gamma-Al<sub>2</sub>O<sub>3</sub> Kovarik, Libor; Genc, Arda; Wang, Chongmin; Kwak, Ja Hun; Szanyi, János; Peden, Charles HF, *J.Phys.Chem. C* 117 179-186 (2013)

### **Subtask 2.2: An energy-based approach to bifunctional molecular catalysis for CO<sub>2</sub> reduction and fuel utilization**

Bullock, R. M. (2011) "A Mercurial Route to a Cobalt Dihydrogen Complex." *Angew. Chem. Int. Ed.*, **50**: 4050.

DuBois, D. L.; Bullock, R. M. (2011) "Molecular Electrocatalysts for the Oxidation of Hydrogen and the Production of Hydrogen – The Role of Pendant Amines as Proton Relays." *Eur. J. Inorg. Chem.*, **2011**: 1017.

Galan, B. R.; Schöffel, J.; Linehan, J. C.; Seu, C.; Appel, A. M.; Roberts, J. A. S.; Helm, M. L.; Kilgore, U. J.; Yang, J. Y.; DuBois, D. L.; Kubiak, C. P. (2011) "Electrocatalytic Oxidation of Formate by [Ni(P<sup>R</sup><sub>2</sub>N<sup>R'</sup><sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>CN)]<sup>2+</sup> Complexes." *J. Am. Chem. Soc.*, **133**: 12767.

Roberts, J. A. S.; Appel, A. M.; DuBois, D. L.; Bullock, R. M. (2011) "Comprehensive Thermochemistry of W-H Bonding in the Metal Hydrides  $\text{CpW}(\text{CO})_2(\text{IMes})\text{H}$ ,  $[\text{CpW}(\text{CO})_2(\text{IMes})\text{H}]^{+}$ , and  $[\text{CpW}(\text{CO})_2(\text{IMes})(\text{H})_2]^{+}$ . Influence of an N-Heterocyclic Carbene Ligand on Metal Hydride Bond Energies." *J. Am. Chem. Soc.*, **133**: 14604.

Roberts, J. A. S.; DuBois, D. L.; Bullock, R. M. (2011) "Experimental and Digital Simulation Studies of the Electrochemical Oxidation of the Metal Anion  $[\text{CpW}(\text{CO})_2(\text{IMes})]^{-}$  and the 17-Electron Metal Radical  $\text{CpW}(\text{CO})_2(\text{IMes})^{\bullet}$ . Kinetics and Thermodynamics of Capture and Release of MeCN by a Metal Radical and a Metal Cation." *Organometallics*, **30**: 4555.

Roberts, J. A. S.; Franz, J. A.; van der Eide, E. F.; Walter, E. D.; Petersen, J. L.; DuBois, D. L.; Bullock, R. M. (2011) "Comproportionation of Cationic and Anionic Tungsten Complexes Having an N-Heterocyclic Carbene Ligand To Give the Isolable 17-Electron Tungsten Radical  $\text{CpW}(\text{CO})_2(\text{IMes})^{\bullet}$ ." *J. Am. Chem. Soc.*, **133**: 14593.

Tronic, T. A.; Rakowski DuBois, M.; Kaminsky, W.; Coggins, M. K.; Liu, T.; Mayer, J. M. (2011) "Directing Protons to the Dioxygen Ligand of a Ruthenium(II) Complex with Pendent Amines in the Second Coordination Sphere." *Angew. Chem. Int. Ed.*, **50**: 10936.

Jain, A.; Reback, M. L.; Lindstrom, M. L.; Thogerson, C. E.; Helm, M. L.; Appel, A. M.; Shaw, W. J. "Investigating the Role of the Outer-Coordination Sphere in  $[\text{Ni}(\text{P}^{\text{Ph}_2}\text{N}^{\text{Ph-R}_2})_2]^{2+}$  Hydrogenase Mimics." *Inorg. Chem.* **2012**, *51*, 6592.

Lense, S.; Ho, M.-H.; Chen, S.; Jain, A.; Raugei, S.; Linehan, J. C.; Roberts, J. A. S.; Appel, A. M.; Shaw, W. (2012) "Incorporating Amino Acid Esters into Catalysts for Hydrogen Oxidation: Steric and Electronic Effects and the Role of Water as a Base." *Organometallics*, **31**: 6719.

Liu, T.; Chen, S.; O'Hagan, M. J.; Rakowski DuBois, M.; Bullock, R. M.; DuBois, D. L. (2012) "Synthesis, Characterization, and Reactivity of Fe Complexes Containing Cyclic Diazadiphosphine Ligands: The Role of the Pendant Base in Heterolytic Cleavage of  $\text{H}_2$ ." *J. Am. Chem. Soc.*, **134** : 6257.

Seu, C. S.; Appel, A. M.; Doud, M. D.; DuBois, D. L.; Kubiak, C. P. (2012) "Formate oxidation via  $\beta$ -deprotonation in  $[\text{Ni}(\text{P}^{\text{R}}_2\text{N}^{\text{R}^1}_2)_2(\text{CH}_3\text{CN})]^{2+}$  complexes." *Energy Environ. Sci.*, **5**: 6480.

van der Eide, E. F.; Liu, T.; Camaioni, D. M.; Walter, E. D.; Bullock, R. M. (2012) "Facile Thermal W-W Bond Homolysis in the N-Heterocyclic Carbene-Containing Tungsten Dimer  $[\text{CpW}(\text{CO})_2(\text{IME})]_2$ ." *Organometallics*, **31**: 1775.

van der Eide, E. F.; Yang, P.; Walter, E. D.; Liu, T.; Bullock, R. M. (2012) "Dinuclear Metalloradicals Featuring Unsupported Metal-Metal Bonds." *Angew. Chem. Int. Ed.*, **51**: 8361.

Wiedner, E. S.; Yang, J. Y.; Chen, S.; Raugei, S.; Dougherty, W. G.; Kassel, W. S.; Helm, M. L.; Bullock, R. M.; Rakowski DuBois, M.; DuBois, D. L. (2012) "Stabilization of Nickel Complexes with  $\text{Ni}^0\cdots\text{H-N}$  Bonding Interactions Using Sterically Demanding Cyclic Diphosphine Ligands." *Organometallics*, **31**: 144.

Eide, E. F. v. d.; Hou, G.-L.; Deng, S. H. M.; Wen, H.; Yang, P.; Bullock, R. M.; Wang, X.-B (2013) "Metal-Centered 17-Electron Radicals  $\text{CpM}(\text{CO})_3^{\bullet}$  (M = Cr, Mo, W): A Combined Negative Ion Photoelectron Spectroscopic and Theoretical Study." *Organometallics*, **32**: 2084.

Liu, T.; DuBois, D. L.; Bullock, R. M (2013) "An iron complex with pendent amines as a molecular electrocatalyst for oxidation of hydrogen." *Nat. Chem.*, **5**: 228.

### **Subtask 3.1: Fundamental studies of water splitting on model $\text{TiO}_2$ , $\text{RuO}_2$ and mixed $\text{TiO}_2$ - $\text{RuO}_2$ catalysts**

Deskins, N. A., R. Rousseau and M. Dupuis (2011). "Distribution of  $\text{Ti}^{3+}$  Surface Sites in Reduced  $\text{TiO}_2$ ." *Journal of Physical Chemistry C* **115**: 7562-7572.

Du, Y., D. J. Kim, T. Varga, Z. Wang, J. Szanyi and I. Lyubinetsky (2011). "Formation of single-phase BaO nanoclusters." *Thin Solid Films* **519**: 5335-5338.



- Henderson, M. A., N. A. Deskins, R. T. Zehr and M. Dupuis (2011). "Generation of organic radicals during photocatalytic reactions on TiO<sub>2</sub>." *Journal of Catalysis* **279**: 205-212.
- Henderson, M. A. and K. M. Rosso (2011). "Oxidation of H<sub>2</sub>S by coadsorbed oxygen on the alpha-Cr<sub>2</sub>O<sub>3</sub>(0001) surface." *Surface Science* **605**: 555-563.
- Henderson, M. A. (2011). "A surface science perspective on TiO<sub>2</sub> photocatalysis." *Surface Science Reports* **66**: 185-297.
- Henderson, M. A. and M. D. Robbins (2011). "Methylene bromide chemistry and photochemistry on rutile TiO<sub>2</sub>(110)." *Surface Science* **605**: 1834-1841.
- Henderson, M. A. (2011). "Surface Chemistry of Trimethyl Phosphate on alpha-Fe<sub>2</sub>O<sub>3</sub>." *Journal of Physical Chemistry C* **115**: 23527-23534.
- Petrik, N. G. and G. A. Kimmel (2011). "Electron- and Hole-Mediated Reactions in UV-Irradiated O<sub>2</sub> Adsorbed on Reduced Rutile TiO<sub>2</sub>(110)." *Journal of Physical Chemistry C* **115**: 152-164.
- Petrik, N. G. and G. A. Kimmel (2011). "Oxygen Photochemistry on TiO<sub>2</sub>(110): Recyclable, Photoactive Oxygen Produced by Annealing Adsorbed O<sub>2</sub>." *The Journal of Physical Chemistry Letters* **2**: 2790-2796.
- Shen, M. M. and M. A. Henderson (2011). "Impact of Solvent on Photocatalytic Mechanisms: Reactions of Photodesorption Products with Ice Overlayers on the TiO<sub>2</sub>(110) Surface." *Journal of Physical Chemistry C* **115**: 5886-5893.
- Shen, M. and M. A. Henderson (2011). "Site Competition during Coadsorption of Acetone with Methanol and Water on TiO<sub>2</sub>(110)." *Langmuir* **27**: 9430-9438.
- Shen, M. and M. A. Henderson (2011). "Identification of the Active Species in Photochemical Hole Scavenging Reactions of Methanol on TiO<sub>2</sub>." *The Journal of Physical Chemistry Letters* **2**: 2707-2710.
- Du, Y., N. G. Petrik, N. A. Deskins, Z. Wang, M. A. Henderson, G. A. Kimmel and I. Lyubinetsky (2012). "Hydrogen reactivity on highly-hydroxylated TiO<sub>2</sub>(110) surfaces prepared via carboxylic acid adsorption and photolysis." *Physical Chemistry Chemical Physics* **14**: 3066-3074.
- Du, Y., D. J. Kim, T. C. Kaspar, S. E. Chamberlin, I. Lyubinetsky and S. A. Chambers (2012). "In-situ imaging of the nucleation and growth of epitaxial anatase TiO<sub>2</sub>(001) films on SrTiO<sub>3</sub>(001)." *Surface Science* **606**: 1443-1449.
- Henderson, M. A. (2012). "Visible light induced photodesorption of NO from the alpha-Cr<sub>2</sub>O<sub>3</sub>(0001) surface." *Surface Science* **606**(3-4): 505-509. (Corrigendum: *Surface Science* **606**: 1467)
- Kim, B., Z. J. Li, B. D. Kay, Z. Dohnalek and Y. K. Kim (2012). "The effect of oxygen vacancies on the binding interactions of NH<sub>3</sub> with rutile TiO<sub>2</sub>(110)-1 x 1." *Physical Chemistry Chemical Physics* **14**: 15060-15065.
- Kim, B., Z. J. Li, B. D. Kay, Z. Dohnalek and Y. K. Kim (2012). "Unexpected Nondissociative Binding of N<sub>2</sub>O on Oxygen Vacancies on a Rutile TiO<sub>2</sub>(110)-1 x 1." *Journal of Physical Chemistry C* **116**: 1145-1150.
- Lin, X., Y. Yoon, N. G. Petrik, Z. J. Li, Z. T. Wang, V. A. Glezakou, B. D. Kay, I. Lyubinetsky, G. A. Kimmel, R. Rousseau and Z. Dohnalek (2012). "Structure and Dynamics of CO<sub>2</sub> on Rutile TiO<sub>2</sub>(110)-1x1." *Journal of Physical Chemistry C* **116**: 26322-26334.
- Shen, M., D. P. Acharya, Z. Dohnalek and M. A. Henderson (2012). "Importance of Diffusion in Methanol Photochemistry on TiO<sub>2</sub>(110)." *Journal of Physical Chemistry C* **116**: 25465-25469.
- Shen, M. M. and M. A. Henderson (2012). "Role of Water in Methanol Photochemistry on Rutile TiO<sub>2</sub>(110)." *Journal of Physical Chemistry C* **116**: 18788-18795.
- Wang, Z. T., N. A. Deskins and I. Lyubinetsky (2012). "Direct Imaging of Site-Specific Photocatalytical Reactions of O<sub>2</sub> on TiO<sub>2</sub>(110)." *Journal of Physical Chemistry Letters* **3**: 102-106.

Wang, Z. T., N. A. Deskins, M. A. Henderson and I. Lyubinetsky (2012). "Inhibitive Influence of Oxygen Vacancies for Photoactivity on TiO<sub>2</sub>(110)." *Physical Review Letters* **109**: 266103.

Henderson, M. A., M. Shen, Z. T. Wang and I. Lyubinetsky (2013). "Characterization of the Active Surface Species Responsible for UV-Induced Desorption of O<sub>2</sub> from the Rutile TiO<sub>2</sub>(110) Surface." *Journal of Physical Chemistry C* **117**: 5774-5784.

Henderson, M. A. and I. Lyubinetsky (2013). "Molecular-Level Insights into Photocatalysis from Scanning Probe Microscopy Studies on TiO<sub>2</sub>(110)." *Chemical Reviews*: in press.

Herman, G. S., Z. T. Zehr and M. A. Henderson (2013). "Characterization of Oxygen and Titanium Diffusion at the Anatase TiO<sub>2</sub>(001) Surface." *Surface Science* **612**: L5-L8.

Lin, X., Z.-T. Wang, I. Lyubinetsky, B. D. Kay and Z. Dohnalek (2013). "Interaction of CO<sub>2</sub> with oxygen adatoms on rutile TiO<sub>2</sub>(110)." *Physical Chemistry Chemical Physics* **15**: 6190-6195.

### **Subtask 3.2: Activation of small molecules with bi-functional amphiphilic catalyst complexes**

Abhi Karkamkar, Kshitij Parab, Doinita Neiner, Thomas K. Nielsen, Herman Cho, Donald M. Camaioni, Tom Autrey (2013). "Thermodynamic Study of Heterolytic Hydrogen Activation by Frustrated Borane-Amine Lewis Pairs." Invited *Dalton Trans.*, **42**: 615. DOI: 10.1039/c2dt31628e. invited (BES)

Liem X. Dang, Gregory K. Schenter, Tsun-Mei Chang, Shawn M. Kathmann and Thomas S. Autrey (2012). "The Role of Solvent on the Thermodynamics and Kinetics of Forming Frustrated Lewis Pairs." *J. Phys. Chem. Lett.*, **3**: 3312. DOI: 10.1021/jz301533a. (BES)

Donald M. Camaioni, Bojana Ginovska-Pangovska, Gregory K. Schenter, Shawn M. Kathmann, and Tom Autrey (2012). "Analysis of the Activation and Heterolytic Dissociation of H<sub>2</sub> by "Frustrated" Lewis Pairs: NH<sub>3</sub> and BX<sub>3</sub> (X = H, F and Cl)." *J. Phys Chem A.*, **116**: 7228. 10.1021/jp3039829 (LDRD, BES)

Arshad Aijaz, Abhi Karkamkar, Young Joon Choi, Nobuko Tsumori, Ewa Rönnebro, Tom Autrey, Hiroshi Shioyama, Qiang Xu (2012). "Immobilizing Highly Catalytically Active Pt Nanoparticles inside the Pores of Metal-Organic Framework: A Double Solvents Approach." *J. Am. Chem. Soc.*, **134**: 13926. DOI: 10.1021/ja3043905 (BES)

Thomas K. Nielsen, Abhi Karkamkar, Mark Bowden, Flemming Besenbacher, Torben R. Jensen, Tom Autrey (2013). "Methods to stabilize and destabilize ammonium borohydride. Invited *Dalton Trans.*, **42**: 680. DOI: 10.1039/C2DT31591B (BES)

Zhenguang Huang, Tom Autrey (2012). "Boron-nitrogen-hydrogen ("BNH") compounds: recent developments in hydrogen storage, applications in hydrogenation and catalysis, and new syntheses." *Energy Environ. Sci.*, **5** DOI:10.1039/C2EE23039A. Invited Review (BES)

Shawn M. Kathmann, Christopher J. Mundy, Gregory K. Schenter, Tom Autrey, Philippe Aeberhard, Bill David, Martin O. Jones, Timmy Ramirez-Cuesta (2012). "Understanding Vibrational Anharmonicity and Phonon Dispersion in Solid Ammonia Borane." *J. Phys. Chem C*, **116**: 5926.

Tom Autrey, Mark Bowden, Abhi Karkamkar (2011). "Control of hydrogen release and uptake in amine borane molecular complexes: Thermodynamics of ammonia borane, ammonium borohydride, and the diammoniate of diborane." *Faraday Disc.*, **151**: 157.

Mark Bowden and Tom Autrey (2011). "Characterization and Mechanistic Studies of the Dehydrogenation of NH<sub>x</sub>BH<sub>x</sub> Materials." Invited paper. *Current Opinion in Solid State & Materials Science.*, **15**: 73.

## **New Approaches to Selective Carbon-Hydrogen Bond Activation Using Dual Catalysis and Artificial Metalloenzymes.**

Jared C. Lewis

The University of Chicago, Department of Chemistry, Chicago, IL 60637

email: [jaredlewis@uchicago.edu](mailto:jaredlewis@uchicago.edu)

Progress toward the development of two new platforms for selective C-H bond activation, namely concurrently operating (dual) transition metal catalysts and artificial metalloenzymes built from catalytically active small molecules and protein scaffolds, is presented. In the former case, details on the nature of metal catalysts employed, mechanistic studies, and an unprecedented non-directed C-H arylation reaction are described. In the latter case, extensive studies on the characterization of two different artificial metalloenzymes systems are outlined. Initial results toward catalysis using hybrid systems for C-H insertion reactions of metal-carbene and -oxo complexes are also included. Finally, a brief overview of the long-term relation of these projects, that is, using artificial metalloenzymes constructs to control selectivity in dual transition metal catalyzed reactions, will be detailed.

**Reactivity of Phenyl Ethyl Alcohols Over Cerium Oxide**

Leading PI: Steven H. Overbury

Contact: Chemical Science Division, Oak Ridge National Laboratory, 1 Bethel Valley Rd, Oak Ridge, TN 37831. Email: [luttermanda@ornl.gov](mailto:luttermanda@ornl.gov); [overburysh@ornl.gov](mailto:overburysh@ornl.gov)

A key scientific challenge for the utilization of highly oxygenated molecules is to understand the fundamental chemistry by which the oxygen functional groups may be converted by both thermochemical and catalytic means. Furthermore, understanding structure-catalysis relationships is of vital importance for developing new catalysts capable of enhanced product selectivity. We have shown that the product selectivity of tethered phenyl ethers are greatly affected by pore confinement in pyrolysis reactions in the presence of mesoporous silicas (MCM-41). These ethers were chosen as models for linkages found in lignin. We have also investigated the difference in ethanol reactivity and product selectivity based on the surface structure of cerium oxide catalysts, where the two main reaction pathways are dehydration and dehydrogenation. Here, we describe product selectivity comparing the reactivity of 1-phenyl ethanol and 2-phenyl ethanol over cerium oxide, where selectivity is determined by the molecular structure of the substrate of interest. The insights gained here provide bases for rational design of better and novel catalytic materials. In addition, we describe future directions to investigate the interfacial interactions of oxygenated model compounds on tailored porous and non-porous metal oxide surfaces.

**Acknowledgements:** This Research is sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy.

# Selective Hydrogenation of Acrolein: Particle Size, Supports, Alloys and Single Sites

Haojuan Wei<sup>1</sup>, A. Jeremy Kropf<sup>2</sup>, Neil Schweitzer<sup>2</sup>, Christopher L. Marshall<sup>2</sup>, Jeffrey T. Miller<sup>2</sup> Randall Meyer<sup>1</sup>

<sup>1</sup>University of Illinois at Chicago, Department of Chemical Engineering, Chicago IL 60607

<sup>2</sup>Argonne National Laboratory, Chemical Sciences and Engineering Division, 9700 S. Cass Ave., Lemont, IL 60439

Many factors may contribute to the performance of heterogeneous catalysts: choice of active metal, particle size effects, support effects, alloying, and process conditions. We have chosen the selective hydrogenation of acrolein as a model reaction for this study to understand what factors influence the selectivity and activity in the selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehyde to  $\alpha,\beta$ -unsaturated alcohol. For the selective hydrogenation of acrolein to allyl alcohol, it is a particularly difficult reaction to obtain selectivity towards C=O bond hydrogenation as the hydrogenation of C=C bond is about 35 kJ/mol easier than that of C=O bond thermodynamically. Thus kinetic control in this system is required. In the particular case of acrolein, the lack of substituents at C=C bond makes it especially vulnerable to hydrogenation. Although previous research has made great progress in understanding some of the factors (choice of metal, process conditions) which may improve selectivity, no catalyst exists with both high activity and selectivity. Therefore we studied this reaction systematically from three aspects: 1) particle size effects; 2) support effects; 3) alloy effects (utilizing single atom alloy to improve the performance of catalysts). We found that both selectivity and activity of the catalyst increased as the particle size increased for Ag/SiO<sub>2</sub> catalysts<sup>1</sup>. It is speculated that the adsorption mode of the acrolein molecule is critical to high selectivity and that the extended terraces of the larger particles allows for favorable adsorption configurations. Although this trend in selectivity was found to extend to other supports (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>), the activity of Ag/Al<sub>2</sub>O<sub>3</sub> dropped with increasing particle size. We have also examined a variety of Ag alloys. Surprisingly when a very low loading (0.01wt%) of a d-band transition metal (eg. Pd) was impregnated into the Ag nanoparticle, the catalyst activity greatly increased with simultaneous improvements in selectivity. EXAFS measurements suggest that the Pd is dispersed throughout the Ag nanoparticle and at low concentration Pd atoms are effectively isolated from one another creating a type of single atom alloy catalyst (similar to the work of Sykes et al.<sup>2</sup>). Finally we have also explored a different variety of single site catalysts which involve the creation of isolated metal centers in a SiO<sub>2</sub> matrix. Although selectivities for some of these systems are quite high, deactivation remains a serious hurdle.

## References

- (1) Wei, H.; Gomez, C.; Guo, N.; Wu, T.; Lobo-Lapidus, R. J.; Marshall, C.; Miller, J. T.; Meyer, R. J. *Journal of Catalysis* **2013**, 298, 18.
- (2) Kyriakou, G.; Boucher, M. B.; Jewell, A. D.; Lewis, E. A.; Lawton, T. J.; Baber, A. E.; Tierney, H. L.; Flytzani-Stephanopoulos, M.; Sykes, E. C. H. *Science* **2012**, 335, 1209.

## Knowledge-based Catalyst Design: Computational Method Development, Water Oxidation, Stereoselective C-H Functionalization and Nitrogen Fixation

Djamaladdin G. Musaev

Emerson Center for Scientific Computation, Department of Chemistry, Emory University, 1515 Dickey Dr. Atlanta, GA, 30322, [dmusaev@emory.edu](mailto:dmusaev@emory.edu); 404-727-2382

We developed [1] the Reactive Force Field (ReaxFF) parameters for investigating the dynamic properties of the polyoxometalates (POM) in water. Molecular dynamics simulations were performed for  $[\text{Nb}_6\text{O}_{19}\text{H}_x]^{(8-x)-}$ ,  $x=0-8$ , submerged in bulk water at 298 K. Analysis of the MD trajectories showed facile H atom transfer between the protonated polyoxoanion core and bulk water.

