
**Pacific Northwest
National Laboratory**
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Pacific Northwest National Laboratory Catalysis Highlights for FY2007

B. C. Garrett (Editor)

November 2007



Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

To reduce the nation's dependency on imported oil and to reduce emissions of greenhouse gases, the U.S. Department of Energy (DOE) and other federal and private agencies are investing in understanding catalysis. This report focuses on catalysis research conducted by Pacific Northwest National Laboratory (PNNL) and its collaborators.

Using sophisticated instruments in DOE's Environmental Molecular Sciences Laboratory, a national scientific user facility, research was conducted to answer key questions related to the nation's use of automotive fuels. Research teams investigated how hydrogen can be safely stored and efficiently released, critical questions to use this alternative fuel. Further, researchers are answering key questions to design molecular catalysts to control the transfer of hydrogen atoms, hydrides, and protons, important to hydrogen production. In dealing with today's fuels, researchers examined adsorption of noxious nitrous oxides in automotive exhaust.

Beyond automotive fuel, our researchers worked on catalysts to harness solar power. These catalysts include the rutile and anatase forms of titanium dioxide. Basic research was conducted on designing catalysts for these and other applications. Our scientists examined how to build catalysts with the desired properties atom by atom and molecule by molecule.

In addition, this report contains brief descriptions of the outstanding accomplishments of catalysis experts at PNNL. Highlights include leadership and recognition in professional societies, such as the newly elected leader of a prestigious professional society and three staff being named American Association for the Advancement of Science Fellows. Further, the Laboratory's staff made strong contributions in publishing, working on the editorial boards of several highly cited journals.

If you have questions on this research, contact Bruce C. Garrett, Pacific Northwest National Laboratory, Chemical & Materials Sciences Division, PO Box 999, Richland, WA 99352; 509-372-6344; bruce.garrett@pnl.gov.

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Science Highlights

Improved Understanding of Metal-Hydrogen and Carbon-Hydrogen Bonds

An improved understanding of how metal-hydrogen and carbon-hydrogen bonds are made and broken can lead to the rational design of new molecular catalysts that are needed in many types of reactions relevant to energy use and storage. Hydrogen atom transfer reactions are fundamentally important in many catalytic reactions. Hydrogen atom transfers *from* metal hydrides *to* carbon-centered radicals are involved in certain types of hydrogenation processes, for example. A research team from Pacific Northwest National Laboratory and Brookhaven National Laboratory has begun to investigate the *opposite* process—hydrogen atom transfer *from* a carbon-hydrogen bond *to* a metal-centered radical, a reaction that is relevant to activation of carbon-hydrogen bonds in hydrocarbons, as a step in their conversion to higher-value chemicals and fuels.

Reactivity studies of osmium suggest that it forms very strong bonds to carbon and hydrogen, so it was chosen for the initial studies. Laser flash photolysis of $[\text{Cp}(\text{CO})_2\text{Os}]_2$ and observation of the infrared spectrum of the CO region by transient infrared spectroscopy show that the osmium-osmium bond is homolytically cleaved, resulting in the formation of the osmium-centered radical, $\text{Cp}(\text{CO})_2\text{Os}\cdot$. Density functional theory computations give infrared bands that are in agreement with the experimental spectrum, confirming the identity of this transient species as the metal-centered radical $\text{Cp}(\text{CO})_2\text{Os}\cdot$. When the photolysis of $[\text{Cp}(\text{CO})_2\text{Os}]_2$ is carried out in the presence of 1,4-cyclohexadiene, carbon-to-metal hydrogen atom transfer occurs, leading to the formation of $\text{Cp}(\text{CO})_2\text{OsH}$. This is the first reported direct observation of carbon-to-metal hydrogen atom transfer; the rate constant was determined to be $k_{\text{H}} = (2.1 \pm 0.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 22°C.

Principal Investigators:

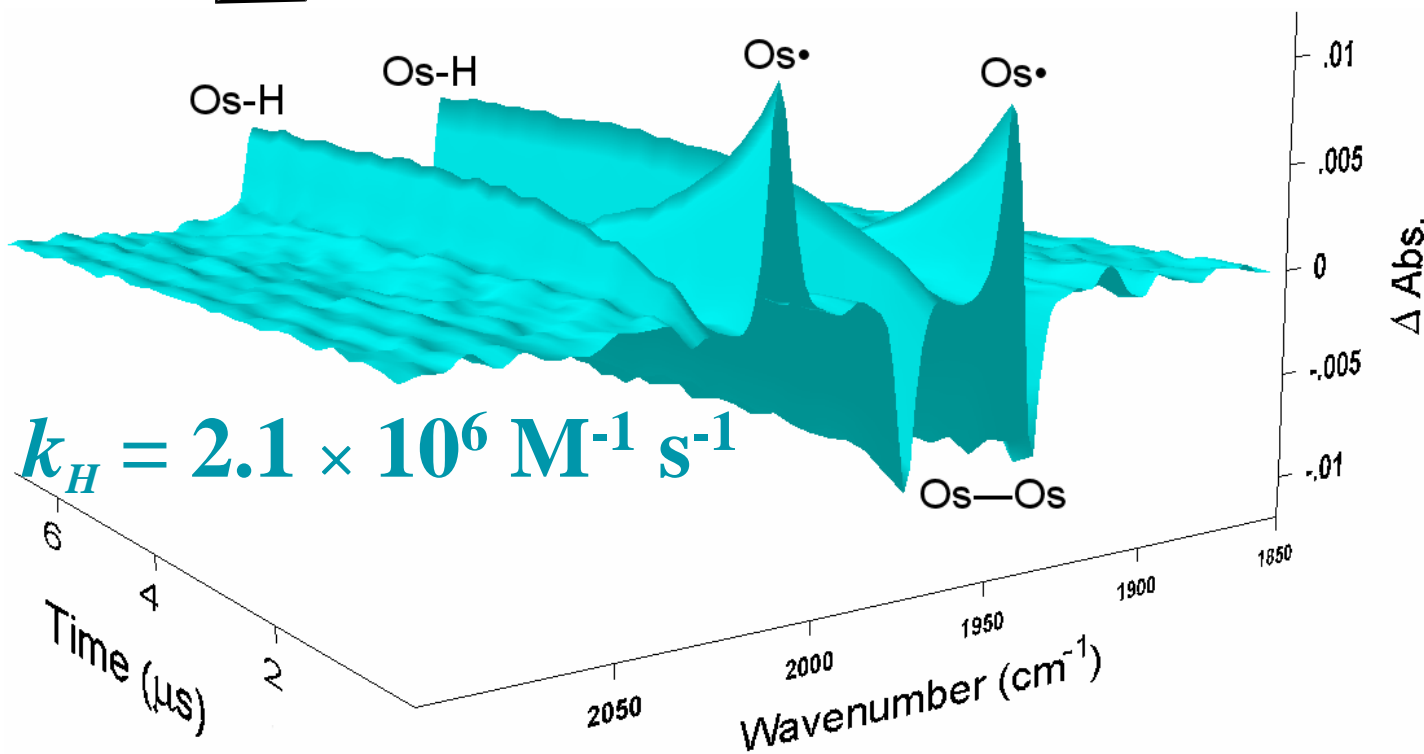
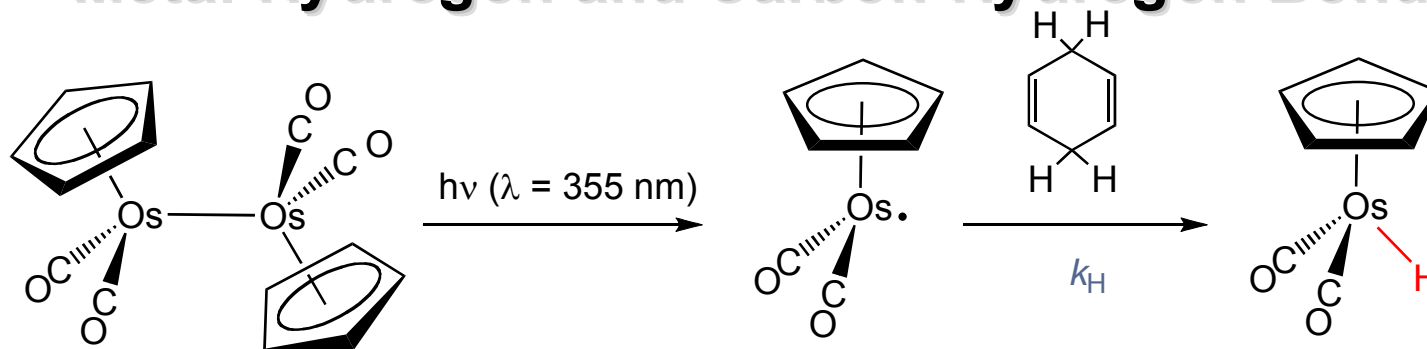
R. Morris Bullock and Etsuko Fujita

Citations:

Zhang, J, DC Grills, KW Huang, E Fujita, and RM Bullock. 2005. “Carbon-to-Metal Hydrogen Atom Transfer: Direct Observation Using Time-Resolved Infrared Spectroscopy.” *Journal of the American Chemical Society* 127:15684-15685.