Water oxidation catalysts (WOCs)  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  (henceforth  $\text{Co}_4\text{POM}$ ), developed previously [2], have attracted much recent attention because of their reported stability and catalytic activity. Our additional studies [3] provide compelling evidence that under our experimental conditions,  $\text{Co}_4\text{POM}$  functions as a molecular catalyst, not simply as a precursor for a cobalt oxide ( $\text{CoO}_x$ ) WOC. Stability and kinetics studies show that the nature of the buffer, particularly phosphate, affects Co speciation. We documented that catalytic  $\text{O}_2$  evolution by  $\text{Co}_4\text{POM}$ ,  $\text{Co}^{2+}(\text{aq})$ , and  $\text{CoO}_x$  have different dependences on buffers, pH, and WOC concentration. A new experiment, involving extraction of  $\text{Co}_4\text{POM}$  but not  $\text{Co}^{2+}(\text{aq})$  or  $\text{CoO}_x$  into toluene from water, and other experiments in this work make it clear that POM WOC studies cannot be meaningfully compared if the concentrations of soluble species are varied. Recently, we reported [4] another molecular, homogeneous catalyst,  $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{VW}_9\text{O}_{34})_2]$ , that is by far the fastest WOC to date. *(This part of my research is collaborative with C. Hill and K. Morokuma and funded by DOE-BES Catalysis: DE-FG02-03ER15461)*

We are investigating transition metal catalyzed C-H bond functionalization. We reported [5] the mechanisms and factors controlling allylic amine and aziridine formation in  $[\text{Ru}_2(\text{hp})_4\text{Cl}]$ , (where  $\text{hp}$  = hydroxypyridinato) and  $[\text{Ru}_2(\text{esp})_2(\text{SbF}_6)]$ . It was found that the energy barrier required for allylic amine formation is 0.99 (1.26) kcal/mol smaller than that for aziridine formation. We analyzed the factors controlling the selectivity of these reactions and made intriguing predictions. In addition, we have recently discovered that mono-protected amino acid ligands (MPAA) can promote Pd(II)-catalyzed enantioselective C-H activation reactions with both pyridine and carboxylic acid directing groups [6]. Computational investigations allowed us to gain insights into the mechanisms and important elementary steps of the reaction, nature of active species, a ligand coordination mode to the Pd(II) and transition state structure of the C-H activation step. The findings later were supported by kinetic studies. Based these new data we were able to improve reaction efficiency and increase catalyst TON. *(This part of my research is funded by CCI-NSF in Stereoselective C-H Functionalization (CHE-0943980)).*

We continue our efforts to search for better catalysts for dinitrogen hydrogenation. Recently, we have shown [7] that the  $\text{Zr}_2\text{Pd}_2$  and  $\text{Zr}_2\text{Pt}_2$  clusters might be very reactive

for dinitrogen hydrogenation. Currently, we embed these clusters on the metal-oxide support and elucidate the effect of the support-cluster interactions on the catalytic activity of the nano-clusters. [8] *(This part of my research is currently not funded.)*

## References:

1. A. L. Kaledin, A. C. T. van Duin, C. L. Hill, D. G. Musaev „Parameterization of Reactive Force Field: Dynamics of the  $[\text{H}_x\text{Nb}_6\text{O}_{19}]^{(8-x)}$  Lindqvist Polyoxoanion in Bulk Water“, *J. Phys. Chem. A*, **2013**, *in press*
2. Q. Yin, J. M. Tan, C. Besson, Y. V. Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle, C. L. Hill „A soluble molecular fast organic-structure-free water oxidation catalyst based on abundant metals“ *Science*, **2010**, 328, 342-345.
3. J. W. Vickers, H. Lv, J. M. Sumliner, J. Fielden, G. Zhu, Z. Luo, D. G. Musaev, Y. V. Geletii, C. L. Hill, „Hydrolytic stability studies of  $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ . Additional evidence that transition-metal substituted polyoxometalates are molecular water oxidation catalysts.“, *J. Am. Chem. Soc.*, **2013**, *in revision*
4. J. Song, H. Lv, Y. V. Geletii, D. G. Musaev, P. Kögerler, J. Bacsá, C. L. Hill, „A Robust Molecular Water Oxidation Catalyst as Fast as the Oxygen Evolving Center“, *Nature*, **2013**, *in revision*
5. M. E. Harvey, D. G. Musaev, J. Du Bois „A diruthenium catalyst for selective allylic C-H amination: Reaction development and mechanistic insight gained through experiment and theory“ *J. Am. Chem. Soc.*, **2011**, 133, 17207-17216
6. D. G. Musaev, A. Kaledin, B.-F. Shi, J.-Q. Yu, „On the origin of enantioselectivity of the Pd(II)-catalyzed C-H bond activation reactions: A combined experimental and computational approach“ , *J. Am. Chem. Soc.*, **2012**, 134, 1690-1698
7. D. G. Musaev, „Theoretical Prediction of a New Dinitrogen Reduction Process: The Utilization of four Dihydrogen Molecules and  $\text{Zr}_2\text{Pt}_2$  Cluster“, *J. Phys. Chem B* **2004**, 108, 10012-10018.
8. A. E. Kuznetsov, D. G. Musaev, „Does the MgO(100)-support facilitate the reaction of dinitrogen and dihydrogen molecules catalyzed by  $\text{Zr}_2\text{Pd}_2$  Clusters? A Computational Study“, *Inorg. Chem.*, **2010**, 49, pp 2557-2567

*Catalytic Deoxydehydration of Carbohydrates and Polyols to Chemicals and Fuels*

Postdoc: Dr. Sanjeev Maradur;

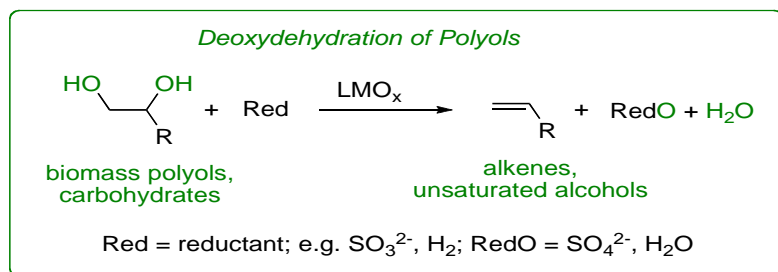
Students: Garry Chapman, Michael McClain, Camille Boucher-Jacobs and Daniel Bamper

Collaborators: Prof. Kendall Houk and PDF Dr. Peng Liu at UCLA (computational)

Contact: Department of Chemistry and Biochemistry, Stephenson Life Sciences Research Center  
University of Oklahoma, Norman, OK 73019, *knicholas@ou.edu*; 405-325-3696

**Goals**

The long term, practical objective of this project is to develop catalytic processes for the deoxydehydration (DODH) of biomass-derived carbohydrates and polyols to produce unsaturated alcohols and hydrocarbons of value as chemical feedstocks and fuels. Achievement of this objective will be enabled through fundamental reactivity studies that will provide new knowledge and a deeper understanding of the means by which oxo-metal complexes ( $LMO_n$ ) can activate and transform polyhydroxylic substrates.

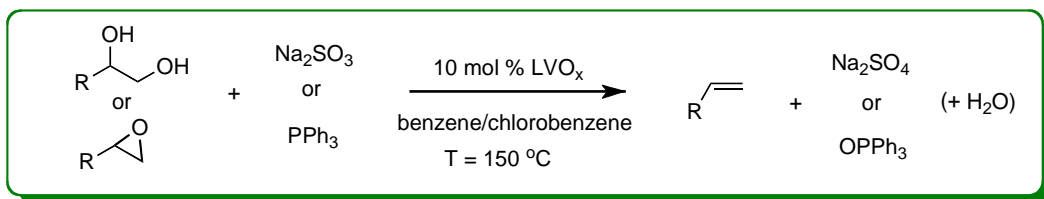
**DOE Interest**

The above achievements constitute an important step towards the development of large-scale processes for the production of value-added products, olefins and unsaturated oxygenates, from abundant biomass-derived polyol feedstocks.

**Recent Progress**

*1. Non-precious metal catalysts for the glycol-to-olefin (DODH) reaction.* A number of economical metavanadate salts and polyoxo-vanadium complexes (e.g. (polyamine) $\text{VO}_2^+$  and [(2,6-pyridinedicarboxylate) $\text{VO}_2^-$ ]) have been evaluated as catalysts for the DODH of representative glycols, providing the first examples of efficient DODH catalyzed by non-precious metal compounds. With various metavanadate salts and sulfite as the reductant low to moderate

yields of olefins (10-40%) are obtained with



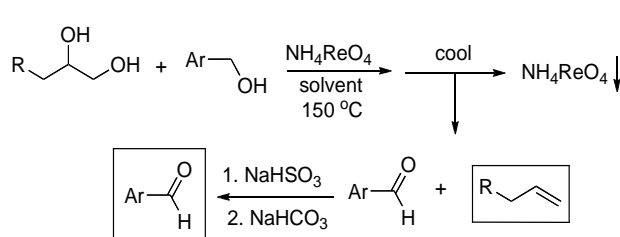
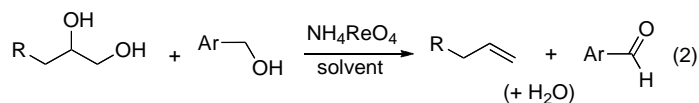


10 mol% catalyst loading at 150 °C. Significantly improved efficiencies were obtained with (dipic)VO<sub>2</sub><sup>-</sup> catalyst both for glycol DODH and for epoxide deoxygenation. The yields obtained with these economical vanadium catalysts are comparable to the best oxo-rhenium catalyst systems reported to date, albeit with somewhat lower activity. Initial promising DODH activities with several oxo-molybdenum complexes and polyoxomolybdates. MoO<sub>2</sub>Cl<sub>2</sub>(DMF)<sub>2</sub>/PPh<sub>3</sub> was found to have the highest DODH activity of all systems studied to date, but it suffers rapid deactivation.

2. *Development of an Efficient System for the Re-catalyzed DODH of Glycols.* Practical limitations of the reported oxo-rhenium based DODH systems include inefficient catalyst recovery and lifetime and the separation of the olefinic products from the redox co-product, e.g. ketone derived from sec-alcohol reductant. We found that representative glycols were converted to corresponding olefins in good to excellent yields when heated with 1.0 equiv of benzyl alcohol in aromatic solvents in the presence of 1-10 mol% of NH<sub>4</sub>ReO<sub>4</sub> (APR). Importantly, the co-product aryl aldehyde, e.g. benzaldehyde, could be easily separated from the olefinic product by reversible formation of its bisulfite adduct. Another attractive feature of the APR/BA DODH system is the catalyst recoverability and longevity; the sparing solubility of APR in aromatic solvents at rt results in its nearly quantitative precipitation after the DODH reactions. The robust nature and retained catalytic activity of

recovered APR was demonstrated through six react-cool-recharge batch reaction cycles with diethyl tartrate/PhCH<sub>2</sub>OH/APR/benzene.

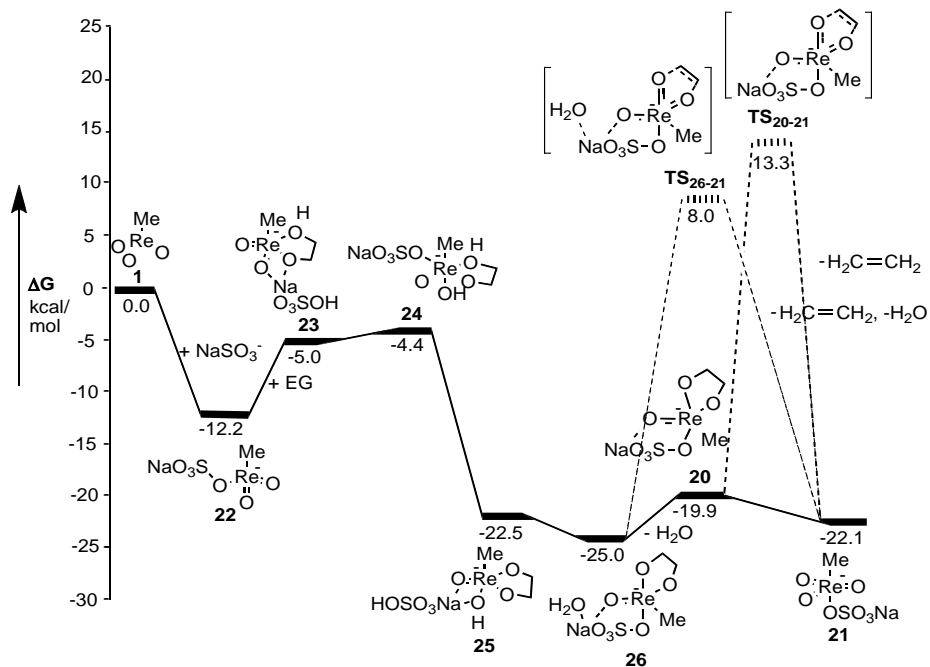
The olefins are formed regioselectively (no C=C isomers detected) and potentially acid- or water sensitive ether and ester linkages are well tolerated. A stereoselective syn-elimination of the glycol hydroxyl groups was indicated by the conversion of rac-diethyl tartrate to trans-diethyl fumarate, indicative of a concerted release of olefin from a M-glycolate intermediate.



3. *Computational Analysis of the Sulfite-MeReO<sub>3</sub> DODH Catalytic Cycle.* The mechanism of the MeReO<sub>3</sub>-catalyzed deoxydehydration of glycols to olefins by sulfite salts has been investigated with DFT calculations. Potential intermediates and transition states were evaluated for the three stages of reaction: a) dehydration of the glycol by an oxo-rhenium complex to form a Re-(O,O-glycolate); b) sulfite-induced O-transfer (to sulfate and a reduced oxo-Re); and c) fragmentation of the Re<sup>v</sup>-glycolate to give the olefin and to regenerate MeReO<sub>3</sub>. Alternative pathways have been analyzed differing in the order of steps (a) and (b), whether and which sulfite/sulfate species are coordinated; and the mechanism of sulfite association/sulfate loss is also evaluated. Transition states and activation energies are calculated for several of the key transformations,

including the H-transfer glycol dehydration, the LMeRe<sup>v</sup>O(glycolate) fragmentations (L=H<sub>2</sub>O, NaSO<sub>3</sub><sup>-</sup>, NaSO<sub>4</sub><sup>-</sup>), and NaSO<sub>3</sub><sup>-</sup> attack on oxo-Re<sup>vii</sup> species. The lowest energy catalytic pathway identified involves:

NaSO<sub>3</sub><sup>-</sup> attack on an oxo-oxygen of MeReO<sub>3</sub> to produce MeRe<sup>v</sup>O<sub>2</sub>(OSO<sub>3</sub>Na)<sup>-</sup> (**22**); glycol coordination by **22**, followed by a series of H-transfer steps to Re=O and/or Re-OSO<sub>3</sub>Na<sup>-</sup> to MeRe<sup>v</sup>O(glycolate)(OSO<sub>3</sub>Na)(H<sub>2</sub>O)<sup>-</sup> (**26**); concerted fragmentation of the Re<sup>v</sup>-glycolate **26** to



olefin and MeReO<sub>3</sub>(OSO<sub>3</sub>Na)<sup>-</sup> (**21**); and dissociation of NaSO<sub>4</sub><sup>-</sup> from **21** to regenerate MeReO<sub>3</sub> (**1**). Fragmentation of the Re-glycolate **26** is turnover-limiting.

## Future Plans

We will follow up, extend and probe more deeply into the reactivity and mechanistic aspects of these systems. We will concentrate our efforts on: 1) defining the scope and mechanism of the LVO<sub>2</sub>-catalyzed DODH reaction, including its extension to new reductants; 2) elucidating the mechanism of the alcohol-driven L<sub>4</sub>ReO<sub>2</sub><sup>+</sup>-catalyzed DODH (L effects; rate law; mechanism); 3) carrying out DFT-computational studies of these systems; 4) developing catalyst/reductant systems for the efficient DODH conversion of abundant higher polyols to value-added olefinic products; and 5) starting a new venture seeking to couple the reductive DODH reaction with C-C bond-forming reactions; e.g. DODH/olefin metathesis and pinacol coupling/DODH, as a means of producing C8-C12 hydrocarbons from abundant biomass-derived C4-C6 polyols.

## Publications: 2012-2013

1. Mechanism of sulfite-driven, MeReO<sub>3</sub>-catalyzed deoxydehydration of glycols, Liu, Peng; Nicholas, Kenneth M. *Organometallics* **2013**, *32*, 1821-1831.
2. Catalytic Deoxydehydration of Glycols with Alcohol Reductants, Boucher-Jacobs, Camille; Nicholas, Kenneth M. *ChemSusChem* **2013**, *6*, 597-599.

## **Molecular approaches toward the development of efficient heterogeneous catalysts and electrocatalysts for chemical energy conversion and storage**

Eranda Nikolla

*Chemical Engineering and Materials Science  
Wayne State University, Detroit, MI*

Dwindling fuel resources and high levels of CO<sub>2</sub> emissions have increased the need for renewable energy resources and more efficient energy conversion and storage systems. The goal of our research group is to design active, selective and stable catalysts and electrocatalysts for energy generation and storage technologies. We employ a combined experimental and theoretical approach, including various spectroscopies, microscopies and quantum chemical calculations to study processes at the gas/solid and liquid/solid interfaces with the aim of guiding the development of efficient and environmentally friendly materials for chemical energy conversion and storage.

I will discuss our work on developing active and stable electrocatalysts for co-electrolysis of CO<sub>2</sub> and H<sub>2</sub>O to synthesis gas using solid oxide electrolyzers. In this project, DFT calculations are employed to identify the chemical/electrochemical steps that limit the activity and stability of solid oxide electrocatalysts and devise ways to improve the electrocatalyst performance. I will also discuss our efforts to develop stable O<sub>2</sub>-electrode materials for Li-air batteries. While Li-air battery is a promising energy storage technology, its commercial application is limited by the performance of the O<sub>2</sub>-electrode. We have employed in-situ infrared spectroscopy and electro-kinetic measurements to shed light on elementary processes that limit the performance these devices. Based on this understanding we devised ways to improve their performance by developing stable O<sub>2</sub>-electrode materials. The last project that will be discussed is focused on the development of heterogeneous catalysts for the isomerization of sugars - a step toward biomass conversion to valuable chemicals.

## Zinc Catalysts for On Demand Hydrogen Generation and Carbon Dioxide Functionalization

Students: Aaron Sattler, Ahmed Al-Harbi, Ashley Zuzek, Yi Rong, Wesley Sattler, Michelle Neary  
Contact: Department of Chemistry, Columbia University, New York, NY 10027;  
parkin@columbia.edu.

### Goals

The specific objectives and research goals of the research performed during the recent grant period have been to obtain information that is relevant to metal mediated transformations that produce useful chemicals from natural resources. For example, considerable effort is currently being directed towards (i) the implementation of a “hydrogen economy”, in which hydrogen serves as a fuel, and (ii) the use of ubiquitous carbon dioxide as a renewable C<sub>1</sub> source for the synthesis of useful chemicals. However, the practical realization of both of these objectives presents daunting challenges. As an illustration, a principal problem with respect to the utilization of carbon dioxide as a chemical feedstock is concerned with the fact that it is not only thermodynamically a very stable molecule, but it is also kinetically resistant to many chemical transformations. Likewise, the energy efficient storage of hydrogen with a high volumetric energy density is a critical prerequisite to the implementation of a hydrogen economy. The discovery of new catalytic methods for (i) the rapid generation of hydrogen and (ii) the functionalization of CO<sub>2</sub> are crucial for advancing the use of hydrogen as a fuel and for utilizing CO<sub>2</sub> as an effective C<sub>1</sub> source for commodity chemicals.

### DOE Interest

An important objective of the Mission of the U. S. Department of Energy is to “Catalyze the timely, material, and efficient transformation of the nation’s energy system and secure U.S. leadership in clean energy technologies”. The research performed is of direct relevance to this goal because on demand production of hydrogen is essential for establishing a future hydrogen economy to transform the nation’s energy system. In addition, the effective utilization of carbon dioxide as a raw material for the chemical industry will contribute considerably to the efficient implementation of clean energy technologies. Furthermore, a fundamental understanding of the chemical aspects of catalysis is important because, as emphasized by the Catalysis Science core research area of the Department of Energy, Basic Energy Sciences: “Catalysts are crucial to creating new, energy-efficient routes for the production of basic chemical feedstocks and value-added chemicals.”

### Recent Progress

#### *1. Zinc Catalysts for On Demand Hydrogen Generation and Carbon Dioxide Functionalization*

We have discovered that zinc, an abundant post-transition metal, can serve as a catalyst for the hydrolysis of Si–H bonds. Specifically, the [*tris*(2-pyridylthio)methyl]zinc hydride complex, [ $\kappa^3$ -Tptm]ZnH is an effective room temperature catalyst for the release of three equivalents of H<sub>2</sub> from PhSiH<sub>3</sub>, a commercially available trihydrosilane. In addition to [ $\kappa^3$ -Tptm]ZnH serving as a catalyst for

the hydrolysis of Si–H bonds, the trimethylsiloxide complex  $[\kappa^4\text{-Tptm}]\text{ZnOSiMe}_3$  may also be employed as an effective precatalyst because it reacts with  $\text{PhSiH}_3$  to generate the hydride complex.

As an illustration of the effectiveness of  $[\kappa^4\text{-Tptm}]\text{ZnOSiMe}_3$  as a precatalyst, 1 mol % (per Si–H bond) is capable of achieving quantitative liberation of three equivalents of  $\text{H}_2$  from a mixture of  $\text{PhSiH}_3$  and water, with a turnover frequency (TOF) of  $1.0 \times 10^4 \text{ h}^{-1}$  for release of the first equivalent. Alcoholysis also provides a means to liberate  $\text{H}_2$  from silanes and, in this regard, the zinc-catalyzed methanolysis of  $\text{PhSiH}_3$  is even more efficient than is the hydrolysis reaction. For example, only 0.001 mol % (per Si–H bond) of  $[\kappa^4\text{-Tptm}]\text{ZnOSiMe}_3$  can achieve quantitative liberation of three equivalents of  $\text{H}_2$  from a mixture of  $\text{PhSiH}_3$  and MeOH in toluene, corresponding to a turnover number (TON) of  $10^5$ . The evolution of  $\text{H}_2$  is also very rapid, with release of the first equivalent occurring in less than two minutes, corresponding to an impressive TOF of  $1.6 \times 10^6 \text{ h}^{-1}$ .

$[\kappa^3\text{-Tptm}]\text{ZnH}$  is also a hydrosilylation catalyst. For example,  $[\kappa^3\text{-Tptm}]\text{ZnH}$  catalyzes the insertion of acetaldehyde and acetone into all three Si–H bonds of  $\text{PhSiH}_3$  to give  $\text{PhSi}(\text{OEt})_3$  and  $\text{PhSi}(\text{OPr}^i)_3$ , respectively. Furthermore,  $[\kappa^3\text{-Tptm}]\text{ZnH}$  catalyzes the hydrosilylation of  $\text{CO}_2$ , as illustrated by the formation of triethoxysilyl formate by reaction of  $\text{CO}_2$  with  $(\text{EtO})_3\text{SiH}$ . Access to silyl formates from  $\text{CO}_2$  is of interest because they have potential for serving as formylating agents, thereby providing a means to convert  $\text{CO}_2$  into other useful compounds. In this regard,  $\text{HCO}_2\text{Si}(\text{OEt})_3$  reacts immediately with  $\text{Me}_2\text{NH}$  to give *N,N*-dimethylformamide,  $\text{Me}_2\text{NCHO}$ .

## 2. Analysis of Benzyl Ligand Coordination Modes in Zirconium Compounds

Benzylzirconium compounds are employed for the synthesis of catalysts for olefin polymerization. In this regard, benzyl ligands coordinate to transition metal centers in manifold ways. For example, in addition to  $\eta^1$ -coordination, interaction *via* the phenyl group is also possible, with  $\eta^2$ ,  $\eta^3$ ,  $\eta^4$ ,  $\eta^5$ , and  $\eta^7$ -coordination modes having been discussed in the literature. The coordination mode of a benzyl ligand is not only expected to influence the intrinsic reactivity of the  $\text{M}-\text{CH}_2\text{Ph}$  bond, but could also provide a means to modulate the reactivity of a metal center by stabilizing coordinatively unsaturated centers. Therefore, we have analyzed the structures of zirconium benzyl compounds and have demonstrated that a benzyl ligand attached to zirconium is intrinsically flexible, such that this may contribute to the reactivity of this class of compounds. For example, while the  $\text{Zr}-\text{CH}_2-\text{Ph}$  bond angles of an orthorhombic form of  $\text{Zr}(\text{CH}_2\text{Ph})_4$  have been reported to range from  $87.0(3)^\circ$  to  $99.1(3)^\circ$ , we obtained the structure of a monoclinic form that exhibits an even greater range of  $\text{Zr}-\text{CH}_2-\text{Ph}$  bond angles, namely  $81.6(1)^\circ$  to  $106.7(2)^\circ$ .

Consistent with this large range in  $\text{Zr}-\text{CH}_2-\text{Ph}$  bond angle, density functional theory calculations demonstrated that little energy is required to perturb the  $\text{Zr}-\text{CH}_2-\text{Ph}$  bond angles in this compound. In order to eliminate the buffering effect provided by the other benzyl ligands, geometry optimization calculations were also performed on  $\text{Me}_3\text{ZrCH}_2\text{Ph}$ , which features only one benzyl ligand. Significantly, while the most stable geometry optimized structure possesses a  $\text{Zr}-\text{C}-\text{C}$  bond angle of  $92.8^\circ$ , the energy of the molecule changes by less than  $2 \text{ kcal mol}^{-1}$  over the range  $80 - 125^\circ$ . Thus, the flexibility of the benzyl ligands in  $\text{Zr}(\text{CH}_2\text{Ph})_4$  is not merely attributable to a buffering effect due to the presence of other benzyl ligands, but is intrinsic to the  $\text{Zr}-\text{CH}_2-\text{Ph}$  moiety. Specifically, the energy required to decrease the  $\text{Zr}-\text{CH}_2-\text{Ph}$  bond angle is compensated by interaction of the phenyl group with

the electronically unsaturated zirconium center, while the energy required to increase the Zr–CH<sub>2</sub>–Ph bond angle is compensated by the formation of agostic interactions with the methylene group.

### Future Plans

Future studies will include, for example: (i) the use of zinc hydride compounds as catalysts for other transformations of organic substrates, (ii) the use of tridentate [O<sub>3</sub>] donor ligands to synthesize counterparts of metallocenes that have catalytic functions, and (iii) an investigation of bond cleavage reactions relevant to catalytic systems.

### Publications (2010 – 2013)

1. “Cleaving Carbon–Carbon Bonds by Inserting Tungsten into Unstrained Aromatic Rings.” Aaron Sattler and Gerard Parkin *Nature* **2010**, *463*, 523-526.
2. “Metal–Metal Bonding in Bridging Hydride and Alkyl Compounds.” Gerard Parkin *Structure and Bonding* **2010**, *136*, 113-145.
3. “Synthesis and Structural Characterization of Tris(2-oxo-1-t-butylimidazolyl) and Tris(2-oxo-1-methylbenzimidazolyl)hydroborato Complexes: A New Class of Tripodal Oxygen Donor Ligand.” Ahmed Al-Harbi, Wesley Sattler, Aaron Sattler and Gerard Parkin *Chem. Commun.* **2011**, *47*, 3123-3125.
4. “Carbon–Sulfur Bond Cleavage and Hydrodesulfurization of Thiophenes by Tungsten” Aaron Sattler and Gerard Parkin *J. Am. Chem. Soc.* **2011**, *133*, 3748-3751.
5. “Modeling Aspects of Hydrodesulfurization by Molybdenum Hydride Compounds: Desulfurization of Thiophene and Benzothiophene and C–S Bond Cleavage of Dibenzothiophene.” Aaron Sattler, Kevin E. Janak and Gerard Parkin *Inorg. Chim. Acta* **2011**, *369*, 197-202.
6. “Structural Characterization of TaMe<sub>3</sub>Cl<sub>2</sub> and Ta(PMe<sub>3</sub>)<sub>2</sub>Me<sub>3</sub>Cl<sub>2</sub>, a Pair of Five and Seven-Coordinate d<sup>0</sup> Tantalum Methyl Compounds.” Aaron Sattler, Serge Rucolo and Gerard Parkin *Dalton Trans.* **2011**, *40*, 7777-7782.
7. “Formation of a Cationic Alkylidene Complex *via* Formal Hydride Abstraction: Synthesis and Structural Characterization of [W(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CHPM<sub>2</sub>)H]X (X = Br, I).” Aaron Sattler and Gerard Parkin *Chem. Commun.* **2011**, *47*, 12828–12830.
8. “A New Class of Transition Metal Pincer Ligand: Tantalum Complexes that Feature a [CCC] X<sub>3</sub>–Donor Array Derived from a Terphenyl Ligand.” Aaron Sattler and Gerard Parkin *J. Am. Chem. Soc.* **2012**, *134*, 2355–2366.
9. “Zinc Catalysts for On Demand Hydrogen Generation and Carbon Dioxide Functionalization.” Wesley Sattler and Gerard Parkin *J. Am. Chem. Soc.* **2012**, *134*, 17642-17465.
10. “Highly Variable Zr–CH<sub>2</sub>–Ph Bond Angles in Tetrabenzylzirconium: Analysis of Benzyl Ligand Coordination Modes.” Yi Rong, Ahmed Al-Harbi and Gerard Parkin *Organometallics* **2012**, *31*, 8208-8217.
11. “The Occurrence and Representation of Three-Center Two-Electron Bonds in Covalent Inorganic Compounds.” Jennifer C. Green, Malcolm L. H. Green, and Gerard Parkin *Chem. Commun.* **2012**, *48*, 11481–11503.

## New Insights into the Synthesis of Methanol on Copper Catalysts

Lead PI: Johannes A. Lercher

Postdoc: Yong Yang

Collaborators: Charles T. Campbell (University of Washington), Donghai Mei (PNNL), and Charles A. Mims (University of Toronto)

Contact: Institute for Integrated Catalysis, P.O. Box 999, MS: K2-12, Pacific Northwest National Laboratory, Richland, Washington; chuck.peden@pnl.gov

Over the last several years, we have constructed and are now routinely operating a new capability for performing studies of reaction mechanisms of heterogeneously catalyzed reactions [1]. This instrument combines fourier transform infrared spectroscopy (FTIR) of adsorbed species in a reactor that can perform a powerful kinetics measurement, steady-state isotopic transients kinetics analysis (SSITKA). We have demonstrated the utility of this capability with studies of the methanol synthesis reaction over oxide-supported Cu catalysts [2-5]. This presentation will describe results that cast doubt on the previously accepted reaction mechanism, and also provide evidence for a new mechanism. Details on the structure of important reaction intermediates involved in the activation of CO<sub>2</sub> to a useful reduced product, methanol, will be given.

The mechanism of methanol synthesis on copper-based catalysts has been extensively studied and remains a target of research because of the significance of this reaction in the chemical industry and methanol's potential as a liquid energy/hydrogen carrier. A recent DFT and microkinetic modeling study by Grabow and Mavrikakis [6] contains a thorough review of the current state of our understanding of this reaction. These recent models allow for conversion of both CO (by direct hydrogenation) and CO<sub>2</sub> (via formate intermediates) to methanol. Although tracer experiments have shown that CO<sub>2</sub> is the preferred reactant over CO in H<sub>2</sub>:CO:CO<sub>2</sub> mixtures under commercial conditions, the relative importance of these channels under various conditions is still uncertain [6]. Furthermore, the role of water in the reaction mechanism has received little attention, despite long established effects of water and CO<sub>2</sub> in the conversions of syngas [7]. Our recent DFT study has pointed out that water can have significant effects in methanol synthesis and that a separate methanol formation mechanism via a carboxyl intermediate is energetically possible [8]. Here, we will describe particularly strong effects of water on the conversion of both CO and CO<sub>2</sub> at temperatures below those of commercial practice, and support for an intermediate common to both CO and CO<sub>2</sub> [5].

### References

1. Yang, Y; Disselkamp, RS; Campbell, CT; Szanyi, J; Peden, CHF; Goodwin Jr., JG *Rev. Sci. Instrum.* **77** (2006) 094104.
2. Yang, Y; Mims, CA; Disselkamp, RS; Mei, D; Kwak, JH; Szanyi, J; Peden, CHF; Campbell, CT *Catal. Lett.* **125** (2008) 201.
3. Yang, Y; Mims, CA; Disselkamp, RS; Peden, CHF; Campbell, CT *Topics in Catal.* **52** (2009) 1440.
4. Yang, Y; Mims, CA; Disselkamp, RS; Peden, CHF; Campbell, CT *J. Phys. Chem. C* **40** (2010) 17205.
5. Yang, Y; Mims, CA; Mei, D; Peden, CHF; Campbell, CT *J. Catal.* **298** (2013) 10.
6. Grabow, LC; Mavrikakis, M *ACS Catal.* **1** (2011) 365.
7. Parameswaran, VR; Lee, S; Wender, I *Fuel Science Techn. Intl.* **7** (1989) 899.
8. Zhao, Y-F; Yang, Y; Mims, CA.; Peden, CHF; Li, J; Mei, D *J. Catal.* **281** (2011) 199.

## Homogeneous and Interfacial Catalysis in 3D Controlled Environment

Additional PI's: Andreja Bakac, James Evans, Aaron Sadow, Igor Slowing, Javier Vela  
Scientific Staff: Takeshi Kobayashi, Dajiang Liu, Oleg Pestovsky  
Graduate Students: Stacey Althaus, Jake Fleckenstein, Yijun Guo, Kapil Kandel, Naresh Needugurala, Melinda Reichert, Zak Weinstein

Ames Laboratory, U.S. DOE, Iowa State University, Ames, IA 50011-3111  
[mpruski@iastate.edu](mailto:mpruski@iastate.edu)

### Goal

The overarching goal of this collaborative research project is to develop new catalytic principles for bringing together the best features of homogeneous and heterogeneous catalysis and ultimately enable the design of catalysts for efficient conversion of biologically-derived feedstocks, particularly those relevant to liquid-phase processing. The substantial challenges for rational design of catalysts for selective chemical conversions require understanding and control of the catalytic environment and reaction mechanisms. These requirements are addressed through the design of 3D, mesoporous interfacial catalysts. Doing so provides advantages in catalyst recovery, reaction control, sensitivity and efficiency. Our efforts combine expertise in mesoporous catalysis synthesis, transition metal chemistry, kinetics and mechanisms of catalytic reactions, photocatalysis, theoretical modeling and solid-state (SS)NMR.

### DOE Interest

Developing catalytic systems that can coherently unite the best features of the homogeneous and heterogeneous areas of catalysis is a key interest of the DOE, and such catalysts are required for rational design of efficient liquid-solid interfacial processes. By controlling the structure, reactivity and morphology of a mesoporous solid support and its interaction with active sites, these studies provide truly unique opportunities for the design of a new generation of highly efficient and selective catalysts. This research also provides fundamental knowledge about catalysis by deconvoluting the key factors that affect selectivity, reactivity and kinetics.

### Recent Progress

*(1) The effects of porosity of mesoporous silica nanoparticle (MSN) supports on the activity of heterogeneous catalysts.* The catalytic activity of supported amines in the aldol condensation was found to be highly dependent on the length and the width of the pores. Catalytic activity requires pore diameters greater than 2.8 nm.[32] The pore size limitation on the activity is understood in terms of models describing restricted transport of molecules through the pores. The transport approached the behavior of single file diffusion (Fig. 1a,b).[40] SSNMR and kinetic studies of the reaction established the formation of an imine surface species, which gives deactivated catalytic sites and reduces the effective pore width limiting diffusion through the pores of the material (Fig. 1c,d). The deactivation of the catalyst was solved by two approaches: 1) modification of the structure of the active site from a primary to a secondary amine,[32] and 2) addition of water to hydrolyze the product of inhibition.[43] Further investigations into the mechanism of the reaction using SSNMR and reaction kinetics reveals two surprising results: 1) the rates of the reaction using heterogeneous catalysts are two orders of magnitude larger than using comparable homogeneous catalysts, which is attributed to cooperative effects by neighboring silanol

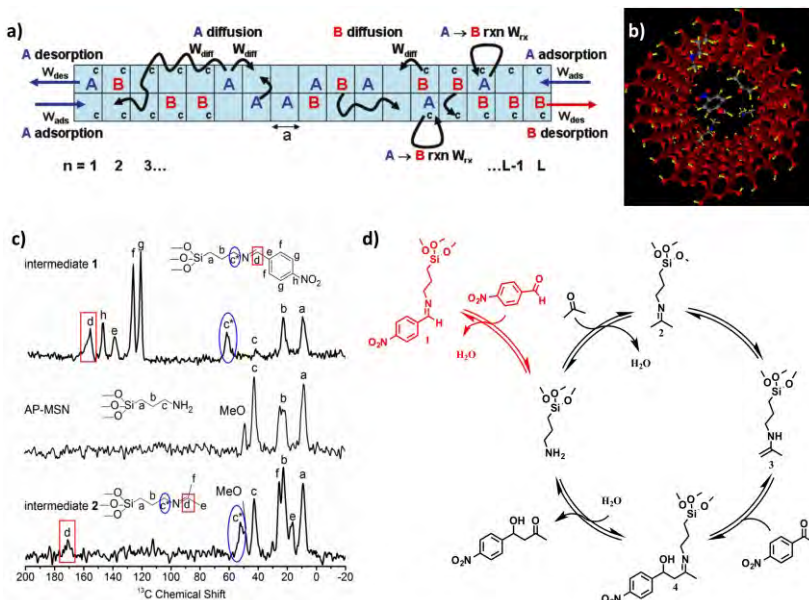


groups,[32] and 2) inverting the polarity of the solvent results in a reversal in the relative activities of the primary and secondary amine catalysts, due to stabilization of additional inhibition products by polar solvents.[43] In addition, water was proven to have an additional effect in shifting the equilibria within the catalytic cycle.[43]

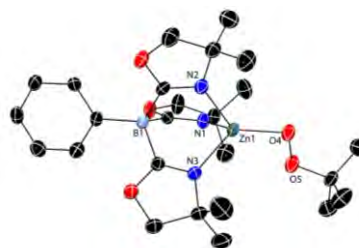
### (2) First row transition metals and oxidations and group transfer.

Our team's significant progress in the study of first row metal mediated catalytic oxidation reactions in interfacial systems give strategies for controlled liquid phase conversion of biological feedstocks. The reaction between  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and hydrogen peroxide (Fenton reaction) at near-neutral pH in the absence of coordinating anions generates Fe(IV) as intermediate, in contrast to the previously established involvement of hydroxyl radicals in acidic solutions. This result implies that changes in reaction conditions or solvent may be used to control reaction mechanism and oxidation products, and this may be particularly important in lignin oxidations.[25] Similarly, control over the coordination environment in zinc alkyls allows controlled oxidation with  $\text{O}_2$  to give crystallographically characterized zinc alkyl peroxides [Fig. 2]. Alkylperoxy-group transfer occurs in reactions with organosilanes, rather than oxidation.[36] Similarly, zinc alkoxides and organosilanes give Si-O bond formation, which provide catalytic approaches to selective condensation (grafting) reactions.[14]

**(3) Catalytic conversions of biorenewables.** Conversions of oxygen-rich substrates, and control over oxidation state, are critical for lignocellulose utilization for fuel and chemical applications. Decarboxylation of alkyl carboxylic acids can be achieved photochemically in the presence of aqua-metal ions. The  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ -assisted reaction generates mixtures of alkanes and alkenes, and the  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ -mediated reaction produces  $\alpha$ -alkenes exclusively.[26] Alternatively, photochemical activation of an oxazolinylborato rhodium dicarbonyl results in a catalytic decarbonylation of primary alcohols to give  $\text{H}_2$ , CO (syngas) and hydrocarbons. The photon is apparently needed to dissociate Rh-CO, and importantly the reactivity of the activated rhodium intermediate is significantly influenced by ancillary ligands.[30] A related reaction has been developed using semiconductor-metal hybrids for sunlight-driven dehydrogenation and hydrogenolysis of benzyl alcohol. Limited metal (Pt, Pd) modification



**Figure 1:** Molecular transport can control the kinetics of catalytic processes within nanoporous supports: when reactants and products are slightly smaller than the pore widths, diffusion can be described by models with restricted passing probabilities (a,b). During the aldol condensation between *p*-nitrobenzaldehyde and acetone the formation of an inhibition intermediate reduces the effective pore width and controls the catalytic cycle, as revealed by surface, kinetic and solid-state NMR analyses (c,d).



**Figure 2:** X-ray structure of a monomeric zinc peroxide.

greatly enhances activity and selectivity and prevents photocatalyst etching and degradation. CdS-Pt favors H<sub>2</sub> (dehydrogenation) over toluene (hydrogenolysis) 8:1, whereas CdS<sub>0.4</sub>Se<sub>0.6</sub>-Pd favors toluene over H<sub>2</sub> 3:1. This work will lead to energy efficient biomass transformations.[48]

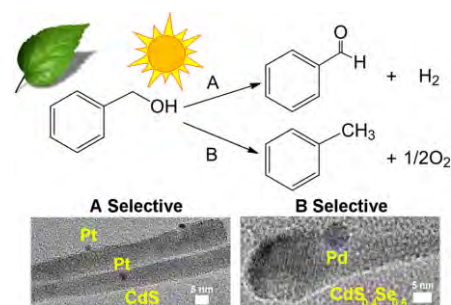
Interfacial oxidations have also been employed in biorenewable conversions. We have developed a bifunctional hybrid material consisting of an enzyme and an organocatalyst supported on mesoporous silica nanoparticles. Alcohol oxidase enzyme was used to catalyze the aerobic oxidation of ethanol into acetaldehyde, which was then subjected to self-aldol condensation catalyzed by aminopropyl groups to give 2,4-hexandienal. This low-temperature (40°C) tandem catalytic process resulted in the upgrade of the carbon content and carbon-to-oxygen ratio of the raw material, improving its properties as a renewable fuel. The site isolation of the two catalytic groups prevented the oxidation of the amines by the enzyme, and led to high product selectivity.[33]

**(4) Studies of mesoporous materials by dynamic nuclear polarization (DNP) NMR.** We investigated the opportunities that this emerging technology can provide for our catalysis program. We systematically studied the enhancement factors in <sup>13</sup>C and <sup>29</sup>Si CP-MAS NMR boosted by DNP of functionalized mesoporous silica, which yielded >1000 improvement in time performance. Specifically, we separated contributions due to: (i) microwave irradiation, (ii) quenching by paramagnetic effects, (iii) the presence of frozen solvent, (iv) the temperature, as well as changes in (v) relaxation and (vi) CP behaviour. The effects of DNP were also ascertained in reference to state-of-the-art <sup>13</sup>C-<sup>1</sup>H and <sup>1</sup>H-<sup>29</sup>Si HETCOR spectra, obtained at room temperature using respectively indirect detection or CPMG refocusing.[44] Furthermore, we showed that DNP can be used to enhance NMR signals of <sup>13</sup>C and <sup>29</sup>Si nuclei located inside nanoparticles at several hundreds of nanometers from radicals trapped in the surrounding solvent.[45]

## Future Plans

Further progress hinges on overcoming significant challenges that we address: (1) the need for synthetic methods that control the structure and catalytic activity of mesoporous scaffolds, (2) fundamental limitations in molecular transport and reactivity, and (3) mechanisms for conversion of biomass-derived feedstocks. Specifically, we will:

- Establish a general platform for the analysis of the effects of transport within nanopores on different catalytic processes.
- Develop methodologies to control and study distribution of multiple functional groups (i.e. catalytic sites, co-catalysts and catalyst modulators) within single mesoporous supports.
- Develop hybrid organic-inorganic multicomponent heterogeneous catalysts for the hydroprocessing of lipids from renewable feedstocks.
- Develop multifunctional platforms for tandem catalytic fragmentation of lignocellulose and subsequent conversion of the products of fragmentation into chemical commodities.
- Graft metal photocatalysts onto semiconductor nanocrystals and mesoporous oxides to develop interfacial catalytic conversions of carbohydrates to syngas and decarboxylation of acids.
- Explore Fe(II)/ozone combination for conversion of furfural and hydroxymethyl furfural to



**Figure 3.** Visible-light promoted dehydrogenation reactions of alcohols using semiconductor nanocrystal sensitizers.

furan carboxylic acids which are useful intermediates and substrates in chemical industries.

- Develop novel strategies and catalysts for metal-assisted photochemical decarboxylation.
- Investigate photoinduced charge transfer mechanisms responsible for the composition-dependent chemistry of semiconductor-metal photocatalysts.
- Investigate the structural and electronic reasons for the enhanced stability of metal-modified photocatalysts against photo-induced etching and degradation.
- Investigate energy and charge transfer between semiconductor quantum dot fluorophores and surface-bound transition metal photocatalysts.
- Further development of SSNMR methodology is planned utilizing DNP, ultrafast MAS, and pulse field gradients. The effort will focus on new multidimensional protocols for studying the internuclear correlations on solid-liquid interfaces and transport phenomena within the pores.
- Modeling of the interplay between transport and reaction in nanoporous systems. We will develop "generalized hydrodynamic" models incorporating both restricted transport and fluctuation effects near pore openings, features needed to predict reactivity. Langevin analyses will assess critical dynamical events within pores which control reactivity.
- Atomistic modeling of catalytic nanomaterials. We will develop atomistic-level models which will be analyzed by kinetic Monte Carlo simulation to assess structure and formation kinetics for catalytic nanomaterials of relevance to this project.

### Publications (2011-present)

1. D.M. Ackerman, J. Wang, J.H. Wendel, D.-J. Liu, M. Pruski, and J.W. Evans, *Catalytic conversion reactions mediated by single-file diffusion in linear nanopores: Hydrodynamic versus stochastic behavior*, J. Chem. Phys., 134, 114107 (2011). DOI: 10.1063/1.3563638
2. M.G. Alemseghed, T.P.A. Ruberu, and J. Vela, *Controlled Fabrication of Colloidal Semiconductor-Metal Hybrid Heterostructures: Site Selective Metal Photo Deposition*, Chem. Mater., 23, 3571-3579 (2011). DOI: 10.1021/cm201513a
3. H.-A. Ho, T.S. Gray, B. Baird, A. Ellern, and A.D. Sadow, *Allylic C-H bond activation and functionalization mediated by tris(oxazolonyl)borato rhodium(I) and iridium(I) compounds*, Dalton Trans., 40, 6500-6514 (2011). DOI: 10.1039/c1dt10249d
4. Y. Huang, S. Xu, and V.S.Y. Lin, *Bifunctionalized Mesoporous Materials with Site-Separated Bronsted Acids and Bases: Catalyst for a Two-Step Reaction Sequence*, Angew. Chem. Int. Ed., 50, 661-664 (2011). DOI: 10.1002/anie.201004572
5. Y. Huang, S. Xu, and V.S.Y. Lin, *New Strategy for Enantioselective Heterogeneous Catalysis: Immobilization of both Metal Nanoparticles and Chiral Modifiers on Mesoporous Silica Nanoparticles*, ChemCatChem, 3, 690-694 (2011). DOI: 10.1002/cctc.201000363
6. Y. Huang, S. Xu, and V.S.Y. Lin, *Changing from Symmetric to Asymmetric Simply by Immobilizing the Catalyst on Mesoporous Silica Nanoparticle*, ChemCatChem, 3, 131-134 (2011). DOI: 10.1002/cctc.201000294
7. B. Jana, A. Ellern, O. Pestovsky, A. Sadow, and A. Bakac, *Synthesis of Monomeric Fe(II) and Ru(II) Complexes of Tetradentate Phosphines*, Inorg. Chem., 50, 3010-3016 (2011). DOI: 10.1021/ic102510c
8. T.W. Kim, Slowing, II, P.W. Chung, and V.S.Y. Lin, *Ordered Mesoporous Polymer-Silica Hybrid Nanoparticles as Vehicles for the Intracellular Controlled Release of Macromolecules*, ACS Nano, 5, 360-366 (2011). DOI: 10.1021/nn101740e
9. T. Kobayashi, K. Mao, S.-G. Wang, V.S.Y. Lin, and M. Pruski, *Molecular ordering of mixed surfactants in mesoporous silicas: A solid-state NMR study*, Solid State Nucl. Magn. Reson., 39, 65-71 (2011). DOI: 10.1016/j.ssnmr.2011.02.001
10. D.C. Leitch, R.H. Platel, and L.L. Schafer, *Mechanistic Elucidation of Intramolecular Aminoalkene Hydroamination Catalyzed by a Tethered Bis(ureate) Complex: Evidence for Proton-Assisted C-N Bond Formation at Zirconium*, J. Am. Chem. Soc., 133, 15453-15463 (2011). DOI: 10.1021/ja202448b

11. D.-J. Liu, J. Wang, D.M. Ackerman, I.I. Slowing, M. Pruski, H.-T. Chen, V.S.Y. Lin, and J.W. Evans, *Interplay between Anomalous Transport and Catalytic Reaction Kinetics in Single-File Nanoporous Systems*, ACS Catal., 1, 751-763 (2011). DOI: 10.1021/cs200115c
12. K. Manna, M.L. Kruse, and A.D. Sadow, *Concerted C-N/C-H Bond Formation in Highly Enantioselective Yttrium(III)-Catalyzed Hydroamination*, ACS Catal., 1, 1637-1642 (2011). DOI: 10.1021/cs200511z
13. K. Manna, S. Xu, and A.D. Sadow, *A Highly Enantioselective Zirconium Catalyst for Intramolecular Alkene Hydroamination: Significant Isotope Effects on Rate and Stereoselectivity*, Angew. Chem. Int. Ed., 50, 1865-1868 (2011). DOI: 10.1002/anie.201006163
14. D. Mukherjee, R.R. Thompson, A. Ellern, and A.D. Sadow, *Coordinatively Saturated Tris(oxazolanyl)borato Zinc Hydride-Catalyzed Cross Dehydrocoupling of Silanes and Alcohols*, ACS Catal., 1, 698-702 (2011). DOI: 10.1021/cs2001016
15. S.R. Neal, A. Ellern, and A.D. Sadow, *Optically active, bulky tris(oxazolanyl)borato magnesium and calcium compounds for asymmetric hydroamination/cyclization*, J. Organomet. Chem., 696, 228-234 (2011). DOI: 10.1016/j.jorganchem.2010.08.057
16. S. Nedd, T. Kobayashi, C.-H. Tsai, I.I. Slowing, M. Pruski, and M.S. Gordon, *Using a Reactive Force Field To Correlate Mobilities Obtained from Solid-State C-13 NMR on Mesoporous Silica Nanoparticle Systems*, J. Phys. Chem. C, 115, 16333-16339 (2011). DOI: 10.1021/jp204510m
17. O. Pestovsky, S.W. Veysey, and A. Bakac, *Kinetics and Mechanism of Hydrogen-Atom Abstraction from Rhodium Hydrides by Alkyl Radicals in Aqueous Solutions*, Chem. Euro. J., 17, 4518-4522 (2011). DOI: 10.1002/chem.201100094
18. T.P.A. Ruberu and J. Vela, *Expanding the One-Dimensional CdS-CdSe Composition Landscape: Axially Anisotropic CdS<sub>1-x</sub>Se<sub>x</sub> Nanorods*, ACS Nano, 5, 5775-5784 (2011). DOI: 10.1021/nn201466b
19. C.-H. Tsai, H.-T. Chen, S.M. Althaus, K. Mao, T. Kobayashi, M. Pruski, and V.S.Y. Lin, *Rational Catalyst Design: A Multifunctional Mesoporous Silica Catalyst for Shifting the Reaction Equilibrium by Removal of Byproduct*, ACS Catal., 1, 729-732 (2011). DOI: 10.1021/cs200222t
20. C.-H. Tsai, J.L. Vivero-Escoto, I.I. Slowing, I.J. Fang, B.G. Trewyn, and V.S.Y. Lin, *Surfactant-assisted controlled release of hydrophobic drugs using anionic surfactant templated mesoporous silica nanoparticles*, Biomaterials, 32, 6234-6244 (2011). DOI: 10.1016/j.biomaterials.2011.04.077
21. D.M. Ackerman, J. Wang, and J.W. Evans, *Generalized Hydrodynamic Treatment of the Interplay between Restricted Transport and Catalytic Reactions in Nanoporous Materials*, Phys. Rev. Lett., 108, 228301 (2012). DOI: 10.1103/PhysRevLett.108.228301
22. S.M. Althaus, K. Mao, G.J. Kennedy, and M. Pruski, *Solid-State NMR Studies of Fossil Fuels using One- and Two-Dimensional Methods at High Magnetic Field*, Energy & Fuels, 26, 4405-4412 (2012). DOI: 10.1021/ef3004637
23. S.R. Alvarado, Y. Guo, T.P.A. Ruberu, A. Bakac, and J. Vela, *Photochemical versus Thermal Synthesis of Cobalt Oxyhydroxide Nanocrystals*, J. Phys. Chem. C, 116, 10382-10389 (2012). DOI: 10.1021/jp301459s
24. J.P. Amoureux and M. Pruski, *MQMAS NMR: Experimental Strategies, NMR of Quadrupolar Nuclei in Solid Materials*, eds. R.R. Wasylshen, S.E. Ashbrook, S. Wimperis, John Wiley & Sons Ltd, Chichester, 143-162 (2012).
25. H. Bataineh, O. Pestovsky, and A. Bakac, *pH-induced mechanistic changeover from hydroxyl radicals to iron(IV) in the Fenton reaction*, Chem. Sci., 3, 1594-1599 (2012). DOI: 10.1039/c2sc20099f
26. J.M. Carraher, O. Pestovsky, and A. Bakac, *Transition metal ion-assisted photochemical generation of alkyl halides and hydrocarbons from carboxylic acids*, Dalton Trans., 41, 5974-5980 (2012). DOI: 10.1039/c2dt30210a
27. C. Fernandez and M. Pruski, *Probing Quadrupolar Nuclei by Solid-State NMR Spectroscopy: Recent Advances*, in *Solid State Nmr*, J.C.C. Chan, Editor 2012. p. 119-188.
28. Y. Guo, K. Marchuk, S. Sampat, R. Abraham, N. Fang, A.V. Malko, and J. Vela, *Unique Challenges Accompany Thick-Shell CdSe/nCdS (n > 10) Nanocrystal Synthesis*, J. Phys. Chem. C, 116, 2791-2800 (2012). DOI: 10.1021/jp210949v
29. K. Hara, S. Akahane, J.W. Wiench, B.R. Burgin, N. Ishito, V.S.Y. Lin, A. Fukuoka, and M. Pruski, *Selective and Efficient Silylation of Mesoporous Silica: A Quantitative Assessment of Synthetic Strategies by Solid-State NMR*, J. Phys. Chem. C, 116, 7083-7090 (2012). DOI: 10.1021/jp300580f
30. H.-A. Ho, K. Manna, and A.D. Sadow, *Acceptorless Photocatalytic Dehydrogenation for Alcohol Decarbonylation and Imine Synthesis*, Angew. Chem. Int. Ed., 51, 8607-8610 (2012). DOI: 10.1002/anie.201203556

31. Y. Huang, W. Deng, E. Guo, P.-W. Chung, S. Chen, B.G. Trewyn, R.C. Brown, and V.S.Y. Lin, *Mesoporous Silica Nanoparticle-Stabilized and Manganese-Modified Rhodium Nanoparticles as Catalysts for Highly Selective Synthesis of Ethanol and Acetaldehyde from Syngas*, *ChemCatChem*, 4, 674-680 (2012). DOI: 10.1002/cctc.201100460
32. K. Kandel, S.M. Althaus, C. Peeraphatdit, T. Kobayashi, B.G. Trewyn, M. Pruski, and I.I. Slowing, *Substrate inhibition in the heterogeneous catalyzed aldol condensation: A mechanistic study of supported organocatalysts*, *J. Catal.*, 291, 63-68 (2012). DOI: 10.1016/j.jcat.2012.04.005
33. K. Kandel, C. Peeraphatdit, B.G. Trewyn, M. Pruski, and I.I. Slowing, *Enzyme-Mesoporous Silica Nanocomposites for Upgrading the Carbon Content of Bio-ethanol*, Preprint Papers - American Chemical Society, Division of Petroleum Chemistry, 57, 202-204 (2012).
34. K. Mao, G.J. Kennedy, S.M. Althaus, and M. Pruski, *Spectral Editing in  $^{13}\text{C}$  Solid-State NMR at High Magnetic Field using Fast MAS and Spin-Echo Dephasing*, *Solid State Nucl. Magn. Reson.*, 47-48, 19-22 (2012). DOI: 10.1016/j.ssnmr.2012.07.003
35. K. Marchuk, Y. Guo, W. Sun, J. Vela, and N. Fang, *High-Precision Tracking with Non-blinking Quantum Dots Resolves Nanoscale Vertical Displacement*, *J. Am. Chem. Soc.*, 134, 6108-6111 (2012). DOI: 10.1021/ja301332t
36. D. Mukherjee, A. Ellern, and A.D. Sadow, *Remarkably Robust Monomeric Alkylperoxyzinc Compounds from Tris(oxazoliny)boratozinc Alkyls and O-2*, *J. Am. Chem. Soc.*, 134, 13018-13026 (2012). DOI: 10.1021/ja303440n
37. T.P.A. Ruberu, H.R. Albright, B. Callis, B. Ward, J. Cisneros, H.-J. Fan, and J. Vela, *Molecular Control of the Nanoscale: Effect of Phosphine-Chalcogenide Reactivity on CdS-CdSe Nanocrystal Composition and Morphology*, *ACS Nano*, 6, 5348-5359 (2012). DOI: 10.1021/nn301182h
38. T.P.A. Ruberu, N.C. Nelson, I.I. Slowing, and J. Vela, *Selective Alcohol Dehydrogenation and Hydrogenolysis with Semiconductor-Metal Photocatalysts: Toward Solar-to-Chemical Energy Conversion of Biomass-Relevant Substrates*, *J. Phys. Chem. Lett.*, 3, 2798-2802 (2012). DOI: 10.1021/jz301309d
39. E. Tavasoli, Y. Guo, P. Kunal, J. Grajeda, A. Gerber, and J. Vela, *Surface Doping Quantum Dots with Chemically Active Native Ligands: Controlling Valence without Ligand Exchange*, *Chem. Mater.*, 24, 4231-4241 (2012). DOI: Doi 10.1021/cm3026957
40. J. Wang, D.M. Ackerman, K. Kandel, I.I. Slowing, M. Pruski, and J.W. Evans. *Conversion reactions in surface-functionalized mesoporous materials: Effect of restricted transport and the catalytic site distribution*. in Materials Research Society Symposium Proceedings. 2012. Pittsburgh: MRS. DOI: 10.1557/opl.2012.229
41. A. Bakac, B.L. Durfey, O. Pestovsky, and K.E. Kristian, *Kinetics and Thermodynamics of Nitric Oxide Binding to Transition Metal Complexes. Relationship to Dioxygen Binding*, *Chem. Sci.*, 4, 2185-2192 (2013). DOI: 10.1039/C3SC50157D
42. Y. Guo, S.R. Alvarado, J.D. Barclay, and J. Vela, *Shape-Programmed Nanofabrication: Understanding the Reactivity of Dichalcogenide Precursors*, *ACS Nano*, 7, 3616-3626 (2013). DOI: 10.1021/nn400596e
43. K. Kandel, S.M. Althaus, C. Peeraphatdit, T. Kobayashi, B.G. Trewyn, M. Pruski, and I.I. Slowing, *Solvent-Induced Reversal of Activities between Two Closely Related Heterogeneous Catalysts in the Aldol Reaction*, *ACS Catal.*, 3, 265-271 (2013). DOI: 10.1021/cs300748g
44. T. Kobayashi, O. Lafon, A.S.L. Thankamony, I.I. Slowing, K. Kandel, D. Carnevale, V. Vitzthum, H. Vezin, J.-P. Amoureux, G. Bodenhausen, and M. Pruski, *Analysis of sensitivity enhancement by dynamic nuclear polarization in solid-state NMR: a case study of functionalized mesoporous materials*, *Phys. Chem. Chem. Phys.*, 15, 5553-5562 (2013). DOI: 10.1039/c3cp00039g
45. O. Lafon, A.S.L. Thankamony, T. Kobayashi, D. Carnevale, V. Vitzthum, I.I. Slowing, K. Kandel, H. Vezin, J.-P. Amoureux, G. Bodenhausen, and M. Pruski, *Mesoporous Silica Nanoparticles Loaded with Surfactant: Low Temperature Magic Angle Spinning C-13 and Si-29 NMR Enhanced by Dynamic Nuclear Polarization*, *J. Phys. Chem. C*, 117, 1375-1382 (2013). DOI: 10.1021/jp310109s
46. M.D. Lesoine, U. Bhattacharjee, Y. Guo, J. Vela, J.W. Petrich, and E.A. Smith, *Subdiffraction, Luminescence-Depletion Imaging of Isolated, Giant, CdSe/CdS Nanocrystal Quantum Dots*, *J. Phys. Chem. C*, 117, 3662-3667 (2013). DOI: 10.1021/jp312231k
47. K. Mao, G.J. Kennedy, S.M. Althaus, and M. Pruski, *Determination of the Average Aromatic Cluster Size of Fossil Fuels by Solid-State NMR at High Magnetic Field*, *Energy & Fuels*, 27, 760-763 (2013). DOI: 10.1021/ef301804p
48. J. Vela, *Molecular Chemistry to the Fore: New Insights into the Fascinating World of Photoactive Colloidal Semiconductor Nanocrystals*, *J. Phys. Chem. Lett.*, 4, 653-668 (2013). DOI: 10.1021/jz302100r

49. J. Wang, D.M. Ackerman, V.S.Y. Lin, M. Pruski, and J.W. Evans, *Controlling reactivity of nanoporous catalyst materials by tuning reaction product-pore interior interactions: Statistical mechanical modeling*, J. Chem. Phys., 138, 134705-134705 (2013). DOI: 10.1063/1.4798463
50. K.K. Tanabe, N.A. Siladke, E.M. Broderick, T. Kobayashi, J.F. Goldston, W.M. H., O.K. Farha, J.T. Hupp, M. Pruski, E.A. Mader, J.M. J.A., and S. Nguyen, *Stabilizing unstable species through single-site isolation: a catalytically active TaV trialkyl in a porous organic polymer*, Chem. Sci., in press (2013). DOI: 10.1039/C3SC22268C
51. K. Manna, W.C. Everett, G. Schoendorff, A. Ellern, T.L. Windus, and A.D. Sadow, *Highly Enantioselective Zirconium-Catalyzed Cyclization of Aminoalkenes*, J. Am. Chem. Soc., in press, (2013). DOI: 10.1021/ja4000189

## Rational Approaches to Design and Optimize Zeolite Catalysts

Jeffrey D. Rimer  
University of Houston, Department of Chemical and Biomolecular Engineering,  
4800 Calhoun Road, Houston, TX 77004  
e-mail: [jrimer@central.uh.edu](mailto:jrimer@central.uh.edu)

Optimizing zeolite catalysts for current and emerging applications requires rational design schemes capable of selectively tailoring zeolite properties, such as crystal size and habit, to improve catalyst activity and lifetime. To address this challenge, a facile synthesis technique was used to control zeolite crystallization. This method relies upon the use of zeolite growth modifiers (ZGMs), which are molecules with molecular recognition for binding to different crystal surfaces and mediating the anisotropic rate of crystallization.[1,2] A systematic analysis of commercially-available molecules revealed ZGMs with high efficacy and versatility for tuning the crystal morphology of several zeolite frameworks (notably MFI and LTL types). The judicious selection of modifiers resulted in substantial changes in crystal size and habit, yielding more than an order of magnitude reduction in the internal diffusion path length with a concomitant increase in the exterior porous surface area. A synergistic combination of techniques was employed to examine the ZGM mode of action, which included: Force spectroscopy to assess ZGM-crystal interactions, atomic force microscopy (AFM) to characterize the effects of ZGM on zeolite surface architecture (e.g. surface roughness), bulk crystal characterization studies to quantify ZGM efficacy, and molecular simulations to examine ZGM binding modes on individual crystal faces. AFM was also used to image surface growth *in situ*, which allows zeolite catalysts to be characterized under realistic synthesis conditions. In conjunction with scattering techniques capable of resolving the size and shape of precursor nanoparticles, the mechanism and kinetics of zeolite surface nucleation and growth were resolved. These studies spanned multiple length scales (macroscopic to molecular) to identify new platforms for zeolite crystal modification. Moreover, these experiments focused on the construction of kinetic phase diagrams to assess the impact of common synthesis parameters on zeolite polymorphism.[3] Collectively, these studies provide quantitative insight into the synergistic effects of ZGM and synthesis parameter selection on phase behavior and crystal properties towards the rational design and optimization of zeolite catalysts.

### References

1. A.I. Lupulescu, J.D. Rimer, *Angew. Chem. Int. Ed.* **51**, 3345 (2012)
2. A.I. Lupulescu, M. Kumar, J.D. Rimer, *J. Am. Chem. Soc.* (2013) in press. DOI: 10.1021/ja4015277
3. M. Maldonado, M.D. Oleksiak, S. Chinta, J.D. Rimer, *J. Am. Chem. Soc.* **135**, 2641 (2013)



## Influence of Multi-Valency, Electrostatics and Molecular Recognition on the Adsorption of Transition Metal Complexes on Metal Oxides: A Molecular Approach to Supported Catalyst Synthesis

Additional PIs: N/A  
 Postdoc: N/A  
 Students: Jason Binz, Megan Strayer  
 Collaborators: Tom Mallouk (Department of Chemistry, Pennsylvania State University)  
 Contacts: Department of Chemical Engineering, The Pennsylvania State University,  
 University Park, PA 16802-4400, rioux@enr.psu.edu

### Goal

Develop a fundamental molecular-level understanding of scalable catalyst synthesis methods, including electrostatic adsorption and covalent interactions between metal precursor and solvated amphoteric supports. A particular emphasis involves understanding how the initial interaction of the transition metal precursor influences catalyst stability (sinter resistance) during heat (calcination and reduction) treatments and ultimately during catalysis under any type of reaction conditions.

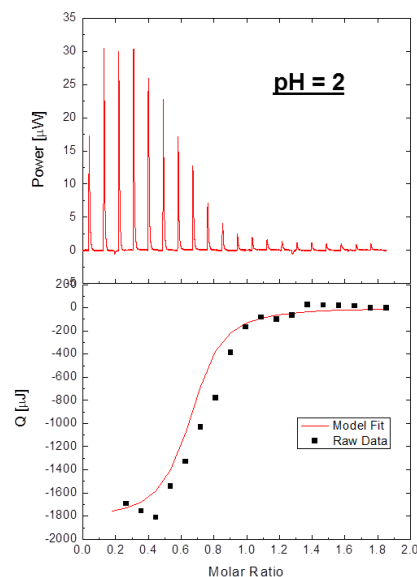
### DOE Interest

Catalyst synthesis is an often overlooked element in the development of a catalytic process. This is evidenced by the lack of fundamental understanding entailing the molecular details of catalyst synthesis. The development of active, selective and stable catalysts requires that we understand catalytic synthesis methods based on a fundamental scientific basis of how the initial interaction of catalyst precursor with an active or inert support ultimately controls the final catalyst structure. The ability to synthesize (*i.e.*, design) catalyst with specific structure which imparts specific function will ultimately impact science and technology of interest to the catalysis program at the Department of Energy. Effective catalyst design will enhance the activity and selectivity of next-generation petroleum-based and biomass feedstock upgrading catalyst.

### Recent Progress

The objectives of the proposal in the first year of the proposal were to (1) to quantify TMC adsorption on charged metal oxide interfaces under electrostatic conditions utilizing isothermal titration calorimetry (ITC) and (2) determine the origin of enhanced sinter-resistant of Rh nanoparticles adsorbed to two-dimensional perovskite materials. The second objective was not included in our original proposal but a recent collaboration with Professor Tom Mallouk (Department of Chemistry, Penn. State University). Both sets of materials have been extensively characterized by in-situ x-ray based synchrotron techniques but we are currently in the process of analyzing this data and it will be reported extensively in the next annual report and in peer-review publications.

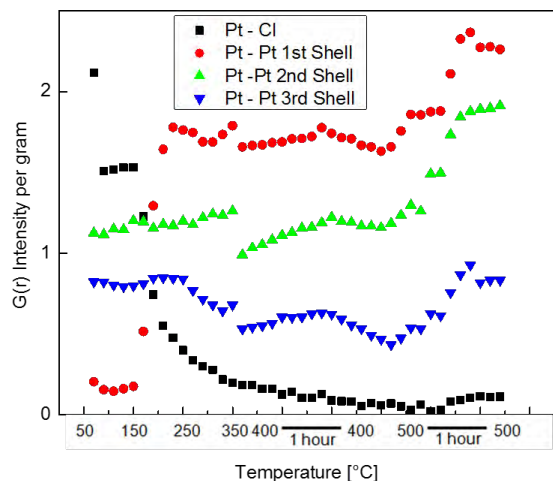
In the first five months of this project, we demonstrated that the thermodynamics of adsorption of solvated transition metal precursors on metal oxides and perovskites can be measured. In some cases, there was a correlation between the stability (propensity for particles to sinter) and the adsorption conditions. We initially focused on electrostatic-driven adsorption which demonstrated under favorable adsorption conditions, stability of the particle correlated with the measured heat of adsorption. A first demonstration of its kind, it



**Figure 1.** (top) Thermogram for the adsorption of CPA on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at bulk pH = 2. (bottom) Integrated heats for the adsorption of CPA onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.



proves that the initial adsorption conditions influence the structure of the final catalyst even after high temperature calcination and reduction. Figure 1 is an example of the adsorption of chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ , CPA) on alumina at  $\text{pH} = 2$ . Under these circumstances, the adsorption is favorable because the negatively charged  $\text{PtCl}_6^{2-}$  ion will adsorb to the positively-charged  $\text{AlOH}_2^+$  groups on the alumina surface. The heat of adsorption under this circumstance is  $-65.4 \text{ kJ mol}^{-1}$  and the equilibrium constant is  $\sim 10^6 \text{ M}^{-1}$ . Surprisingly, this  $\Delta H$  is 2.5 greater than the enthalpy of adsorption at  $\text{pH} = 4$ , the  $\text{pH}$  value that Regalbuto's simplified revised physical adsorption (sRPA) predicts the largest uptake of CPA, which is in agreement with his experimental results. Therefore, these results suggest that kinetic factors, most likely influenced by interfacial effects (Debye layer thickness, ionic strength). We will continue to explore the apparently contradictory results between our thermodynamic observations and those of Regalbuto. We do observe utilizing *in-situ* high-energy x-ray scattering that the solution  $\text{pH}$  during adsorption influences the

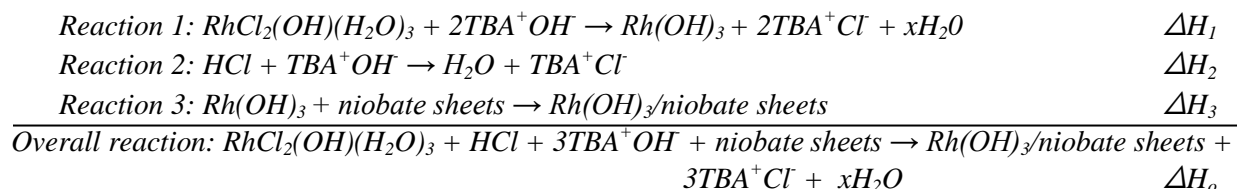


**Figure 2.** Coordination of Pt-Cl and Pt-Pt first and multiple shells for  $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$  prepared at  $\text{pH} = 2$ .

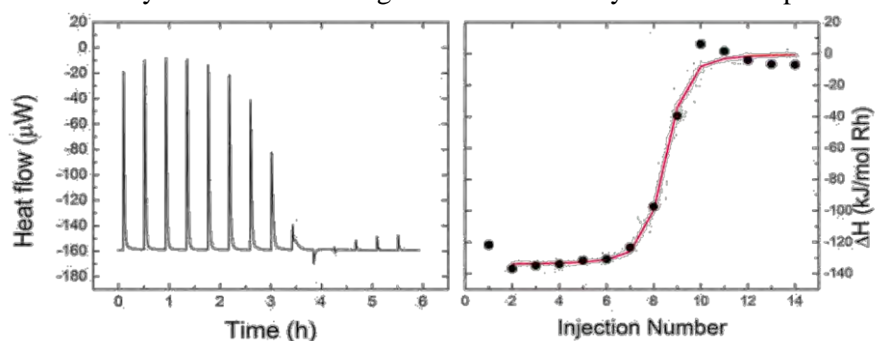
versus injection number is plotted. Integrating the area under each peak in the thermogram gives the differential heat production for each injection of rhodium solution.

In this experiment, numerous reactions are occurring simultaneously, each with their own associated enthalpy. According to Hess's law, the enthalpy of the overall reaction will be the sum of the enthalpies of the individual reactions. The first step of a deposition reaction is to add hydrated rhodium trichloride to water. **Scheme 1** depicts the individual reactions that occur during an experimental deposition reaction of rhodium nanoparticles to niobate sheets. The enthalpy associated with the bonding of the rhodium hydroxide nanoparticles to the oxide support (reaction 3) cannot be measured directly. Therefore, it must be determined by subtracting the enthalpies of the other individual reactions from the enthalpy of the overall reaction. Reaction 1 will determine the enthalpy of the complete hydrolysis of the rhodium solution, while reaction 2 will determine the enthalpy of the interaction of protons with the exfoliated sheets. Reaction 3 is an acid-base reaction which is known from the literature to be  $-57.3 \text{ kJ mol}^{-1}$ . We have confirmed this experimentally with a measured  $\Delta H$  of  $-58 \text{ kJ mol}^{-1}$ .

**Scheme 1.** The individual reactions occurring for a deposition reaction of rhodium hydroxide nanoparticles to niobate nanosheets. According to Hess's law,  $\Delta H_o = \Delta H_1 + \Delta H_2 + \Delta H_3$ .



The first system to be investigated is rhodium hydroxide nanoparticles onto calcium niobate supports



**Figure 3.** (A) Thermogram and (B) integrated heat data for the adsorption of  $\text{Rh}(\text{OH})_3$  onto  $\text{KCa}_2\text{Nb}_3\text{O}_{10}^-$ .

onto calcium niobate supports (**Figure 3**). The enthalpy of the reaction 3 is  $-35 \pm 9 \text{ kJ mol}^{-1}$ . This has been determined by measuring  $\Delta H_1 (= -27 \text{ kJ mol}^{-1})$ ,  $\Delta H_2 (= -58 \text{ kJ mol}^{-1})$  and  $\Delta H_0 (= -120 \text{ kJ mol}^{-1})$  in separate experiments. **Table 1** summarizes the results for  $\text{KCa}_2\text{Nb}_3\text{O}_{10}^-$  and two other perovskite supports ( $\text{KTiNbO}_5$  and  $\text{K}_4\text{Nb}_6\text{O}_{17}$ ).

**Table 1.** Summary of  $\Delta H_3$  and  $\Delta H_0$  values for the adsorption of three perovskite supports.

	$\text{KCa}_2\text{Nb}_3\text{O}_{10}^-$	$\text{KTiNbO}_5$	$\text{K}_4\text{Nb}_6\text{O}_{17}$
$\Delta H_3 (\text{kJ mol}^{-1})$	$-35 \pm 9$	$-26 \pm 6$	$-37 \pm 9$
$\Delta H_0 (\text{kJ mol}^{-1})$	$-120 \pm 7$	$-111 \pm 4$	$-122 \pm 8$

### Future Plans

*Adsorption of multivalent transition metal precursors on well-defined silica supports:* Utilize polyhedral oligomeric silsesquioxanes (POSS) and multivalent, labile precursors to characterize multi-valent effects during catalyst synthesis.

*Kinetics of transition metal precursor adsorption under electrostatic conditions:* Measure the rates of adsorption of charged, hydrated transition metal precursors to solvated amphoteric supports as a function of pH. We are currently developing a streaming potential based measurement to determine the rate at which transition metal precursors adsorb to alumina or silica as function of  $(\text{pH} - \text{PZC}_{\text{support}})$ . We will also measure the rate of adsorption of  $\text{RhCl}_2(\text{OH})(\text{H}_2\text{O})_3$  onto perovskite supports to determine if the kinetics of adsorption differ amongst supports that have the same adsorption thermodynamics.

*Correlation between M-O-M' bonds in metal-doped perovskites:* Our work over the last five months (in collaboration with Tom Mallouk, Chemistry, Penn. State University) has demonstrated that a series of perovskites containing various transition metals yield similar solution-phase thermodynamics for the adsorption of  $\text{RhCl}_2(\text{OH})(\text{H}_2\text{O})_3$ , but display very different behavior with regards to their sinter-resistant. This series of catalysts do not appear to display the same history effect observed with the  $\text{Pt}/\text{SiO}_2$  and  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts synthesized under electrostatic conditions. We will apply extended x-ray absorption and high-energy x-ray scattering with pair distribution function analysis to these materials to determine the connectivity between Rh and the various layered supports.

### Publications (September 2012 – current)

1. E. G. Moschetta, K. M. Gans, R. M. Rioux, "Characterization of sites of different thermodynamic affinities on the same metal center via isothermal titration calorimetry" *J. Catal.* **302** (2013) 1-9.
2. J. M. Binz, P. Erb, R. M. Rioux, Multi-sample Reactor for Low-Temperature X-Ray Absorption Measurements of Supported Heterogeneous Catalysts. Submitted to *J. Synchrotron Radiat.* (4/2013).
3. J. M. Binz and R. M. Rioux. Assessing hydrated metal ion adsorption on solvated amphoteric metal oxides with isothermal titration calorimetry. Submitted to *J. Am. Chem. Soc.* (3/2013; revised version submitted 4/2013).
4. J. M. Binz, N. H. Sturgis and R. M. Rioux. Combined isothermal titration calorimetry and in-situ high-energy x-ray scattering/pair distribution function measurements of catalyst stability: Correlations with pH dependent contacting conditions. Submitted to *Nature Mater.* (4/2013).

## Catalytic Pairs for the Activation of Biomass-derived Oxygenates

Students: William R. Gunther (Ph.D.)  
Helen Luo (Ph.D.)  
Linh Bui (B.S.)  
Contacts: Massachusetts Institute of Technology, 77 Massachusetts Ave 66-456,  
Cambridge, MA 02139; [yroman@mit.edu](mailto:yroman@mit.edu)

**Goal:**

The objective of this project is to understand the mechanistic aspects behind the cooperative activation of oxygenates by catalytic pairs in liquid-phase reactions. Specifically, we investigate how the reactivity of a solid Lewis acid can be modulated by pairing the active site with other catalytic sites at the molecular level, with the ultimate goal of enhancing activation of targeted functional groups. We are also interested in coupling materials or active sites to achieve “one-pot” domino reaction sequences.

**DOE Interest:**

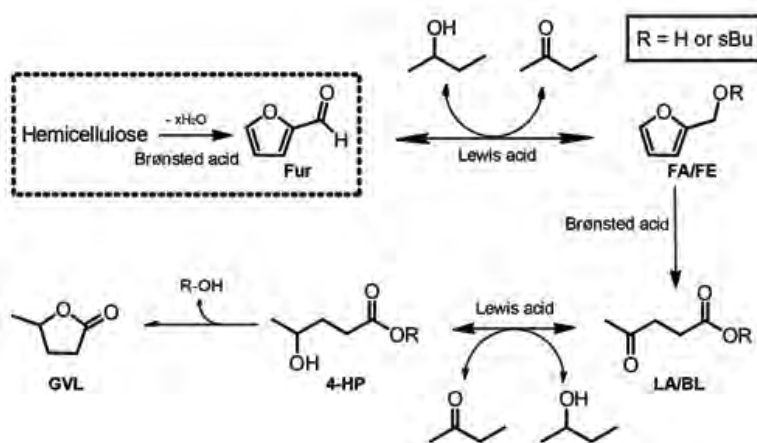
Development of more carbon-efficient and economically viable lignocellulosic biomass conversion technologies is critical for the sustainable production of liquid transportation fuels and chemicals. Development of water-tolerant catalysts or materials that can replace critical materials, such Pt, Pd, Re, and Ir, is a major technical challenge for the bio-refinery of the future. Catalyst design is already playing a central role in creating a new paradigm in the transformation of biomass-derived oxygenates using earth-abundant materials. Materials with engineered catalytic pairs have the potential to unravel new biomass conversion schemes, particularly in the critical areas of C-C bond forming, selective oxidation, metal-free hydrogenation, and hydrogen transfer reactions.

**Recent Progress:**

For the current performance period, one of the technical aims pursued involved coupling Lewis and Brønsted acid sites for the “one-pot” production of gamma-valerolactone (GVL) from furfural (Fur) via sequential transfer hydrogenation (TH) and ring-opening reactions.

Tin- or zirconium-containing zeolites (e.g., Sn- and Zr-Beta) are versatile water-tolerant Lewis acids. Pairing of Lewis and Brønsted acid sites enables multi-step reactions to be performed in a single reactor. In this aim, we demonstrate an integrated catalytic process for the efficient production of GVL from Fur via sequential TH and hydrolysis reactions triggered by zeolites with Brønsted and Lewis acid sites (see Scheme 1). Under optimal reaction conditions a GVL yield of 78

mol% was obtained starting from a 5 wt% Fur solution under using Zr-Beta as a Lewis acid catalyst and an aluminosilicate with MFI topology and nanosheet morphology (Al-MFI-ns) as a Brønsted acid catalyst. Effectively, this catalytic system offers an attractive streamlined strategy for the production of GVL from lignocellulosic biomass without the use of precious metals or high pressures of molecular H<sub>2</sub>.



Scheme 1. Domino reaction for the production of GVL from hemicellulose using a combination of Lewis and Brønsted acids. Fur (Furfural), BL (butyl levulinate), LA (levulinic acid), FA (furfural alcohol), FE (furfuryl ether), 4-HPs (4-hydroxypentanoates), GVL ( $\gamma$ -valerolactone).

### Future Plans:

*Stability tests:* Perform detailed stability tests to assess the impact of thermal conditions on framework atoms and structure crystallinity.

*Optimization studies:* Current mass balances are ~85-90% with oligomeric byproducts that have not been identified. Detailed characterization studies are required to identify the nature of the byproducts so that proper catalyst/process optimization can be performed.

*Kinetic studies:* Rigorous kinetic studies are currently underway to extract the appropriate parameters that describe the kinetics of the various reactions in the sequence. Specifically, a better understanding is needed regarding the interaction between the reactants, the active site, and the various hydrogen donors during the transfer hydrogenation steps.

### Publications:

Bui, L. Luo, H., Gunther, W. and Román-Leshkov, Y. "Domino reaction for the production of gamma-valerolactone from furfural catalyzed by zeolites with Brønsted and Lewis acid sites" (submitted)

## The chemistry of CO<sub>2</sub> on Rutile TiO<sub>2</sub>(110): The role of charge transfer and finite temperature dynamics.

Y. Yoon, X. Lin, Y.G. Wang, N.G. Petrik, Z. Li, Z. Wang, V.-A. Glezakou, B.D. Kay, I. Lyubinetsky, G.A. Kimmel, J. Li, Z. Dohnalek and **R. Rousseau**.

Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, Richland, WA 99352, USA

We provide an overview of ongoing theoretical and experimental studies of CO<sub>2</sub> reactivity and production on the prototypical reducible oxide surface rutile TiO<sub>2</sub>(110)-1x1. Adsorption, binding, and diffusion of CO<sub>2</sub> on reduced, were investigated experimentally using scanning tunneling microscopy, infrared reflection absorption spectroscopy, molecular beam scattering, and temperature programmed desorption and theoretically via *ab initio* molecular dynamics. Following the saturation of bridging oxygen vacancies (V<sub>O</sub>'s), additional CO<sub>2</sub> is found to adsorb on 5-coordinated Ti sites (Ti<sub>5c</sub>) with the initial small fraction stabilized by CO<sub>2</sub> adsorbed on V<sub>O</sub> sites. The Ti<sub>5c</sub>-bound CO<sub>2</sub> is highly mobile at 50 K at coverages of up to 1/2 monolayer (ML). Theoretical studies show that the CO<sub>2</sub> diffusion on Ti<sub>5c</sub> rows proceeds via a rotation-tumbling mechanism with extremely low barrier of 0.06 eV. At 2/3 ML, CO<sub>2</sub> diffusion is hindered and at 1 ML an ordered (2×2) overlayer with a zigzag arrangement of tilted CO<sub>2</sub> molecules develops along the Ti<sub>5c</sub> rows. Out of phase arrangement of the zigzag chains is observed across the rows. An additional 0.5 ML of CO<sub>2</sub> can be adsorbed on O<sub>b</sub> sites with a binding energy only slightly lower than that on Ti<sub>5c</sub> sites presumably due to quadrupole-quadrupole interactions with the Ti<sub>5c</sub>-bound CO<sub>2</sub> molecules. Both CO<sub>2</sub> reduction to CO at V<sub>O</sub> sites and CO + 1/2O<sub>2</sub> → CO<sub>2</sub> are found theoretically to be thermodynamically favorable processes but kinetically hindered due to the non-adiabatic nature of oxide/adsorbate charge transfer. Extensive theoretical studies of Au nanoparticles on supported on reduced TiO<sub>2</sub>(110) have found that the barriers for CO oxidation can be reduced but the reaction energetics and dynamics/morphology of the metal particles is strongly influenced by oxide/metal charge transfer.

## Two-Electron Redox Activity of Trigold Monocations and Related Complexes

Joseph P. Sadighi\*, Thomas J. Robilotto and Brandon K. Tate

Trigold monocations of the general formula  $[(\text{LAu})_3]^+$  (L = N-heterocyclic carbene, NHC) represent the simplest mixed-valent Au(0)/Au(I) complexes isolated to date [1]. Both experimental and theoretical data are consistent with full valence delocalization: the highest occupied molecular orbital is derived largely from gold 6s orbitals, and two-electron oxidation forms three Au(I) centers. When paired with a poorly coordinating anion, the  $[(\text{LAu})_3]^+$  cation is remarkably inert, stable to air and to protic solvents, and resistant to oxidation even by powerful oxygen atom transfer agents. In the presence of soft Lewis-basic anions including bromide or thiocyanate, however, the oxidation potential of the trigold cluster is lowered by up to 600 mV, and exposure to air leads to the formation of dioxygen adducts as indicated by mass spectroscopy. Investigations into the nature of these adducts are ongoing. Small gold clusters have been shown to act as exceptionally active catalysts for certain transformations of organic small molecules [2]. The goal of this inquiry is the development of tunable, well-defined catalysts for aerobic oxidation catalysis.

### References

1. T. J. Robilotto, J. Bacsa, T. G. Gray, J. P. Sadighi, *Angew. Chem. Int. Ed.* **2012**, *51*, 12077–12080.
2. J. Oliver-Meseguer, J. R. Cabrero-Antonino, I. Domínguez, A. Leyva-Pérez, A. Corma, *Science* **2012**, *338*, 1452–1455.

## Surface Chemistry of Polyols on Metals and Metal Oxides

Carsten Sievers,\* John R. Copeland, Guo Shiou Foo

Georgia Institute of Technology – School of Chemical & Biomolecular Engineering

Email: carsten.sievers@chbe.gatech.edu - Phone: 404-385-7685

### Introduction

Aqueous phase processes are expected to play a critical role in the production of renewable chemicals and fuels from biomass. Facile separation makes heterogeneous catalysts an attractive option for high efficiency in these processes. Therefore, it is not surprising that numerous recent publications described heterogeneously catalyzed processes in water including aqueous phase reforming, hydrogenolysis of polyols, dehydration of sugars, and aldol condensation.<sup>1,2</sup> However, little is known about the surface chemistry involved in catalytic conversion of biomass. Historically, a detailed understanding of relevant surface reactions has been a prerequisite for the development of highly active catalysts. Obtaining such insight into the surface chemistry of biomass-derived oxygenates is challenging because the low vapour pressure of most of these substances makes it very difficult to dose them into vacuum cells, which are used in traditional surface science studies. Consequently, new approaches have to be developed. In the present study, IR and NMR spectroscopy are used to understand the surface chemistry of polyols on oxide supports including Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub>. In addition, aqueous phase reforming of glycerol over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is studied under flow conditions using in-situ Attenuated Total Reflection (ATR) IR spectroscopy.

### Experimental

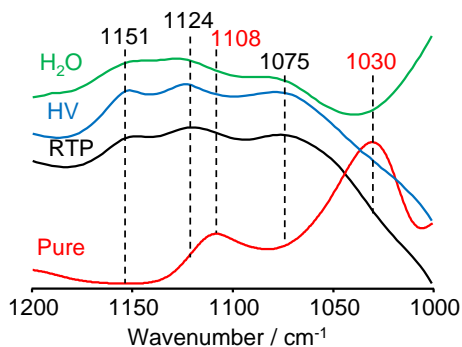
$\gamma$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> (anatase) were purchased from Sigma-Aldrich. ZrO<sub>2</sub> was obtained from Alfa Aesar. The formation of surface species from ethylene glycol, 1,2-propanediol, 1,3-propanediol, and glycerol on metal oxides was studied by impregnation of the oxides with aqueous solutions of the oxygenates. Free water was removed by storing the wet sample in a desiccator jar. Typically an oxygenate loading of 1 wt% was obtained. For IR studies the impregnated oxides were pressed into self-supported wafers and mounted into the high vacuum transmission IR cell. The first spectra were recorded before activation when the wafer still contained significant amounts of physisorbed water. Subsequently, the remaining water was removed at room temperature and 10<sup>-6</sup> mbar. Lastly, the sample was exposed to 1.00 mbar of H<sub>2</sub>O vapor. <sup>2</sup>H solid echo pulse NMR experiments were performed on a Bruker DSX 300 spectrometer. The samples were prepared using deuterium-enriched oxygenates and packed into a custom-made glass sample tubes that were loosely sealed with Teflon tape. DFT calculations on the surface chemistry of glycerol were performed in VASP using the PBE-GGA exchange functional and the PAW method.

In-situ IR spectroscopic studies on aqueous phase reforming of glycerol over a Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were carried out using an ATR IR flow-through cell. All experiments were performed at room temperature. Prior to the start of an experiment, five layers of catalyst were deposited on the internal reflection element (IRE) of the cell. For each layer, a dilute slurry of the catalyst in water was applied followed by evaporation of the water. The IRE was then placed in the cell and any loose catalyst particles were removed by flushing the cell with degassed water for at least 4 h. Prior to glycerol exposure, one of four different pretreatments was used to clean the Pt surfaces: flowing water saturated with helium, oxygen, or hydrogen gas. The fourth treatment consisted of

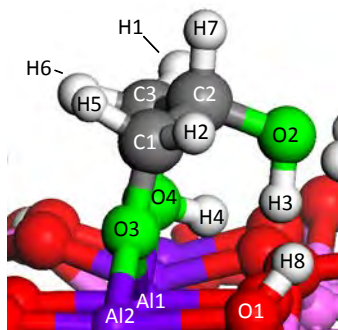
multiple cycles of dissolved oxygen, hydrogen, and helium flows. After the cleaning procedure a background was collected. Then, an aqueous solution of glycerol ( $0.1 \text{ mol L}^{-1}$ ) was introduced to start the reaction.

## Results and Discussion

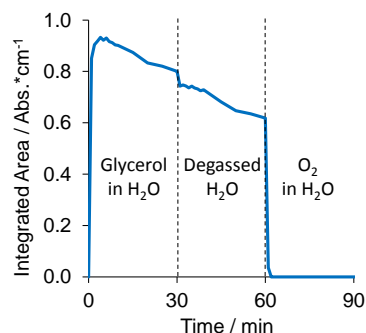
Aqueous phase adsorption isotherms of ethylene glycol, 1,2-propanediol, 1,3-propanediol, and glycerol on  $\gamma\text{-Al}_2\text{O}_3$  indicated that adsorption occurred, but to a lesser extent than on hydrophobic catalysts, such as zeolite ZSM-5.<sup>3</sup> It is concluded that the oxygenates compete with water for adsorption sites. Blue shifts of the C-O stretching bands in the IR spectrum indicated that all of the polyols can strongly bind to the surface of  $\gamma\text{-Al}_2\text{O}_3$ , for example, by formation of alkoxy bonds. In case of glycerol and 1,3-propanediol, the formation of alkoxy bonds is observed even when significant amounts of physisorbed water remain on the surface (Figure 1). In contrast, these species only formed from ethylene glycol and 1,2-propanediol when residual water was removed by evacuation and they were removed when water was reintroduced into the cell. Additional evidence for the formation of strongly bound surface species was obtained from analyzing the line widths in  $^2\text{H}$  solid echo pulse NMR experiments, which indicated that blue shift in the IR spectra were correlated to strong reduction in mobility of the polyol molecules. Oxygenate molecules interact with the surface hydroxyl groups of  $\gamma\text{-Al}_2\text{O}_3$ , as well as the coordinatively unsaturated Al atoms on the  $\gamma\text{-Al}_2\text{O}_3$  surface. DFT calculations were performed to identify the most stable surface species formed from glycerol (Figure 2): Both primary alcohol groups strongly interact with a coordinatively unsaturated surface sites on  $\text{Al}_2\text{O}_3$  forming a multidentate alkoxy, whereas the secondary hydroxyl group forms a hydrogen bond with the surface.<sup>3</sup> Only molecules with sufficient spatial separation between functional groups can form such a surface species. It was also shown that multidentate surface species effectively protect the surface of  $\gamma\text{-Al}_2\text{O}_3$  against hydrolytic attack in hot liquid water.<sup>4,5</sup> Glycerol also formed multidentate alkoxydes on  $\text{TiO}_2$ , which appear to be very similar to the surface species on  $\gamma\text{-Al}_2\text{O}_3$ .<sup>6</sup> However, these species were only formed after removal of physisorbed water. At least eight signals were observed in the  $\nu_{\text{CO}}$  region of the IR spectrum of glycerol on  $\text{ZrO}_2$  after evacuation. This implies the existence of a variety of surface sites that can bind glycerol in different ways.



**Fig. 1.** FTIR spectra of pure glycerol and glycerol on  $\gamma\text{-Al}_2\text{O}_3$  at room temperature and pressure (RTP), in high vacuum (HV) and after reintroduction of water ( $\text{H}_2\text{O}$ )



**Fig. 2.** Most stable surface species formed from glycerol on  $\gamma\text{-Al}_2\text{O}_3$  based on DFT calculations.



**Fig. 3.** Integrated peak area for bridging CO on  $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$  (peak at  $1780 \pm 5 \text{ cm}^{-1}$ ).



Surface reactions of glycerol on Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were elucidated by in-situ ATR IR spectroscopy under flow conditions.<sup>7</sup> To prepare well-defined catalysts layers in a reproducible state several cleaning procedures were applied. When Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was only exposed to degassed water CO was formed from impurities on linear (CO<sub>L</sub>) and bridging (CO<sub>B</sub>) Pt sites. Pretreatment with dissolved oxygen removed carbonaceous impurities from the Pt surface and made more Pt sites available for glycerol conversion. However, residual surface oxygen oxidized the first CO formed from glycerol to CO<sub>2</sub>, which was readily desorbed. Therefore, a delay in CO accumulation was observed. Pretreatment with dissolved hydrogen resulted in blockage of some surface sites by strongly adsorbed hydrogen. When multiple cycles of all of the three dissolved gas flows were used as a pretreatment, the fastest rates of CO formation and highest CO coverages were observed. This indicated that this pretreatment is the best of those studied for creating a clean and active Pt surface for in-situ aqueous phase ATR IR studies. After application of multiple cleaning cycles, exposure to glycerol led to saturation of the sites for CO<sub>L</sub> within 30 min. The concentration of CO<sub>L</sub> on the surface did not change when the cell was purged with degassed water for 30 min. In contrast, the concentration of CO<sub>B</sub> reached a maximum after 4 min of exposure to glycerol and decreased in the presence of the aqueous glycerol solution and degassed water (Figure 3). Since bridging sites bind CO more strongly than linear sites and since traces of oxygen would convert both surface CO species, we suggest that CO<sub>B</sub> is converted by the water-gas shift reaction.<sup>7</sup>

## Conclusions

In aqueous phase, polyols and water compete for adsorption sites on polar metal oxides. Under certain conditions, polyols chemisorb on metal oxides by forming alkoxy bonds. Multidentate surface species are particularly stable. Glycerol in aqueous solution is readily activated over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at room temperature forming surface bound CO. CO on bridging sites can even be converted by water-gas-shift at room temperature.

## Acknowledgements

The authors would like to thank Xuerong Shi and David Sholl for supporting DFT calculations.

## References

- (1) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411-2502.
- (2) Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* **2006**, *106*, 4044-4098.
- (3) Copeland, J. R.; Shi, X.-R.; Sholl, D. S.; Sievers, C. *Langmuir* **2013**, *29*, 581-593.
- (4) Jongorius, A. L.; Copeland, J. R.; Foo, G. S.; Hofmann, J. P.; Bruijninx, P. C. A.; Sievers, C.; Weckhuysen, B. M. *ACS Catalysis* **2013**, *3*, 464-473.
- (5) Ravenelle, R. M.; Copeland, J. R.; Van Pelt, A. H.; Crittenden, J. C.; Sievers, C. *Top. Catal.* **2012**, *55*, 162-174.
- (6) Copeland, J. R.; Santillan, I.; McNew, S. E.; Sievers, C. *J. Phys. Chem. C*, in preparation.
- (7) Copeland, J. R.; Foo, G. S.; Harrison, L. A.; Sievers, C. *Catal. Today* **2013**, *205*, 49-59.

**Fundamental Studies on Well-Defined Oxide Catalysts: From UHV to *in-situ* conditions**

Lead PI: José A. Rodriguez  
Additional PIs: Ping Liu, Sanjaya D. Senanayake  
Postdocs: Kumudu Mudiyansele, Ashleigh E. Baber  
Contact: Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973;  
[djs@bnl.gov](mailto:djs@bnl.gov)

The traditional approach to the optimization of metal/oxide catalysts has focused on the properties of the metal and the selection of the proper oxide for its dispersion. Typically, there is a low concentration of chemically active sites in the oxide, and these may be blocked by the anchoring of the metal particles. By using a second oxide as a support (host), one can create a multifunctional configuration in which metal nanoparticles and chemically active oxide nanoparticles are exposed to the reactants [1]. Thus, the reactants can interact with defect sites of the oxide nanoparticles, metal sites, and metal-oxide interfaces. Deposition of an oxide on sub-monolayer amounts over a second oxide host can create nanostructures which in turn may enhance the overall catalytic properties of the entire system. We have synthesized Nanowires of RuO<sub>x</sub> on TiO<sub>2</sub>(110) by adsorption and decomposition of Ru<sub>3</sub>(CO)<sub>12</sub> with subsequent exposure to O<sub>2</sub> at elevated temperatures, and found a dramatic increase in their catalytic activity with respect to bulk ruthenium oxide [2]. Depositing ceria on TiO<sub>2</sub>(110) leads to the formation of ceria dimers [1]. We uncovered an unexpected electronic influence, coined as 'electronic metal-support interaction' (EMSI), of these ceria dimers on the reactivity of small co-deposited platinum particles for reactions involving water cleavage [3]. The importance of metal-oxide interfaces has long been recognized, but the molecular determination of their properties and role is only now emerging. Atoms with properties ranging from metallic to ionic are available at the metal-oxide interface and create unique reaction sites. We have shown that the activation of an efficient associative mechanistic pathway for the water-gas shift reaction by an oxide-metal interface leads to an increase in the catalytic activity of ceria nanoparticles deposited on Cu(111) or Au(111) by more than an order of magnitude. *In situ* experiments demonstrated that a carboxy species formed at the interface is the critical intermediate in the reaction [4]. Our studies point to a new paradigm in the design of catalysts: The optimization of the oxide phase and the metal-oxide interface in a catalyst can improve substantially its activity and selectivity.

- [1] "Fundamental Studies of Well-Defined Surfaces of Mixed-Metal Oxides: Special Properties of MO<sub>x</sub>/TiO<sub>2</sub>(110) {M = V, Ru, Ce, or W}" D Stacchiola, SD Senanayake, P Liu, JA Rodriguez [Chem. Rev \(doi: 10.1021/cr300316v\)](https://doi.org/10.1021/cr300316v) (2013)
- [2] "Determining the Behavior of RuO<sub>x</sub> Nanoparticles in Mixed-Metal Oxides: Structural and Catalytic Properties of RuO<sub>2</sub>/TiO<sub>2</sub>(110) Surfaces" F Yang, S Kundu, AB Vidal, J Graciani, PJ Ramirez, SD Senanayake, D Stacchiola, J Evans, P Liu, JF Sanz, JA Rodriguez [Angew. Chem. Int. Ed. 50, 1-6](https://doi.org/10.1002/anie.201210077) (2011)
- [3] "A New type of Strong Metal-Support Interaction and the Production of H<sub>2</sub> through the Transformation of Water on Pt/CeO<sub>2</sub>(111) and Pt/CeO<sub>x</sub>/TiO<sub>2</sub>(110) Catalysts" A Bruix, JA Rodriguez, PJ Ramirez, SD Senanayake, J Evans, JB Park, DJ Stacchiola, P Liu, J Hrbek, F Illas [J. Am. Chem. Soc. 134, 8968-8974](https://doi.org/10.1021/cr300316v) (2012)
- [4] "Importance of the Metal-Oxide Interface in Catalysis: In-situ Studies by Ambient-Pressure XPS of the Water-Gas Shift Reaction" K Mudiyansele, SD Senanayake, L Feria, S Kundu, AE Baber, J Graciani, AB Vidal, S Agnoli, J Evans, R Chang, S Axnanda, Z Liu, JF Sanz, P Liu, JA Rodriguez, DJ Stacchiola [Angew. Chem. Int. Ed. \(doi: 10.1002/anie.201210077\)](https://doi.org/10.1002/anie.201210077) (2013)

## In-situ Studies and Catalysis of Transition Metal Oxides

Postdoc: Junjun Shan

Students: Shiran Zhang

Collaborator: Anatoly I Frenkel

Contacts: University of Notre Dame, Department of Chemistry and Biochemistry, Notre Dame, IN 46556, [ftao@nd.edu](mailto:ftao@nd.edu)

### Goal

Explore surface chemistry and structure of transition metal oxide catalysts under reaction conditions and during catalysis, build an intrinsic correlation of the surface chemistry and structure of these oxides to their catalytic performances of important reactions for chemical transformation and energy conversion, and develop catalysts based on the correlation to be built.

### DOE Interest

Catalysis on transition metal oxide catalysts is equivalently important in contrast to that on metals. Fundamental understanding of catalysis on transition metal oxide-based catalysts has been lagged behind that on metals though it is critical in deeply understanding catalysis on oxide catalysts and development of oxide catalysts with high activity and selectivity. Exploration of surface chemistry and structure of oxide catalysts under reaction conditions and during catalysis has remained challenging.

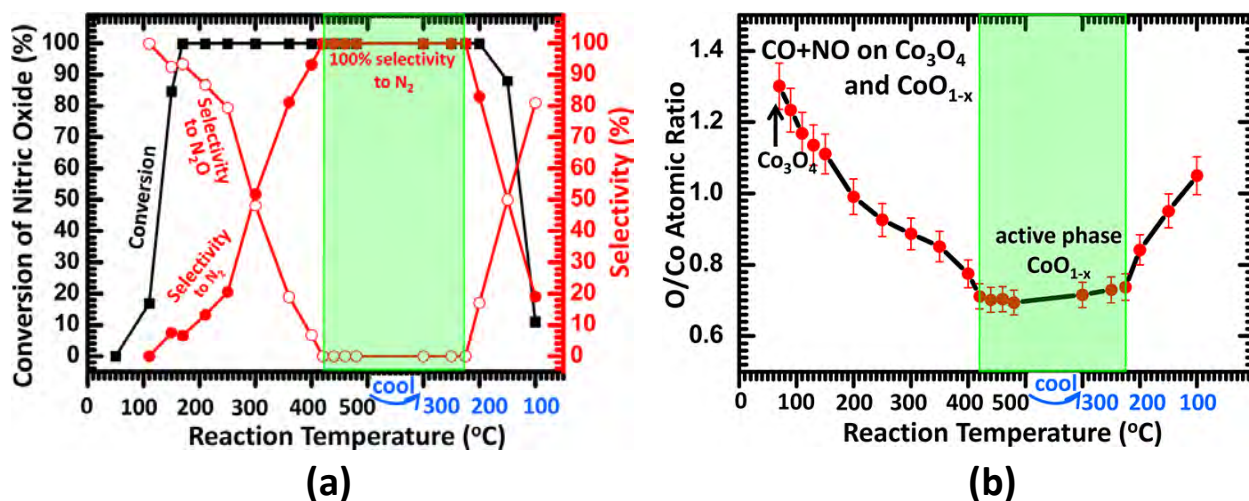
### Recent Progress

*Instrumentation of in-situ studies of surface chemistry and structure:* Ambient pressure high temperature scanning tunneling microscope (APHT-STM) and lab-based ambient pressure X-ray photoelectron spectrometer (AP-XPS) were built. Their functions were tested.

*Fundamental studies of surface chemistry and structure:*  $\text{Co}_3\text{O}_4$  and  $\alpha\text{-MnO}_2$  nanorods were synthesized. Their surface chemistries in terms of oxidation states and surface compositions and defects under different reaction condition were studied. Flexibility of surface structure under reaction conditions was suggested. Phase transformation of bulk of these oxide nanorods under reaction conditions was revealed in in-situ studies using environmental TEM (E-TEM).

*Restructuring during catalysis and correlation to catalytic performance:*  $\text{Co}_3\text{O}_4$  was restructured to nonstoichiometric  $\text{CoO}_{1-x}$  during catalysis of NO reduction with CO. A correlation between surface chemistry tracked with AP-XPS (Figure 1a) and structure examined with E-TEM and the corresponding catalytic performance (Figure 1b) showed that  $\text{CoO}_{1-x}$  is active for NO reduction with 100% selectivity for production of  $\text{N}_2$ . In addition, the restructured  $\text{CoO}_{1-x}$  is also active for other reactions.

*Tuning catalytic performance through introduction of guest metal atoms on surface of oxide:* Pt atoms were deposited on surface of cobalt oxide nanorods. Structural evolution of  $\text{Co}_3\text{O}_4$  with deposited Pt atoms during catalysis was studied with AP-XPS and EXAFS. New catalytic phases restructured from cobalt oxides deposited with Pt atoms were identified through the correlation between catalytic performance and the corresponding surface chemistry.



**Figure 1.** Catalytic performance (selectivity for production of N<sub>2</sub> and activity) (a) and corresponding surface chemistry (b) during catalysis of reducing NO with CO.

### Future Plans

*Fundamental studies of transition metal oxides:* study surface chemistry of MoO<sub>3</sub>, WO<sub>3</sub>, and other oxides with well controlled shapes under reaction conditions and during catalysis to provide insights for understanding catalysis such as selective oxidation of alkanes on them.

*In-situ studies of surfaces of active phases at atom scale:* prepare active phases and visualize surfaces of active phases under reaction conditions and during catalysis with atomic resolution.

*Fundamental studies of active sites for C-H oxidation:* perform in-situ studies of oxide catalysts (oxide nanoparticles and oxide species in microporous materials) under reaction conditions and during catalysis to gain fundamental insights on C-H oxidation catalysis.

### Publications (2012-2013)

1. Zhang, S.; Shan, J.; Zhu, Y.; Nguyen, L.; Huang, W.; Yoshida, H.; Takeda, S.; **Tao, F.\*** "A Correlation between Catalytic Performances of Pure Cobalt Oxide and the Corresponding Surface Chemistries during Catalysis", **Nano Letters** **2013**, *accepted*, DOI: 10.1021/nl4015292.
2. Zhang, S.; Shan, J.; Zhu, Y.; Frenkel, A.; Patlolla, A.; Huang, W.; Yoon, S.; Wang, L.; Yoshida, H.; Takeda, S.; **Tao, F.\*** "WGS Catalysis and In-situ Studies of CoO<sub>1-x</sub>, PtCo<sub>n</sub>/Co<sub>3</sub>O<sub>4</sub>, and Pt<sub>m</sub>Co<sub>m</sub>/CoO<sub>1-x</sub> nanorod catalysts", **J. Am. Chem. Soc.** **2013**, *135*, 8283-8293.
3. Shan, J. J.; Zhu, Y.; Zhang, S.; Zhu, T.; Rouvimov, S.; **Tao, F.\*** "Catalytic Performance and In-situ Surface Chemistry of Pure  $\alpha$ -MnO<sub>2</sub> Nanorods in Selective Reduction of NO and N<sub>2</sub>O with CO", **J. Phys. Chem. C.** **2013**, *117*, 8329-8335.
4. Wang, L.; Zhang, S.; Zhu, Y.; Patlolla, A.; Shan, J.; Yoshida, H.; Takeda, S.; Frenkel, A. I.; **Tao, F.\*** "Catalysis and In-situ Studies of RhCo<sub>n</sub> Nanoclusters Supported on Co<sub>3</sub>O<sub>4</sub> Nanorods", **ACS Catalysis.** **2013**, *3*, 1011-1019.
5. **Tao, F.\***, Nguyen, L.; Zhang, S. "Design of A New Reactor-Like High Temperature Near Ambient Pressure Scanning Tunneling Microscope for Catalysis Studies", **Review of Scientific Instruments.** **2013**, *84*, 034101.
6. **Tao, F.\*** et al. "In-situ Studies of Nanocatalysis", **Acc. Chem. Res.** **2013**, *ASAP*. DOI: 10.1021/ar300245g

7. Ye, Y.; Wang, L.; Zhang, S.; Zhu, Y.; Shan, J.; **Tao, F.\*** “Role of copper in catalytic performance of Fe-Cu-Al-O catalyst for water gas shift reaction” **Chem. Comm.** **2013**, 49, 4385-4387.
8. Nguyen, L.; Cheng, F.; Zhang, S.; **Tao, F.\*** “Visualization of Surfaces in Reactive Environments Using Ambient Pressure Scanning Tunneling Microscopy and Insights on Restructurings of Surfaces of Model Metal Catalysts under Reaction Conditions at Near Ambient Pressure”, **J. Phys. Chem. C** **2013**, 117, 971-977.
9. Zhu, Y.; Zhang, S.; Ye, Y.; Zhang, X.; Wang, L.; Fang, C.; **Tao, F.\***“Catalytic Conversion of Carbon Dioxide to Methane on Cobalt-ruthenium Bimetallic Nanocatalysts and Correlation between Surface Chemistry of Catalysts under Reaction Conditions and Catalytic Performances”, **ACS Catalysis**, **2012**, 2, 2403-2408.
10. Wen, C.; Zhu, Y.; Ye, Y.; Cheng, F.; Wang, P.; **Tao, F.\***“Water-Gas-Shift Reaction on Metal Nanoclusters Encapsulated in Mesoporous Ceria Studied with Ambient Pressure X-ray Photoelec-tron Spectroscopy”, **ACS Nano** **2012**, 6, 9305-9313.
11. **Tao, F.\***; Zhang, S.; Nguyen, L.; Zhang, X. “Action of Bimetallic Nanocatalysts under Reaction Conditions and during Catalysis: Evolution of Chemistry from High Vacuum Conditions to Reaction Conditions”, **Chem. Soc. Rev.** **2012**, 41, 7980-7993 .
12. Pei, Y.; Zhou, G.; Nguyen, L.; Zong, B.; Qiao\*, M.; **Tao, F.\***; Synthesis and catalysis of chemically reduced metal–metalloid amorphous alloys, **Chem. Soc. Rev.** **2012**, 41, 8140-8162.

**DE-SC0001004 Dionisios (Dion) G. Vlachos**  
**Rational Design of Innovative Catalytic Technologies for Biomass Derivative Utilization**

Additional PIs: Mark E. Davis, Douglas J. Doren, Anatoly Frenkel, Raul F. Lobo, Vladimiro Nikolakis, Yuri Roman-Leshkov, Stanley I. Sandler, Michael Tsapatsis  
Postdocs: Samir Mushrif, Raj Gounder  
Students: Vinit Choudhary, Christopher Ho  
Collaborators: Nebojsa Marinkovic (UD), Andrzej Anderko (OLI Systems Inc.)  
Contacts: Catalysis Center for Energy Innovation, University of Delaware, 150 Academy St., Newark, DE 19716, USA, [vlachos@udel.edu](mailto:vlachos@udel.edu)

**Goal**

This work is part of the Catalysis Center for Energy Innovation, an Energy Frontier Research Center. Our overarching goal in CCEI is to develop the enabling science leading to improved or radically new heterogeneous catalytic technologies for viable and economic operation of biorefineries from various lignocellulosic biomass feedstocks. For this presentation, our goal is to understand the mechanisms of isomerization of glucose to fructose and dehydration of fructose to hydroxymethylfurfural and to compare homogeneous and heterogeneous catalysts for this chemistry in order to close the gap between them.

**DOE Interest**

CCEI meets multiple research directions of DOE interest, namely: Our work focuses on one of the most challenging renewable routes and advances several crosscutting research directions: catalysis, nanomaterials, separations, characterization and measurements, and theory, simulation, and modeling. It employs catalysis as an enabling technology and targets both grand challenges of the Basic Research Needs: Catalysis for Energy, namely: (1) understanding reaction mechanisms of converting biomass derivatives into fuels and chemicals in complex, multiphase, multiscale media and (2) the design and controlled synthesis of catalytic surfaces that are suited for the selective thermochemical conversion of biomass-related molecules into fuels and chemicals.

**Recent Progress**

*Tuning Sugars Chemistry via Materials and Solvent Selection:* Water-tolerant solid Lewis acids, such as Sn-Beta zeolite, have emerged as catalysts that mediate glucose isomerization to fructose in water. We have reported that different synthesis and treatment protocols used to prepare Sn-Beta zeolites indeed lead to the formation of different Sn structures, as identified using solid-state  $^{119}\text{Sn}$  magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. We used isotopic labeling studies to show that extra framework  $\text{SnO}_2$  particles isomerized glucose to fructose, but via a base-catalyzed proton transfer mechanism, in both water and methanol solvents (Figure 1). We also discovered that framework Sn sites behaved as Lewis acids in methanol solvent (Figure 1), but catalyze glucose epimerization to mannose via an intramolecular carbon shift (the Bilik reaction). The finding that reactivity differences prevail among Sn sites of different structure provides opportunities to tune the synthesis of Sn-based catalysts and the choice of solvent to influence reaction selectivity in biomass and sugar conversion.



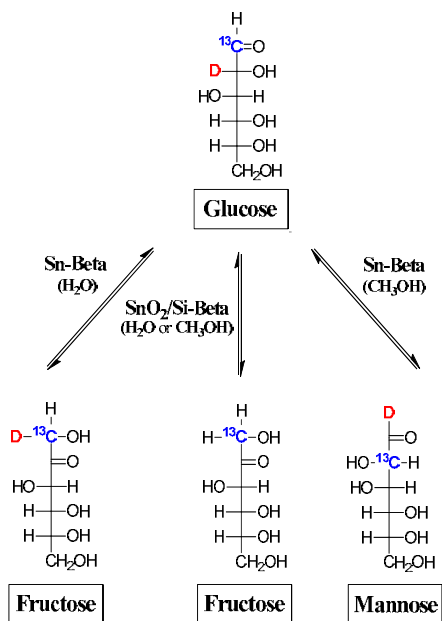


Figure 1. Isotopic labeling experiments revealed that Lewis acid Sn sites in the framework of Sn-BEA catalyze glucose isomerization to fructose in  $\text{H}_2\text{O}$  or glucose epimerization to mannose in methanol. Base sites in non-framework  $\text{SnO}_2$  particles ( $\text{SnO}_2/\text{Si-Beta}$ ) catalyze glucose isomerization to fructose in both solvents.

dehydration and rehydration reactions and side reactions. EXAFS and Car-Parrinello molecular dynamics simulations reveal that glucose molecules displace water molecules from the first coordination sphere of Cr to enable ring opening and isomerization. Isotopic labeling experiments and NMR spectroscopy reveal that the isomerization mechanism entails intrahydride transfer, similar to the Sn-beta zeolite. This establishes for the first time an analogue between heterogeneous and homogeneous isomerization (Lewis acid/Brønsted-base) catalysts.

### Future Plans

**Isomerization Chemistry:** Develop descriptors so we can predict suitable homogeneous Lewis acid/Brønsted-base catalysts and develop design principles for heterogeneous isomerization catalysts.

**Dehydration Chemistry:** Develop reaction mechanisms for quantitative description of data using homogeneous and heterogeneous catalysts.

### Publications (Select Ones in 2010-2013)

1. R. Gounder and M. E. Davis, "Beyond Shape Selective Catalysis with Zeolites: Hydrophobic Void Spaces in Zeolites Enable Catalysis in Liquid Water," *AIChE J.* (2013) In press.
2. V. Choudhary, S. H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N. S. Marinkovic, A. I. Frenkel, S. I. Sandler, and D. G. Vlachos, "Insights into the Interplay of Lewis and Brønsted Acid Catalysts in

**Bifunctional Lewis-Brønsted Homogeneous Acid Catalysts:** We have combined kinetic measurements with a metal salt speciation model to understand bifunctional catalysts and revealed that the hydrolyzed metal ions, such as  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  and  $[\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ , are the most active species in the metal salt catalyzed aldose-ketose isomerization. As a result, the rate of sugar isomerization scales linearly with the concentration of the active species (Figure 2). Additionally, it has been shown that there is a complex synergy between the two catalysts. Brønsted acidity retards aldose-to-ketose isomerization by shifting the thermodynamic equilibrium and thereby decreasing the concentration of the active hydrolyzed metal ions. In contrast, Lewis acidity acidifies the solution resulting in

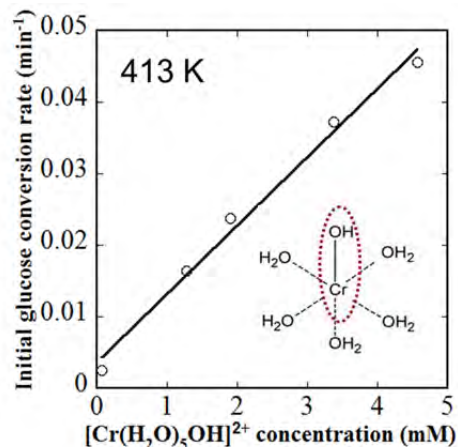


Figure 2. Initial isomerization rate of glucose scales linearly with the concentration of the active species (inset).

- Glucose and Fructose Conversion to 5-(Hydroxymethyl)furfural and Levulinic Acid in Aqueous Media," *J. Am. Chem. Soc.* **135**(10) (2013) 3997-4006.
3. V. Choudhary, S. Caratzoulas, and D. G. Vlachos, "Insights into the Isomerization of Xylose to Xylulose and Lyxose by a Lewis Acid Catalyst," *Carbohydr. Res.* **368** (2013) 89-95.
  4. C. M. Lew, N. Rajabbeigi, and M. Tsapatsis, "One-Pot Synthesis of 5-(Ethoxymethyl)furfural from Glucose using Sn-BEA and Amberlyst Catalysts," *Ind. Eng. Chem. Res.* **51**(14) (2012) 5364-5366.
  5. C. M. Lew, N. Rajabbeigi, and M. Tsapatsis, "Tin-containing zeolite for the isomerization of cellulosic sugars," *Micr. Meso. Mat.* **153** (2012) 55-58.
  6. J. S. Kruger, V. Nikolakis, and D. G. Vlachos, "Carbohydrate dehydration using porous catalysts," *Current Opinion Chem. Eng.* **1**(3) (2012) 312-320.
  7. N. Guo, S. Caratzoulas, D. J. Doren, S. I. Sandler, and D. G. Vlachos, "A Perspective on the Modeling of Biomass Processing," *Energy Environ. Sci.* **5**(5) (2012) 6703-6716.
  8. V. Choudhary, S. I. Sandler, and D. G. Vlachos, "Conversion of Xylose to Furfural using Lewis and Brønsted Acid Catalysts in Aqueous Media," *ACS Catal.* **2**(9) (2012) 2022-2028.
  9. V. Choudhary, R. Burnett, D. G. Vlachos, and S. I. Sandler, "Dehydration of Glucose to 5-(Hydroxymethyl)furfural and Anhydroglucose: Thermodynamic Insights," *J. Phys. Chem. C* **116**(8) (2012) 5116-5120.
  10. R. Bermejo-Deval, R. Gounder, and M. E. Davis, "Framework and Extraframework Tin Sites in Zeolite Beta React Glucose Differently," *ACS Catal.* **2**(12) (2012) 2705-2713.
  11. R. Bermejo-Deval, R. S. Assary, E. Nikolla, M. Moliner, Y. Roman-Leshkov, S. J. Hwang, A. Palsdottir, D. Silverman, R. F. Lobo, L. A. Curtiss, and M. E. Davis, "Metalloenzyme-like Catalyzed Isomerizations of Sugars by Lewis Acid Zeolites," *Proc. Nat. Acad. Sci.* **109**(25) (2012) 9727-9732.
  12. Y. Roman-Leshkov and M. E. Davis, "Activation of Carbonyl-Containing Molecules with Solid Lewis Acids in Aqueous Media," *ACS Catal.* **1**(11) (2011) 1566-1580.
  13. E. Nikolla, Y. Roman-Leshkov, M. Moliner, and M. E. Davis, "One-Pot Synthesis of 5-(Hydroxymethyl)furfural from Carbohydrates using Tin-Beta Zeolite," *ACS Catal.* **1**(4) (2011) 408-410.
  14. V. Choudhary, A. B. Pinar, S. I. Sandler, D. G. Vlachos, and R. F. Lobo, "Xylose Isomerization to Xylulose and its Dehydration to Furfural in Aqueous Media," *ACS Catal.* **1** (2011) 1724-1728.
  15. S. Caratzoulas and D. G. Vlachos, "Converting Fructose to 5-Hydroxymethylfurfural: A Quantum Mechanics/Molecular Mechanics Study of the Mechanism and Energetics," *Carbohydr. Res.* **346**(5) (2011) 664-672.
  16. S. Caratzoulas, T. D. Courtney, and D. G. Vlachos, "Hybrid Quantum Mechanics/Molecular Mechanics-Based Molecular Dynamics Simulation of Acid-Catalyzed Dehydration of Polyols in Liquid Water," *J. Phys. Chem. A* **115**(32) (2011) 8816-8821.
  17. Y. Roman-Leshkov, M. Moliner, J. A. Labinger, and M. E. Davis, "Mechanism of Glucose Isomerization Using a Solid Lewis Acid Catalyst in Water," *Angew. Chemie - Int. Ed.* **49**(47) (2010) 8954-8957.
  18. M. Moliner, Y. Roman-Leshkov, and M. E. Davis, "Tin-containing zeolites are highly active catalysts for the isomerization of glucose in water," *Proc. Nat. Acad. Sci.* **107**(14) (2010) 6164-6168.
  19. R. F. Lobo, "Synthetic Glycolysis," *ChemSusChem* **3**(11) (2010) 1237-1240.



## Enabling Catalytic Strategies for Biomass Conversion

Postdoc: Antonio G. De Crisci  
Students: Jeff Simon, Timothy Blake  
Collaborators: Richard Zare (Stanford)  
Contacts: Robert M. Waymouth, Department of Chemistry, Stanford University, Stanford CA 94305-5080; waymouth@stanford.edu

### Goal

Develop an integrated platform of selective catalysts for converting biomass-derived feedstocks into value-added chemicals and polymers.

### DOE Interest

The development of biomass-derived commodity chemicals is a critical component of biomass energy production and a key element of a sustainable national (or global) energy strategy. The dominance of fossil fuels and the environmental impact of petroleum and coal-based economies highlight the need for alternative and more varied sources of energy and chemicals to provide the energy, materials, products and technologies that improve our lives while preserving the environment for future generations. The utilization of renewable biomass requires selective catalysts that can convert highly hydroxylated biomass feedstocks such as carbohydrates and glycerol into new chemical intermediates and thermoplastics. New scientific advances in the development of selective catalysts to transform these highly functionalized feedstocks will expand the range of options for transforming biomass into useful and environmentally sustainable products.

### Recent Progress

*Selective Polyol Oxidation Catalysts.* We have discovered a family of cationic palladium catalysts that mediate the selective oxidation of unprotected vicinal polyols to alpha-hydroxy ketones. The catalytic oxidation of glycerol affords dihydroxyacetone with selectivities > 95% and can be performed aerobically with Pd loading of 10 mol % or with benzoquinone with loadings as low as 0.1 mol %. Catalytic oxidation of the tetraol threitol selectively generates erythulose with isolated yields up to 86%. These oxidations can be carried out in organic solvents or in water.

*Generation of High-melting Thermoplastics from Glycerol.* We have developed an integrated catalytic strategy for converting glycerol to dihydroxyacetone carbonate polymers. These materials exhibit melting points of up to 250°C, illustrating the potential of utilizing glycerol, a biproduct of biodiesel manufacturing, as a feedstock for new families of thermoplastics.

### Future Plans

*Selective Oxidation Catalysts.* We are extending our oxidation studies to more earth abundant metals, as our mechanistic studies imply that the selective oxidation of polyols can be generalized to other catalyst systems.

*Synthesis of Polycarbonates from Biomass-derived Polyols.* We are developing new catalytic methods to new families of polycarbonates derived from selectively oxidized polyols.

**Publications (2010-2012).**

1. Pearson, D. M.; Conley, N. R.; Waymouth, R. M. "Palladium-Catalyzed Carbonylation of Diols to Cyclic Carbonates" *Adv. Synth. Cat.* **2011**, *353*, 3007-3013.
2. Kim, H.; Hedrick, J. L.; Waymouth, R. M. "Facile Synthesis of Functionalized Lactones and Organocatalytic Ring Opening Polymerization" *ACS Macro Letters*, **2012**, *1*, 845-847.
3. Simon, J.; Olsson, J. V.; Kim, H.; Tenney, I. F.; Waymouth, R. M. "Semicrystalline Dihydroxyacetone Copolymers Derived from Glycerol " *Macromolecules*, **2012**, *45*, 9275-9281.
4. De Crisci, A., Chung, K., Oliver, A., Waymouth, R. M. "Chemo- and Stereoselective Alcohol Oxidation with Chiral Palladium Catalysts" *Organometallics*, **2013**, *32*, 2257-2266.
5. Chung, K.; Banik, S. M.; De Crisci, A. G.; Pearson, D. M.; Blake, T.; Olsson, J. V.; Waymouth, R. M. "Chemoselective Pd-catalyzed Oxidation of Polyols" *J. Am. Chem. Soc.*, **2013**, in press.

# **Additional Abstracts**

This page is intentionally blank.

## Developing the Science of Immobilized Molecular Catalysts

*coPIs:* Marcus Weck (NYU), C. David Sherrill (GT), Seung Soon Jang (GT)

*Post-docs:* Jonas Dimroth (NYU), Niels ten Brummelhuis (NYU), Lori Burns (GT), Nicholas Brunelli (GT), Yan Feng (GT); *Students:* Michael Kahn (NYU), Jie Lu (NYU), Aaron Cohen (NYU), Nina Schuchman (undergrad, NYU), Byeong Jae Chun (GT), Matthew Kennedy (GT), Rebecca Key (GT), Caroline Hoyt (GT)  
School of Chem. and Biomolec. Eng., Georgia Institute of Technology, [cjones@chbe.gatech.edu](mailto:cjones@chbe.gatech.edu)  
Chemistry Department, New York Univ., [marcus.weck@nyu.edu](mailto:marcus.weck@nyu.edu)

### Abstract

Cooperative catalysis, whereby two or more active sites work in concert in promoting a catalytic reaction, is ubiquitous in biological systems. Design and understanding of synthetic cooperative catalysts is the scientific target of this small team program. Past and current work has focused on the utilization of different cooperative M-Salen catalysts (where M has been Co, Al, or Ru), whereby two M-Salen catalysts work together in the rate-limiting step to catalyze the reaction. An interdisciplinary research team that can probe all aspects of catalyst synthesis, structure and properties is exploring this topic from both experimental and theoretical points of view. In particular, researchers at GT and NYU are developing design principles for supported M-Salen catalysts that follow bimetallic (Co- and Al-Salen) reaction pathways, chiefly a family of Co-Salen catalyzed epoxide ring-opening reactions. Increasingly, other cooperative catalytic systems are being considered, including those that utilize organic active sites. Using these model systems, the fundamental principles that can be used to understand and design future classes of supported, cooperative catalysts are being elucidated.

### *DOE Interest*

The work performed in this program elucidates fundamental principles important in the design of supported, cooperative catalysts. These catalysts have the potential of being highly active and selective while straightforward to separate from the reaction medium. A particular focus is placed on understanding catalyst stability and deactivation mechanisms, which are critical issues that limit the current widespread use of catalysts of this type. Stable supported molecular catalysts would facilitate environmentally-benign, green chemical processing, providing a substantial energy advantage in chemical processing.

### *Goals and Accomplishments for 2012-2013*

In past work, a key aspect of our program has been to elucidate how metal salen complexes should be immobilized to obtain optimal catalytic properties, and to learn what factors affect their long term stability as catalysts. In particular, we hypothesized that different immobilization strategies will be required for the two broad classes of reactions that metal salen complexes catalyze – (i) reactions that involve a single metal center vs. (ii) reactions that are bimolecular in metal complex. In the past year, work has focused on cooperative catalytic reactions involving two M-Salen catalysts, as well as on bio-inspired, cooperative catalysis. In this regard, systems to study cascade reactions in shell-cross-linked micelles and bio-inspired cooperative aminosilica catalysts for aldol coupling reactions are being studied. Specifically, our current and future work aims to develop (i) cooperative catalysts that use two different types of sites (e.g. acid and base), (ii) compartmentalized catalysts (a commonly occurrence in biological systems), and (iii) techniques for carrying out one pot reaction cascades, with localization of different active sites in different environments. Key foci and accomplishments over the last twelve months were:

- (a) Systematic studies of DFT functionals for applicability to various metal salen complexes.
- (b) Assessment of the reactivity of our cooperative Co-Salen catalysts in epoxide ring-opening reactions with organic nucleophiles targeting both enantioselective and regioselective reactions.
- (c) Development of “shell cross-linked micelles” and multicompartment micelles as nanoreactors for catalytic reactions.
- (d) Development of immobilized Co-Salen complexes on a number of supports and evaluating their structure-activity relationships in hydrolytic kinetic resolution (HKR) of epoxides with theory and

experiment.

- (e) Design of Co(III)-X<sub>3</sub>L ligand complexes for epoxide ring-opening reactions and elucidation of their reactivity and electronic structure.
- (f) Investigation of cooperative Co-Salen catalysis of HKR using theory.
- (g) Investigation of catalyst design principles for silica-supported amine catalysts in cooperative aldol and nitroaldol reactions.

### *Scientific Impact*

The team's past contributions (2003-2009) regarding catalyst stability and the role of leaching in palladium-catalyzed coupling reactions has broadly impacted the palladium chemistry community. Our review in *Advanced Synthesis and Catalysis* in 2006 was the most cited paper of the 11785 published in 2006 in any focused catalysis or organic synthesis journal. We authored the lead publication in the journal *Inorganic Chemistry's* 2007 "Forum on Palladium Chemistry for Organic Synthesis."

Our focus on catalysts designed to enhance cooperativity (2006-present) has led to new insights and guidelines in designing supported metal complex catalysts for these types of reactions, which have been reviewed in an *Accounts of Chemical Research* article in 2008. Studies showed that our catalyst based on a mixture of different sized macrocycles using ROMP of cyclooctene-based salen monomers can be fractionated into macrocycles of specific sizes. This catalyst in the form of a mixture of macrocycles is on par with the most active catalysts for the enantioselective ring-opening of terminal epoxides with water, phenols, aliphatic alcohols or amines. The largest sized macrocycles, when separated from the mixture, are even more active, on a per Co basis, making these large macrocycles the most active catalyst known for these reactions. Our work routinely appears in top journals (*JACS*, *Chem. Eur. J.*, *Adv. Synth. Catal.*), and when it is published in specialty journals, it routinely is cited for quality by the editors (4 Editor's Choice Papers in *J. Mol. Catal. A. Chem.*).

### **Publications in 2012-2013**

#### Funded solely by this grant

1. "Highly Crosslinked Polycyclooctyl-Salen Cobalt (III) for the Hydrolytic Kinetic Resolution of Terminal Epoxides" Michael G. C. Kahn and Marcus Weck *Catal. Sci. Tech.* **2012**, 2, 386-389.
2. "Poly(styrene) Resin-Supported Co (III) Salen Cyclic Oligomers: Highly Active and Easily Recycled HKR Catalysts" Michael G.C. Kahn, Joakim H. Stenlid, and Marcus Weck *Adv. Synth. Catal.* **2012**, 354, 3016-3024.
3. "Co(salen) Macrocycles as Catalysts for the Regioselective Aminolytic Kinetic Resolution of Epoxyhexane" Nina S. Schuchman, Matthew Kennedy, C. David Sherrill, and Marcus Weck *Org. Lett.* *submitted*.
4. "Tuning Acid-Base Cooperativity to Create Next Generation Silica-Supported Organocatalysts." Nicholas A. Brunelli, Christopher W. Jones, *J. Catal.*, *submitted*.
5. "Evaluation of Enantiopure and Non-Enantiopure Co(III)-Salen Catalysts and their Counter-ion Effects in the Hydrolytic Kinetic Resolution (HKR) of Racemic Epichlorohydrin." Rebecca E. Key, Krishnan Venkatasubbaiah, Christopher W. Jones, *J. Mol. Catal. A. Chem.* **2013**, 366, 1-7. Editor's Choice Paper.
6. "Tuning Cooperativity by Controlling the Linker Length of Silica-Supported Amines in Catalysis and CO<sub>2</sub> Capture." Nicholas A. Brunelli, Stephanie A. Didas, Krishnan Venkatasubbaiah, Christopher W. Jones, *J. Am. Chem. Soc.* **2012**, 134, 13950-13953.
7. "Cooperative Catalysis with Acid-Base Bifunctional Mesoporous Silica: Impact of Grafting and Co-condensation Synthesis Methods on Material Structure and Catalytic Properties." Nicholas A. Brunelli, Krishnan Venkatasubbaiah, Christopher W. Jones, *Chem. Mater.* **2012**, 24, 2433-2442.
8. "Catalytic Regioselective Epoxide Ring Opening with Phenol using Homogeneous and Supported Analogues of Dimethylaminopyridine." Nicholas A. Brunelli, Wei Long, Krishnan Venkatasubbaiah, Christopher W. Jones, *Top. Catal.*, **2012**, 55, 432-438.

**Fundamentals of Catalysis and Chemical Transformations**

Co-PIs: AC Buchanan, Sheng Dai, De-en Jiang, Edward W. Hagaman, Michelle Kidder, Danny Lutterman, David R. Mullins, Adyita Savara, Zili Wu

Postdocs: Amanda Mann, Lance Gill, Peter Albrecht, Zhenan Qiao, Florencia Calaza, Meijun Li, J. Christopher Bauer, T.-L. (Alex) Chen,

Graduate students: Andrew Binder

Collaborators: Larry Allard, Ariana Beste, Viviane Schwartz, Ken Herwig, Jane Howe, Ye Xu, M.L.Poutsma

Contact: S.H. Overbury, Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6201, [overburysh@ornl.gov](mailto:overburysh@ornl.gov)

**Goals**

Our objective is to achieve a detailed understanding of how oxygenates adsorb, transform and react with one another and with the surface on highly uniform model catalysts and functionalized catalyst surfaces. The hypothesis is that this approach may lead to general methods for design of improved catalysts. We investigate the role of surface site geometry, oxygen availability, confinement, molecule substituents, surface functional groups and metal support interactions in controlling selectivity in reactions catalyzed on shaped and functionalized oxides surfaces and metal particles supported on them.

**DOE interest**

New catalysts hold the key to technology innovation in efficient and clean production and utilization of fuels and chemicals. This work provides a research basis for preparing, testing and understanding catalysts with potential application in these technologies. One end-use application is the conversion of biomass which is limited by a need for new, stable and more selective catalysts. Success in our project may lead to a general understanding of catalytic oxygenate transformations that may lead to improved catalysts.

**Recent Progress**

*Oxygenate chemistry on monolithic CeO<sub>2</sub>*: Highly oriented films of CeO<sub>2</sub>(111) and CeO<sub>2</sub>(100) have been used as model surfaces to typify the surface chemistry of oxygenates on reducible oxides. Recently we have focused on the comparison of these two surface structures to explore the role of site geometry upon the surface chemical transformations. We have explored adsorption and evolution of methanol and water and find that the increased ease of vacancy formation on the (100) surface compared to the (111) surface plays a role in altering the selectivity for decomposition compared to desorption. Another focus area is the effect of structure on the transformations of the oxygenates, especially small alcohols and aldehydes.

We have examined the surface intermediates that form as a function of temperature, coverage and oxidation state of the surface on these two surfaces. Temperature-dependent adsorption and reaction of acetaldehyde (CH<sub>3</sub>CHO) on a fully oxidized and a highly reduced thin-film CeO<sub>2</sub>(111) surfaces have been investigated using a combination of reflection-absorption IR spectroscopy (RAIRS) and periodic density functional theory (DFT+U) calculations. On the fully oxidized surface, acetaldehyde adsorbs weakly through its carbonyl O interacting with a lattice Ce<sup>4+</sup> cation in the η<sup>1</sup>-O configuration. This state desorbs at 210 K without reaction. On the highly reduced surface, new vibrational signatures appear below 220 K due to a dimer state formed from the coupling of the carbonyl O and the acyl C of two acetaldehyde

molecules. This dimer decomposed above 400 K to produce enolate ( $\text{CH}_2\text{CHO}^-$ ). Calculated activation barriers for the coupling of acetaldehyde, the decomposition of the dimer state, and the recombinative desorption of enolate and H as acetaldehyde, agree with TPD for acetaldehyde adsorbed on reduced  $\text{CeO}_2(111)$ . The results demonstrate that surface oxygen vacancies play a crucial role in stabilizing and activating acetaldehyde for coupling reactions.

Acetaldehyde adsorption on  $\text{CeO}_2(100)$  is stronger than on the (111) surface and desorption extends through a larger T range from 200 K to above 400 K. In addition to the parent molecule, above 400 K additional products are observed. Total decomposition to CO,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are the principal pathways with a small amount of dehydration to produce acetylene at 700 K. In addition, a notable product is the small amount of crotonaldehyde that is evident at 430 K, a result of the aldol condensation coupling reaction between two acetaldehyde molecules. The adsorption and reaction on  $\text{CeO}_2(100)$  is consistent with trends previously observed for the other oxygenates. Specifically, stronger adsorption results from a greater number of coordination vacancies around the Ce cation on  $\text{CeO}_2(100)$  compared to  $\text{CeO}_2(111)$ . The CO and  $\text{CO}_2$  products result from dehydrogenation of the adsorbed acetaldehyde by the basic O anions. The water desorption results from the relative ease with which the H reacts with the surface O.

*Shaped nanocrystals to explore structure reactivity relationships:* Oriented single crystals have limited surface area and the UHV environment is challenging for probing catalytic pathways. To bridge this gap we have initiated studies of chemisorption and reactions on shaped nanoparticles that have well defined surface structures included cubes that terminate on {100} surfaces, octahedra that terminate on {111} and rods that terminate on a mixture of defective but low index terminations. Using these nanoshapes we have probed structure dependence in chemisorption and reaction rates.

Adsorption and desorption of a probe molecule, methanol, were followed by *in situ* IR and Raman spectroscopy to probe surface species and mass spectrometry to probe temperature dependent evolution of desorption products. Upon methanol adsorption, on-top, bridging and three-coordinate methoxy species are formed on rods and cubes while only on-top methoxy is present on the octahedra. The distribution of the methoxy species is believed to be determined by the coordination status of surface Ce cations and the amount of defect sites on the three nanoshapes. During the TPD the methoxy species are gradually dehydrogenated into  $\text{H}_2$  and CO *via* formate intermediates. Formyl is also evident on the rods. Methoxy is more reactive on the rods, resulting in desorption of  $\text{H}_2$  and CO at lower temperature (< 583 K) than on cubes and octahedra. Higher than stoichiometric H/CO ratio is observed in the methanol-TPD products, attributed to retention of some amount of formate and carbonate on the ceria nanoshapes as revealed by *in situ* IR. A small amount of methanol and formaldehyde desorbs below 423 K from the three surfaces due to the disproportionation of methoxy. UV Raman and IR results indicate that the ceria nanoshapes are slightly reduced at room temperature by methanol adsorption, and become more reduced during methanol desorption. The degree of reduction is dependent on the surface structure of the nanoshapes.

Shaped  $\text{CeO}_2$  nanoparticles have also been used to explore the effect of surface structure upon the surface chemistry and catalytic selectivity for the ethanol selective oxidation reaction.  $\text{CeO}_2$  octahedra, cubes and rods were synthesized using previously published methods. Adsorption and desorption behavior on these nanoshapes was determined by a combination of temperature programmed desorption (TPD) and *in situ* DRIFTS. Activity and selectivity were measured in steady state and in temperature programmed surface reaction (TPSR). Shape dependent differences are observed in surface adsorbates, their transformation temperatures and the selectivity for dehydration, dehydrogenation and decomposition. Ethoxide and acetate are the primary surface species present under both TPD and TPSR conditions for all shapes. Different rates of  $\alpha$ - and  $\beta$ -CH bond scission on the different shapes are responsible for different product



selectivity. Structure dependent, reductive vacancy formation and availability of reactant O<sub>2</sub> combine to control surface H which in turn plays a role in controlling product selectivity

*Au catalysts, clusters and bimetallic catalysts for oxygenate reactions:* We have explored various salts as supports, including phosphates and sulfates, that may stabilize Au catalysts for gas phase reactions such as CO oxidation. Au catalysts containing BaSO<sub>4</sub> nanocrystals (5–8 nm) were prepared by *in situ* growth method using amphiphilic sulfonate (SDBS) as the sulfate source, leading to new, highly stable, nonreducible but “active” Au catalyst supports that may be preferable to the typical reducible oxides for low-temperature CO oxidation. The results suggest a unique interaction between Au nanoparticles and nanosized BaSO<sub>4</sub> supports. We have also explored another strategy for stabilizing ultra-small gold clusters under thermal treatment. By this strategy, thiolated gold clusters (Au<sub>25</sub>, Au<sub>144</sub>), after removal of the protecting thiolate ligands by thermal treatment, can be stabilized onto heterostructured mesoporous supports. The essence of this strategy lies in use of the heterostructured binary oxide supports (M<sub>x</sub>O<sub>y</sub>-mSiO<sub>2</sub>) synthesized through a combination of a transition-metal oxide and an ordered mesoporous silica. Monodispersed Au clusters can be readily absorbed into the pores of this heterostructured oxide. The size of the clusters is maintained after removing the thiolate ligands by thermal treatment in air, making this method superior to *in vacuo* treatment. Small gold clusters supported on these heterostructured mesoporous supports were found to be active for CO oxidation.

We have developed a synthetic methodology to create supported, nanoscale AuCuPd ternary alloy nanoparticles through the diffusion of Cu<sup>0</sup> and Pd<sup>0</sup> atoms in an organic solvent using hexadecylamine as a reductant and ligand stabilizer. Subjecting the AuCuPd catalyst to reductive or oxidative pretreatment conditions greatly affected the catalytic activity for the oxidation of CO. In situ XRD and EXAFS indicated that oxidizing the catalyst to 300 °C produced a AuPd alloy core that was separated from CuO and a small amount of PdO. Oxidation at 500 °C resulted in the segregation of PdO and CuO to form a decorated Au rich particle. Forming a PdO and CuO rich surface on the AuPd or Au-rich core decreased O<sub>ads</sub> spill over from Cu to Au or Pd sites and hindered access to the Au active sites resulting in decreased catalytic activity. Reducing the catalyst under H<sub>2</sub> formed a AuCuPd alloy with a Cu rich surface and formed the most active catalyst. It is likely that Cu, a base metal, helped to lower the activation energy through the activation O<sub>2</sub> that could migrate to Au or Pd sites. However, AuCu/SiO<sub>2</sub> demonstrated an opposite structure-activity relationship. Reduced AuCu alloy was the least active catalyst and improved after it was oxidized to form a Au-CuO hybrid particle.

Au<sub>15</sub>(SR)<sub>13</sub> is the smallest, stable thiolated gold nanocluster experimentally identified so far and its elusive structure may hold the key to the origin of the nucleus in the formation of thiolated gold nanoclusters. By an extensive exploration of possible isomers by DFT, we arrive at a novel structure for Au<sub>15</sub>(SR)<sub>13</sub> with high stability and whose optical-absorption features match experiment. This structure features a cyclic [Au(I)-SR] pentamer interlocked with one staple trimer motif protecting the tetrahedral Au<sub>4</sub> nucleus, together with another trimer motif. This structure suggests that Au<sub>15</sub>(SR)<sub>13</sub> is a transitional composition from the [Au(I)-SR]<sub>x</sub> polymer (Au<sub>10</sub>(SR)<sub>10</sub>) to larger Au<sub>n</sub>(SR)<sub>m</sub> clusters that have only the staple motifs; and that the nucleation process starts from the Au<sub>4</sub> core. We have also explored the interaction between gold nanoclusters and a fully hydroxylated surface, Mg(OH)<sub>2</sub> basal plane, by using a DFT-enabled local basin-hopping technique for global-minimum search. We find strong interaction of Au clusters with the surface -OH *via* a short bond between edge Au atoms and O atoms of the OH groups. We expect that this strong interaction is ubiquitous on hydroxylated support surfaces and helps the gold clusters against sintering, thereby contributing to their CO-oxidation activity at low temperatures.

*Dynamics and reactions of tethered oxygenates:* Product selectivity and reactions rates in pyrolysis of phenethyl phenyl ether confined in mesoporous silica by covalent tethers to the pore walls have been

measured as a function of tether density and the presence of co-tethered spacer molecules. The phenyl shift rearrangement resulting from H-abstraction at the  $\beta$ -carbon is inhibited by H-bonding interactions of the ether oxygen with surface silanols. Spacer molecules further inhibit the ring rearrangement pathway. The origin of these effects on the rearrangement path are described in the context of steric constraints, pore confinement, hydrogen bonding and the rigidity of the spacer molecules. Diffusive motions of another system, tethered diphenylpropane, were probed by quasi-elastic neutron scattering. The results support a model where the DPP molecules prefer an orientation allowing close proximity to the MCM-41 pore surface and are forced into the pore interior by either the steric effect of small pore diameter or by increased competition for surface area at high molecule surface coverage.

### Future Directions

Additional DFT computations will be performed to understand better how surface site geometry affects the rates of  $\alpha$ - and  $\beta$ -CH bond scission, and how this alters product selectivity. Probe molecules will be chosen to examine substituent group effects on the CH bond cleavage of the adsorbed reactants. Adsorption of various ‘test’ gases (pyridine, acetonitrile, CO, CO<sub>2</sub>...) on the CeO<sub>2</sub> nanoshapes will be used to quantify how structure affects acid-base parameters and bonding interactions. We will examine increasingly more complicated oxygenates such as polyols to understanding how adjacent hydroxyls react and compete for sites. Experimental studies of reaction selectivity and surface intermediates on the CeO<sub>2</sub> shapes will be supplemented with computer simulations to build a detailed understanding of the reaction pathways. Following a similar approach, work will continue on characterizing ketonization of acids, especially acetic acid, on the ceria nanoshapes. We will initiate studies of Au clusters deposited on CeO<sub>2</sub> nanoshapes with the goal of creating highly uniform model catalysts that have known support structure and identically sized Au particles. The stability and temperature dependent evolution of these catalysts will be studied microscopically, and their reactivity/selectivity will be characterized and compared to the CeO<sub>2</sub> and Au reactivity to elucidate metal-support effects on the model surfaces. Effect of acid phosphate groups on mesoporous silica will be examined for reactions of tethered alkyl phenyls.

### Publication list (2011-2013)

Albrecht, P. M.; Mullins, D. R., Adsorption and Reaction of Methanol over CeOx(100) Thin Films, *Langmuir* **2013**, *in press*.

Allard, L. F.; Overbury, S. H.; Bigelow, W. C.; Katz, M. B.; Nackashi, D. P.; Damiano, J., Novel MEMS-Based Gas-Cell/Heating Specimen Holder Provides Advanced Imaging Capabilities for In Situ Reaction Studies, *Microscopy and Microanalysis* **2012**, *18*(4), 656-666.

Bauer, J. C.; Mullins, D.; Li, M. J.; Wu, Z. L.; Payzant, E. A.; Overbury, S. H.; Dai, S., Synthesis of silica supported AuCu nanoparticle catalysts and the effects of pretreatment conditions for the CO oxidation reaction, *PhysChem ChemPhys* **2011**, *13*(7), 2571-2581.

Bauer, J. C.; Veith, G. M.; Allard, L. F.; Oyola, Y.; Overbury, S. H.; Dai, S., Silica-Supported Au-CuOx Hybrid Nanocrystals as Active and Selective Catalysts for the Formation of Acetaldehyde from the Oxidation of Ethanol, *ACS Catalysis* **2012**, *2*(12), 2537-2546.

Beste, A.; Buchanan, A. C., III, Computational Investigation of the Pyrolysis Product Selectivity for alpha-Hydroxy Phenethyl Phenyl Ether and Phenethyl Phenyl Ether: Analysis of Substituent Effects and Reactant Conformer Selection, *J. Phys. Chem. A* **2013**, *117*, , 3235–3242.

Beste, A.; Buchanan, A. C., III, Kinetic Simulation of the Thermal Degradation of Phenethyl Phenyl Ether, a Model Compound for the  $\beta$ -O-4 Linkage in Lignin, *Chem. Phys. Lett.* **2012**, *550*, 19-24.

Beste, A.; Buchanan, A. C., III, The Role of Carbon-Carbon Phenyl Migration in the Pyrolysis Mechanism of  $\beta$ -O-4 Lignin Model Compounds: Phenethyl Phenyl Ether and  $\alpha$ -Hydroxy Phenethyl Phenyl Ether, *J. Phys. Chem. A* **2012**, *116*, 12242-12248.

Beste, A.; Buchanan, A. C., III, Kinetic Analysis of the Phenyl-shift Reaction in  $\beta$ -O-4 Lignin Model Compounds: A Computational Study. *J. Org. Chem.* **2011**, *76*, 2195.

Beste, A.; Buchanan, A. C., III, Challenges in the Computation of Rate Constants for Lignin Model Compounds, in *Rate Constant Calculation for Thermal Reactions: Methods and Applications*. DaCosta, H., Fan, M., Eds.; John Wiley & Sons, Inc.: Hoboken, NJ **2012**, Chapter 7, pp. 191-238.

Brooks, J. D.; Chen, T.-L.; Mullins, D. R.; Cox, D. F., Reactions of ethylidene on a model chromia surface: 1,1-dichloroethane on stoichiometric  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> (10-12), *Surface Science* **2011**, *605*, 1170.

Calaza, F. C.; Xu, Y.; Mullins, D. R.; Overbury, S. H., Oxygen Vacancy-Assisted Coupling and Enolization of Acetaldehyde on CeO<sub>2</sub>(111), *JACS* **2012**, *134*(43), 18034-18045.

Calaza, F. C.; Chen, T. L.; Mullins, D. R.; Overbury, S. H., Structure and Reactivity of Alkyl Ethers Adsorbed on CeO<sub>2</sub>(111) Model Catalysts, *Topics Catalysis* **2011**, *54*(1-4), 56-69.

Chen, T.-L.; Mullins, D. R., Adsorption and Reaction of Acetaldehyde over CeO<sub>x</sub>(111) Thin Films, *J Phys Chem C* **2011**, *115*, 3385.

Chen, T.-L.; Mullins, D. R., Ethylene Glycol Adsorption and Reaction over CeO<sub>x</sub>(111) Thin Films, *J Phys Chem C* **2011**, *115* 13725-13733.

Fulvio, P. F.; Mayes, R. T.; Bauer, J. C.; Wang, X. Q.; Mahurin, S. M.; Veith, G. M.; Dai, S., "One-pot" synthesis of phosphorylated mesoporous carbon heterogeneous catalysts with tailored surface acidity, *Catalysis Today* **2012**, *186*(1), 12-19.

Hagaman, E. W.; Chen, B.; Jiao, J.; Parsons, W., Solid-State <sup>17</sup>O-NMR Study of Benzoic Acid Adsorption on Metal Oxide Surfaces. *Solid State Nucl. Magn. Reson.* **2012**, *41*, 60.

Jiang, D.E.; Overbury, S. H.; Dai, S., Structures and Energetics of Pt Clusters on TiO<sub>2</sub>: Interplay between Metal–Metal Bonds and Metal–Oxygen Bonds, *J Phys Chem C* **2012**, *116*(41), 21880-21885.

Jiang, D. E.; Dai, S., The Role of Low-coordinate Oxygen on Co<sub>3</sub>O<sub>4</sub>(110) in Catalytic CO Oxidation, *PhysChem ChemPhys* **2011**, *13*, 978.

Jiang, D. E.; Overbury, S. H.; Dai, S., Interaction of Gold Clusters with a Hydroxylated Surface, *J Phys Chem Lett* **2011**, *2*(10), 1211-1215.

Kidder, M. K.; Chaffee, A. L.; Nguyen, M.-H. T.; Buchanan, A. C., III, Pyrolysis of Phenethyl Phenyl Ether Tethered in Mesoporous Silica. Effects of Confinement and Surface Spacer Molecules on Product Selectivity. *J. Org. Chem.* **2011**, *76*, 6014.

Kintzel, E. J. J.; Kidder, M. K.; Buchanan, A. C., III; Britt, P. F.; Mamantov, E.; Zamponi, M.; Herwig, K. W., The Dynamics of 1,3-Diphenylpropane Tethered to the Interior Pore Surfaces of MCM-41, *J. Phys. Chem. C* **2012**, *116*, 923.

Li, M. J.; Wu, Z. L.; Overbury, S. H., CO oxidation on phosphate-supported Au catalysts: Effect of support reducibility on surface reactions, *J Catal* **2011**, *278*(1), 133-142.

Lee, J. W.; Buchanan, III, A. C.; Evans, B. R.; Kidder, M. K., Partial Oxidation of Biochar for Enhanced Cation Exchange Capacity in *Advanced Biofuels and Bioproducts*. Lee, J. W., Ed.; Springer: New York, NY **2012**, Chapter 4, pp. 35-45.

Liu, Z. G.; Chai, S. H.; Binder, A.; Li, Y. Y.; Ji, L. T.; Dai, S., Influence of calcination temperature on the structure and catalytic performance of CuO<sub>x</sub>-CoO<sub>y</sub>-CeO<sub>2</sub> ternary mixed oxide for CO oxidation, *Appl Catal A - General* **2013**, *451*, 282-288.

Ma, G. C.; Binder, A.; Chi, M. F.; Liu, C.; Jin, R. C.; Jiang, D. E.; Fan, J.; Dai, S., Stabilizing gold clusters by heterostructured transition-metal oxide-mesoporous silica supports for enhanced catalytic activities for CO oxidation, *Chem Comm* **2012**, *48*(93), 11413-11415.

Ma, Z.; Dai, S., Development of Novel Supported Gold Catalysts: A Materials Perspective, *Nano Res* **2011**, *4*, 3-32.

Mullins, D. R.; Albrecht, P. M.; Chen, T.-L.; Calaza, F.; Biegalski, M. D.; Christen, H. M.; Overbury, S. H., Water Dissociation on CeO<sub>2</sub>(100) and CeO<sub>2</sub>(111) Thin Films, *J. Phys. Chem. C* **2012**, *116*, 19419–19428.

Mullins, D. R.; Albrecht, P. M.; Calaza, F. C., Variations in Reactivity on Different Crystallographic Orientations of Cerium Oxide, *Top Catal* **2013**, *in press*.

Pei, Y.; Shao, N.; Li, H.; Jiang, D. E.; Zeng, X. C., Hollow Polyhedral Structures in Small Gold–Sulfide Clusters, *ACS Nano* **2011**, *5*, 1441.

Poutsma, M. L., Evolution of Structure-Reactivity Correlations for the Hydrogen Abstraction Reaction by Chlorine Atom, *J. Phys. Chem. A* **2013**, *117*, 687-703.

Poutsma, M. L., Review of Rate Constants and Exploration of Correlations of the Halogen Transfer Reaction of Tri-substituted Carbon-Centered Radicals with Molecular Halogens, *J. Org. Chem* **2012**, *77*, 2619-2636.

Poutsma, M. L., Chain Elongation during Thermolysis of Tetrafluoroethylene and Hexafluoropropylene: Modeling of Mechanistic Hypotheses and Elucidation of Data Needs. *J. Anal. Appl. Pyrol.* **2011**, *92*, 25.

Qian, H. F.; Jiang, D. E.; Li, G.; Gayathri, C.; Das, A.; Gil, R. R.; Jin, R. C., Monoplatinum Doping of Gold Nanoclusters and Catalytic Application, *JACS* **2012**, *134*(39), 16159-16162.

Qiao, Z. A.; Huo, Q. S.; Chi, M. F.; Veith, G. M.; Binder, A. J.; Dai, S., A "Ship-In-A-Bottle" Approach to Synthesis of Polymer Dots@Silica or Polymer Dots@Carbon Core-Shell Nanospheres, *Advanced Materials* **2012**, *24*(45), 6017.

Singh, J. A.; Overbury, S. H.; Dudney, N. J.; Li, M.; Veith, G. M., Gold Nanoparticles Supported on Carbon Nitride: Influence of Surface Hydroxyls on Low Temperature Carbon Monoxide Oxidation, *ACS Catalysis* **2012**, *2*, 1138–1146.

Tenney, S. A.; He, W.; Ratliff, J. S.; Mullins, D. R.; Chen, D. A., Characterization of Pt-Au and Ni-Au Clusters on TiO<sub>2</sub>(110), *Top Catal* **2011**, *54*, 42.

Tian, C.; Chai, S.-H.; Mullins, D. R.; Zhu, X.; Binder, A.; Guo, Y.; Dai, S., Heterostructured BaSO<sub>4</sub>–SiO<sub>2</sub> mesoporous materials as new supports for gold nanoparticles in low-temperature CO oxidation, *Chem Comm* **2013**, *49* 3464-3466.

Tian, C. C.; Chai, S. H.; Zhu, X.; Wu, Z. L.; Binder, A.; Bauer, J. C.; Brown, S.; Chi, M. F.; Veith, G. M.; Guo, Y. L.; Dai, S., In situ growth synthesis of heterostructured LnPO<sub>4</sub>-SiO<sub>2</sub> (Ln = La, Ce, and Eu) mesoporous materials as supports for small gold particles used in catalytic CO oxidation, *J Mater Chem* **2012**, *22*(48), 25227-25235.

Waksburg, A.; Nguyen, M.-H. T.; Chaffee, A. L.; Kidder, M. K.; Buchanan, A. C., III; Britt, P. F., Molecular Dynamics Modeling of Tethered Organics in Confined Spaces. *Mol. Simul.* **2011**, *37*, 1266.

Wu, Z.; Li, M.; Overbury, S. H., Probing the surface sites of ceria nanoshapes via methanol adsorption and reaction, *ACS Catalysis* **2012**, *2*, 2224 - 2234.

Wu, Z.; Li, M.; Overbury, S. H., Raman Spectroscopic Study of the Speciation of Vanadia Supported on Ceria Nanocrystals with Defined Surface Planes, *ChemCatChem* **2012**, *4*(10), 1653-1661.

Wu, Z.; Li, M.; Overbury, S. H., On the Structure Dependence of CO Oxidation over CeO<sub>2</sub> Nanocrystals with Well-Defined Surface Planes, *J Catal* **2012**, *285*, 61-73.

Wu, Z.; Schwartz, V.; Li, M.; Rondinone, A.; Overbury, S. H., Support Shape Effect in Metal Oxide Catalysis: Ceria Nanoshapes Supported Vanadia Catalysts for Oxidative Dehydrogenation of Isobutane, *J Phys Chem Lett* **2012**, *3* 1517–1522.

Yang, X.; Wu, Z.; Moses-Debusk, M.; Mullins, D. R.; Mahurin, S. M.; Geiger, R. M.; Kidder, M. K.; Narula, C. K., Heterometal Incorporation in M-Exchanged Zeolites Enables Low Temperature Catalytic Activity of NOx Reduction, *J. Phys. Chem. C* **2012**, *116*, 23322-23331.

Yin, H. F.; Ma, Z.; Chi, M. F.; Dai, S., Heterostructured catalysts prepared by dispersing Au@Fe<sub>2</sub>O<sub>3</sub> core-shell structures on supports and their performance in CO oxidation, *Catalysis Today* **2011**, *160*(1), 87-95.

Yunker, J. M. B., A.; Buchanan, I., A. C., Computational Study of Bond Dissociation Enthalpies for Lignin Model Compounds: β-5 Arylcoumaran, *Chem. Phys. Lett* **2012**, *545*, 100-106.

Yunker, J. M.; Beste, A.; Buchanan, A. C., III, Computational Study of Bond Dissociation Enthalpies for Lignin Model Compounds: Intramolecular Hydrogen Bonding in Phenethyl Phenyl Ethers. *ChemPhysChem.* **2011**, *12*, 3556.

# Participant List

This page is intentionally blank.

## Catalysis Research Meeting

June 30 – July 2, 2013

### Participant List

Mahdi Abu-Omar  
Purdue University  
mabuomar@purdue.edu

Aaron Appel  
Pacific Northwest National Laboratory  
Aaron.Appel@pnnl.gov

Bart Bartlett  
University of Michigan  
bartmb@umich.edu

Matthias Batzill  
University of South Florida  
mbatzill@usf.edu

Ali Belkacem  
Lawrence Berkeley National Laboratory  
abelkacem@lbl.gov

John Berry  
University of Wisconsin  
berry@chem.wisc.edu

Theodore Betley  
Harvard University  
betley@chemistry.harvard.edu

Aditya Bhan  
University of Minnesota  
abhan@umn.edu

Thomas Bligaard  
SLAC National Accelerator Laboratory  
bligaard@SLAC.Stanford.EDU

Janet Bluemel  
Texas A&M University  
bluemel@tamu.edu

Suzanne Blum  
University of California  
blums@uci.edu

Phillip Britt  
Oak Ridge National Laboratory  
brittpf@ornl.gov

R M Bullock  
Pacific Northwest National Laboratory  
morris.bullock@pnnl.gov

Emilio Bunel  
Argonne National Laboratory  
ebunel@anl.gov

Eugene Chen  
Colorado State University  
eugene.chen@colostate.edu

Peng Chen  
Cornell University  
pc252@cornell.edu

Malcolm Chisholm  
Ohio State University  
chisholm.4@osu.edu

Phillip Christopher  
University of California  
christopher@enr.ucr.edu

Geoffrey Coates  
Cornell University  
gc39@cornell.edu

Christophe Copéret  
ETH Zurich  
ccoperet@ethz.ch

Robert Crabtree  
Yale University  
robert.crabtree@yale.edu

Thomas Cundari  
University of North Texas  
t@unt.edu

## Catalysis Research Meeting

June 30 – July 2, 2013

### Participant List

Paul Dauenhauer  
University of Massachusetts  
dauenhauer@ecs.umass.edu

Huw Davies  
Emory University  
hmdavie@emory.edu

Zdenek Dohnalek  
Pacific Northwest National Laboratory  
Zdenek.Dohnalek@pnnl.gov

Richard Finke  
Colorado State University  
rfinke@lamar.colostate.edu

Annaliese Franz  
University of California  
akfranz@ucdavis.edu

Michel Gagne  
University of North Carolina  
mgagne@unc.edu

Bruce Garrett  
Pacific Northwest National Laboratory  
bruce.garrett@pnnl.gov

Bruce Gates  
University of California  
bcgates@ucdavis.edu

Alan Goldman  
Rutgers University  
alan.goldman@rutgers.edu

Lars Grabow  
University of Houston  
grabow@uh.edu

Jeffrey Greeley  
Purdue University  
jgreeley@purdue.edu

Thomas Gunnoe  
University of Virginia  
tbg7h@virginia.edu

Alexander Harris  
Brookhaven National Laboratory  
alexh@bnl.gov

John Hartwig  
University of California  
jhartwig@berkeley.edu

Andreas Heyden  
University of South Carolina  
heyden@cec.sc.edu

Jason Hicks  
University of Notre Dame  
Jhicks3@nd.edu

Adam Hock  
Illinois Institute of Technology  
ahock@iit.edu

George Huber  
University of Wisconsin  
huber@enr.wisc.edu

Cynthia Jenks  
Ames Laboratory  
cjenks@ameslab.gov

Rongchao Jin  
Carnegie Mellon University  
rongchao@andrew.cmu.edu

Christopher Jones  
Georgia Institute of Technology  
cjones@chbe.gatech.edu

Alexander Katz  
University of California  
askatz@berkeley.edu



## Catalysis Research Meeting

June 30 – July 2, 2013

### Participant List

Robert Knowles  
Princeton University  
rknowles@princeton.edu

Harold Kung  
Northwestern University  
hkung@northwestern.edu

Johannes Lercher  
Pacific Northwest National Laboratory  
johannes.lercher@pnnl.gov

Jared Lewis  
University of Chicago  
jaredlewis@uchicago.edu

Wenbin Lin  
University of Chicago  
wlin@unc.edu

Suljo Linic  
University of Michigan  
linic@umich.edu

Raul Lobo  
University of Delaware  
lobo@udel.edu

Daniel Lutterman  
Oak Ridge National Laboratory  
luttermanda@ornl.gov

Diane Marceau  
U.S. Department of Energy  
diane.marceau@science.doe.gov

Tobin Marks  
Northwestern University  
t-marks@northwestern.edu

Christopher Marshall  
Argonne National Laboratory  
marshall@anl.gov

Paul Maupin  
U.S. Department of Energy  
paul.maupin@science.doe.gov

James Medlin  
University of Colorado  
medlin@colorado.edu

Randall Meyer  
University of Illinois  
rjm@uic.edu

Scott Miller  
Yale University  
scott.miller@yale.edu

Raul Miranda  
U.S. Department of Energy  
raul.miranda@science.doe.gov

Liviu Mirica  
Washington University  
mirica@wustl.edu

Noritaka Mizuno  
University of Tokyo  
tmizuno@mail.ecc.u-tokyo.ac.jp

Djamaladdin Musaev  
Emory University  
dmusaev@emory.edu

Kenneth Nicholas  
University of Oklahoma  
knicholas@ou.edu

Eranda Nikolla  
Wayne State University  
erandan@wayne.edu

Jens Norskov  
SLAC National Accelerator Laboratory  
norskov@stanford.edu

## Catalysis Research Meeting

June 30 – July 2, 2013

### Participant List

Justin Notestein  
Northwestern University  
j-notestein@northwestern.edu

Gerard Parkin  
Columbia University  
parkin@columbia.edu

Charles Peden  
Pacific Northwest National Laboratory  
chuck.peden@pnnl.gov

Marek Pruski  
Iowa State University  
mpruski@iastate.edu

Lawrence Que  
University of Minnesota  
larryque@umn.edu

Jeffrey Rimer  
University of Houston  
jrimer@central.uh.edu

Robert Rioux  
Pennsylvania State University  
rioux@engr.psu.edu

Jose Rodriguez  
Brookhaven National Laboratory  
rodriguez@bnl.gov

Yuriy Roman  
Massachusetts Institute of Technology  
yroman@mit.edu

Roger Rousseau  
Pacific Northwest National Laboratory  
Roger.Rousseau@pnnl.gov

Joseph Sadighi  
Georgia Institute of Technology  
joseph.sadighi@chemistry.gatech.edu

Aaron Sadow  
Ames Laboratory  
sadow@iastate.edu

Susannah Scott  
University of California  
sscott@engineering.ucsb.edu

Carsten Sievers  
Georgia Institute of Technology  
carsten.sievers@chbe.gatech.edu

Dario Stacchiola  
Brookhaven National Laboratory  
djs@bnl.gov

Steven Tait  
Indiana University  
tait@indiana.edu

Don Tilley  
University of California  
tdtilley@berkeley.edu

F. Dean Toste  
University of California  
fdtoste@berkeley.edu

Dionisios Vlachos  
University of Delaware  
vlachos@udel.edu

Robert Waymouth  
Stanford University  
waymouth@stanford.edu

Robert Weber  
Pacific Northwest National Laboratory  
Robert.Weber@pnnl.gov

Zili Wu  
Oak Ridge National Laboratory  
wuz1@ornl.gov

**Bullets from the  
Session Chairs and Contributors**

Moderator: Alex Katz (U.C. Berkeley)

- **Invited Speaker:** Christophe Copéret (ETH Zurich)  
"Controlled functionalization and Molecular Understanding of surfaces: Towards supported Single-Site Catalysts and Beyond"
- T. Don Tilley (U.C. Berkeley, LBNL)  
"Molecular Routes to Single-Site Catalytic Surface Species for Selective Oxidations"
- Steven Tait (Indiana U.)  
"Metal/Organic Surface Catalyst for Low-Temperature Methane Oxidation: Bi-Functional Union of Metal-Organic Complex and Chemically Complementary Surface"
- Tobin Marks (Northwestern U.)  
"Supported Organometallic Complexes: Surface Chemistry, Spectroscopy, Catalysis and Homogeneous Models"

## Session 1: Katz's Bullets

Molecular understanding of chemistry on surfaces has progressed tremendously and allowed development of supported catalysts with performances oftentimes equaling or exceeding what is observed for their molecular analogues.

- Speakers spoke about first-coordination-sphere site requirements in Lewis acid sites on inorganic-oxide supports, which are responsible for selective activation of small molecules such as hydrogen (for olefin hydrogenation using frustrated Lewis acid-base pairs), methane, hydrogen peroxide, and dinitrogen, and the synthesis of these types of active-site environments.
- Speakers also spoke about the importance of second-sphere environment for sites on surfaces within the context of enabling catalysis in water via enclosure of active site within hydrophobic environments. Some of these environments can be enforced using organic ligands coordinated to anchored active sites on surfaces, particularly in systems involving multiple metals where the ligand serves to preferentially organize one metal relative to the other (as in new systems for olefin polymerization).
- There are continuing opportunities to borrow on knowledge bases from homogeneous catalysis and use this information for the molecular design of solid catalysts consisting of more efficient catalytic sites.
- Characterization of sites on solid catalysts can be performed using emerging NMR spectroscopic techniques such as DNP to greatly enhance sensitivity, as well as other tools (HAADF-STEM, EXAFS, and XANES though there was less discussion on operando spectroscopy), and unprecedented detail of reaction mechanism using computational tools.
- As we look to the future, supported catalysts could be superior to molecular ones because bimolecular decomposition can be suppressed and highly active species can be generated; the main problem is to control their synthesis and to understand their structure.
- Items for future topics: (i) explore the intentional and controlled synthesis of highly under-coordinated surface species and surface species consisting of multiple organized metal atoms using generalizable and modular approaches and (ii) investigate new reactivities and detailed mechanistic studies using such sites.

## Session 1: Tobin Marks' Bullets

- True understanding of a molecule-based surface catalytic system requires accurate, operando active site quantification, the application of multiple physical/structural characterization techniques (as many operando as possible) detailed kinetic analysis, and exploration of substrate scope and limitations.
- Ideally such systems should also be characterized by high-level quantum chemical techniques which are bench-marked against physical observables of the catalytic system. The computational effort should focus both on understanding known reaction pathways, but more importantly, should be used to guide catalyst synthesis and the discovery of new catalytic transformations.
- Ideal synthetic routes to catalyst precursors should be sufficiently flexible to allow exploration of steric and electronic effects, and their connection with catalytic observables.
- The support should be treated as an active component of the catalytic system, and synthetic strategies should strive to similarly modify the support steric and electronic characteristics.
- We don't know enough about how to position multiple, cooperating catalytic entities in proximity on the surface.
- While the research effort should have a fundamental scientific flavor, we must be conversant in, and never lose sight of, the technological implications of what we are trying to accomplish.

Moderator: Ted Betley (Harvard U.)

- Susannah Scott (U.C. Santa Barbara)  
"Exploring the Relationship between Homogeneous and Heterogeneous Reaction Kinetics"
- Justin Notestein (Northwestern U.)  
"Templating Routes to Supported Oxide Catalysts by Design"
- Liviu Mirica (Washington U.–St. Louis)  
"Novel Palladium Catalysts for the Oxidative Oligomerization of Methane & Carbon Dioxide Reduction"
- Aaron Appel (PNNL)  
"An Energy-Based Approach to Bifunctional Molecular Catalysis for CO<sub>2</sub> Reduction and Fuel Utilization"

## Session 2: Betley's Bullets

- From Susannah Scott's talk, the discussion centered on the applicability of kinetic models being invoked to cover both homo- and heterogeneous catalytic systems.
- A wonderful followup for this concept was Notestein's talk about the immobilization of homogeneous catalysts on oxide surfaces. Should Scott's methodology be generally applicable, the immobilized catalyst systems would be a great showcase for this.
- A big disconnect between the homogeneous catalyst community and groups that immobilize these systems onto surfaces is whether the chemistry manifest by these molecular centers is really duplicated upon immobilization, or is a fundamentally new chemical species generated with disparate or enhanced reactivities. The last two talks really speak to this.
- Mirica's talk really hammered home how tailoring of the molecular entity turns out desirable chemistry paying special attention to understanding of the electronic structure of the reactive species. Too often the inorganic field relies of "structure-function" relationships, but not necessarily highlighting the electronic-structure to function relationship should be front and center.
- This idea was also highlighted by Appel's talk on PNNL's work on CO<sub>2</sub> reduction. The molecular architectures are evolving to directly target certain chemical function and PNNL's work on H<sub>2</sub> and CO<sub>2</sub> really highlight this.

### Session 3: Gunnoe's Bullets

Moderator: Brent Gunnoe (U. Virginia)

- **Invited Speaker:** Huw Davies (Emory U.)  
"Center Approach to C-H Functionalization"
- Dean Toste (U.C. Berkeley, LBNL)  
"Selective Reactions of Carbon-Carbon  $\pi$ -Bonds Catalyzed by Cations and Anions"
- **Invited Speaker:** Scott Miller (Yale U.)  
"Asymmetric Catalysis in Complex Molecular Environments"

- Talks focused primarily on stereoselective catalytic transformations using transition metal and organic catalysts.
- Common theme in all three presentations was the role of theory to understand catalyst selectivity and predict design of improved catalysts. Demonstrate that the synergy of theory and experiment continues to develop/evolve.
- The selective functionalization of CH bonds, both for large scale processes (alkane, arene conversions) and synthetic organic chemistry, continues to be one of the foremost synthetic challenges. One particular challenge for synthetic chemistry of complex organic molecules is understanding how to tune selectivity, in particular functionalization of strong CH bonds in the presence of weaker CH bonds.
- Stereoselective functionalization of CH bonds via carbene insertion using di-rhodium catalysts has been demonstrated. Ligand tuning to control selectivity is enhanced by understanding, in detail, the role of carbene substituents and ligands. Collaborative approach that involves organic chemists, inorganic/coordination chemists and computational chemists provides tools necessary to understand and optimize these catalysts.
- Selective functionalization of complex organic molecules is possible using organocatalysts, and the use of modeling can be powerful tool to predict selectivity.
- With complex natural products, the rapid study and development of catalysts are inhibited by the challenging nature of product characterization.
- Increased sophistication for the synthesis and characterization of materials provides new opportunities to control selectivity via secondary interactions. Opportunities for such materials to be used to control tandem catalytic events. Challenge: Robust materials that provide enhanced selectivity at elevated temperatures.

Moderator: Morris Bullock  
(PNNL)

- **Invited Speaker:** Wenbin Lin (U. Chicago)  
"Metal-organic Frameworks as Single Site Solid Catalysts"
- Larry Que (U. Minnesota)  
"Bio-inspired Nonheme Iron Catalysts for Hydrocarbon Oxidations"
- John Hartwig (U.C. Berkeley–LBNL)  
"Studies on Homogeneous Catalysis for Efficient Synthesis from Chemical Feedstocks"

## Session 4: Bullock's Bullets

- Wenbin Lin

Metal-organic frameworks offer several attributes for catalysis:

- Can be recycled
- Can add functionality
- High porosity and large channels can be obtained
- Different reactivity and selectivity compared to homogeneous catalysts
- Tandem catalysis can be achieved
- Energy applications (solar energy, water splitting, artificial photosynthesis) showing promise in recent studies

- Larry Que

Non-heme iron catalysts for selective oxidations of C-H and C=C bonds  
Challenge is to avoid Fenton chemistry (formation of  $\bullet\text{OH}$ )  
Isotope labeling of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  provide key probes for mechanistic understanding  
Dihydroxylation usually has one O from  $\text{H}_2\text{O}_2$  and one from  $\text{H}_2\text{O}$   
Both Fe(III) and Fe(V) intermediates have been detected  
Hydrogen bonding can promote heterolytic cleavage  
High catalyst loading (10-20%) still required in many cases  
Holy Grail – use of  $\text{O}_2$  as oxidant

- John Hartwig

Metal catalysts for addition of N-H to C=C bonds  
Addition of O-H bonds (hydro-etherification) not well-developed, but has now been achieved with addition of phenols to alkenes  
Hydroarylation of unactivated alkenes in some cases, with activated ( $\text{CF}_3$ ) arenes  
Multi-dimensional screening vs. one-dimensional screening, with analysis by mass spec, led to discovery of hydroamination of an alkyne by a Cu catalyst (not a precious metal)



Moderator: Mahdi Abu-Omar (Purdue U.)

- **Invited Speaker:**  
Noritaka Mizuno (U. of Tokyo)  
"Design of Polyoxometalate-Based Molecular Catalysts for Bridging the Gap between Homogeneous and Heterogeneous Catalysis"
- Harold Kung (Northwestern)  
"Nanoconfinement Effects in Heterogeneous Catalysis"
- Geoffrey Coates (Cornell)  
"Development and Application of New Carbonylation Catalysts: Improvements in Regioselectivity, Stereoselectivity, Activity and Exploration of New Reactions"
- Robert Crabtree (Yale U.)  
"Moving to Nonprecious Metal Catalysis"

### Session 5: Abu-Omar's Bullets

- Mechanistic understanding is key to drive catalyst design and future improvements on reaction selectivity and rates.
- Cooperative catalysis in both homogeneous and heterogeneous systems is an emerging area with promise in emulating nature.
- Fundamental studies and deep understanding was a characteristic of the talks and creativity in the field.
- Approaches in catalysis research include (a) advancement based on mechanistic understanding, (b) combinatorial searches or optimizations, and (c) chemical intuition driven systematic ligand modifications. Each of these approaches appears to have advantages and disadvantages.
- The interaction of theory and experiment is increasing. However, there is a need for more proactive predictive/guiding power from theory.
- Size selection moving from homogeneous to heterogeneous catalysis.

Moderator: Richard Finke  
(Colorado State U.)

- **Invited Speaker:** Alan Goldman (Rutgers U.)  
"Addition of O-H Bonds to Olefins Catalyzed by Pincer-Iridium Complexes"
- Malcolm Chisholm (Ohio State U.)  
"Developing s-block Element Catalysis and New Chemical Transformations"
- Christopher Marshall (ANL)  
"Fundamental Understanding and Control of Selectivity and Deactivation in Biomass Conversion Catalysts"
- Eugene Chen (Colorado State U.)  
"Catalytic Conversion of Glucose and Cellulose into HMF and Subsequent Upgrading to Value-Added Chemicals and Liquid Fuels"
- Raul Lobo (U. Delaware)  
"Selective Catalytic Dehydration and Hydrodeoxygenation Reactions for the Production of Fuels and Chemicals from Biomass"

## Session 6: Finke's Bullets

Noticeable highlights from this session:

- Facile C-H activation-initiated, "indirect / back-door" mechanisms for activating strong C–F, O–H bonds
- Controlling ionic, labile metal catalysts via appropriate ligand chemistry
- The importance of catalyst deactivation studies en route to catalyst optimization
- The true catalyst may not be what the *Nature* or *Science* paper claims!
- Non-metal, for example NHCarbene, organo-catalysis can be clean and productive
- Some basic, bio-mass intermediate, catalytic conversions—and the still underexplored nature of biomass conversions and catalysis
- The careful, skeptical use of DFT in supporting or refuting proposed mechanistic pathways
- The importance and use of kinetic and mechanistic studies in rational catalytic reaction development
- Organocatalysis for biomass conversion and upgrading can be atom-economical, efficient, and selective.

Moderator: Bruce Gates (U.C. Davis)

- Johannes Lercher (PNNL, T.U. Munich)  
"Understanding Elementary Steps of Catalytic Conversions in Water to Achieve Complex Transformations"
- Suljo Linic (U. Michigan)  
"Photo-Catalysis on Plasmonic Metal Nanoparticles"
- Andreas Heyden (U. South Carolina)  
"Theoretical Investigation of Heterogeneous Catalysis at the Solid-Liquid Interface for the Conversion of Lignocellulosic Biomass Model Molecules"

## Session 7: Gates' Bullets

- Lercher
  - Conversion of lignin-derived biomass compounds, especially phenol to cyclohexanol to cyclohexane
  - Metal/zeolite catalyst
  - Bifunctional catalyst important to convert alcohol—dehydration plus HDO
  - EXAFS spectra show no effect of water on palladium hydride; XANES and EXAFS show nickel on carbon reduced to metal; some oxidation of iron in NiFe.
  - In bifunctional metal/zeolite catalyst, the acidic zeolite sites are dissociated in the presence of water
  - Alkylation can occur of aromatics can occur, controlled by pore environment; La beta zeolite favors alkylation over dehydration
- Linic
  - Ag nanoparticles doped with Co for ORR—synthesis and nanoparticle stability
  - Plasmonic photocatalysis with copper—rare, clear demonstration of surface plasmon effect
- Heyden
  - Calculations for complex reactions of biomass-derived compounds in water, including HDO of organic acids (e.g., decarbonylation and decarboxylation on Pt(111))
  - Considering solvation models, optimizing solvent by calculations
  - Water has significant effects on adsorption and reaction; water facilitates C–OH bond cleavage and C–H bond cleavage in propanoic acid

## Session 8: Waymouth's Bullets

Moderator: Robert Waymouth  
(Stanford U.)

- Jens Norskov (SLAC, Stanford U.)  
"Theoretical Description of CO<sub>2</sub> Reduction"
- Aditya Bhan (U. Minnesota)  
"One-Pot Catalytic Conversion of Biomass and Alkanes: Kinetically Coupling Deoxygenation and Dehydrogenation Pathways"
- Jose Rodriguez (BNL)  
"Catalysis: Reactivity and Structure"

- Jens Norskov

--Scaling Relationships provide a means of correlating catalytic behavior complex catalytic reactions on surfaces: Good correlations between calculated thermodynamics of bound intermediates and catalytic behavior.

--Reactivity dominates on step edges.

--Scaling predictions can be predictive to identify new catalysts (Ni<sub>5</sub>Ga<sub>3</sub>)

In some cases, scaling laws provide insights on when more complex bifunctional catalysts are needed to catalyze particularly challenging reactions (N<sub>2</sub> reduction).

- Aditya Bhan

--Where can we get hydrogen to upgrade biomass? Use of methane for hydrogen transfer reactions.

--MoC in ZSM-5 methane to benzene; influence of oxygenates of forward rates. Oxygenates modify catalyst bed and generate hydrogen.

- Jose A. Rodriguez

--Electronic effects of supports on metal overlayers. Supports such as TiC, CeO<sub>2</sub> influence reactivity of metal adlayers.

--Au<sub>4</sub> on TiC - hydrodesulfurization: thiophene binds strongly to small clusters or adlayer of Au...larger Au nanoparticles don't bind effectively.

--Metal-support interactions exhibit significant electronic effects on metal catalysts.

Moderator: Christopher Jones  
(Georgia Inst. Tech.)

- Zili Wu (ORNL)  
"Revealing the Surface Structure of Ceria Nanocrystals with Well-Defined Facets"
- Will Medlin (U. Colorado)  
"Selectivity Control through Modification of Metal Catalysts with Organic Monolayers"

### Session 9: Jones' Bullets

- Wu
  - well-defined nanomaterials used to study crystal plane effects on catalysis with metals for years
  - similar studies based on oxides more rare
  - ceria nanomaterials gives insights into crystal plane effects for fixed nanoparticle size
  - evaluated via high resolution TEM and operando studies
- Medlin
  - controlling C-O vs. C-C bond scission in furanics on metal catalysts
  - control adsorption via control of access to surface by design of organic thiol Au surface modifiers
  - allows significant control over selectivity with large reduction in rates