These results were highlighted as an “Editor’s Choice” in the Nov. 4, 2005, issue of *Science*.

Improved Understanding of Metal-Hydrogen and Carbon-Hydrogen Bonds



Identifying Nucleation Sites for Catalytic Phase on γ -Al₂O₃

The formation of many catalysts at a molecular level is a mystery. Using a unique nuclear magnetic resonance (NMR) spectrometer, located at the U.S. Department of Energy's Environmental Molecular Sciences Laboratory, a national scientific user facility, Pacific Northwest National Laboratory scientists have, for the first time, observed where and how BaO—an absorber of NO_x products in exhaust streams—interacts with a penta-coordinated Al³⁺ atom on the surface of an aluminum lattice of Al₂O₃. The results of this study provide fundamental knowledge that suggests exactly where the nucleation site occurs and may contribute to an atom-by-atom approach for building better catalysts.

In their studies, the researchers readily observed penta-coordinate Al³⁺ ions in γ -Al₂O₃ using ultra-high-field ²⁷Al magic angle spinning NMR at an ultra-high magnetic field of 21.1 T and at sample spinning rates of up to 23 kHz. Under these experimental conditions, a peak in the NMR spectrum at ~23 ppm with relatively low intensity, assigned to 5-coordinated Al³⁺ ions, is clearly distinguished from the two other peaks representing Al³⁺ ions in tetra- and octahedral coordination. Spin-lattice ²⁷Al relaxation time measurements show that these penta-coordinated Al³⁺ sites are located on the surface of the γ -alumina support. Catalytic phases nucleate at these penta-coordinated sites.

Investigators:

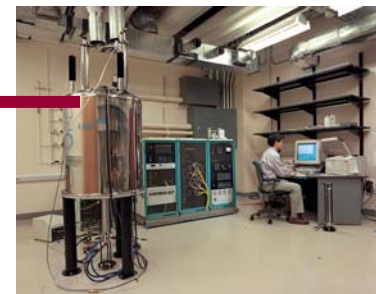
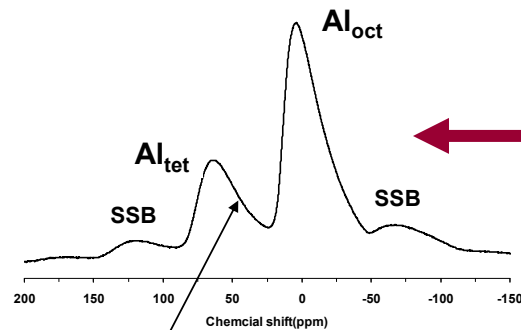
Ja Hun Kwak, Jian Zhi Hu, Do Heui Kim, Janos Szanyi, and Charles HF Peden

Citations:

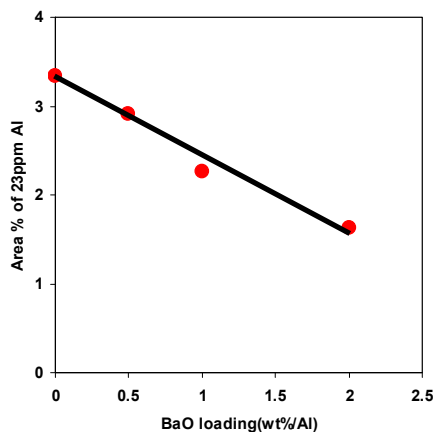
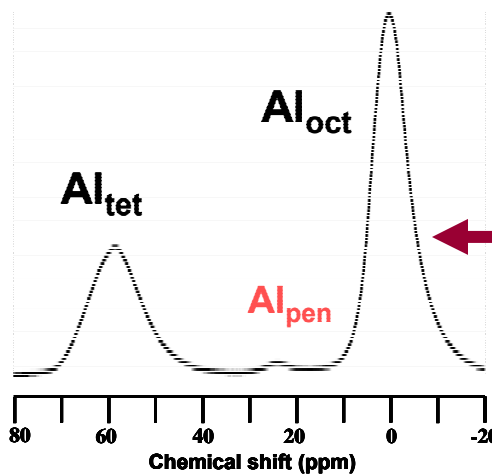
Kwak, JH, JZ Hu, DH Kim, J Szanyi, and CHF Peden. 2007. "Penta-coordinated Al³⁺ Ions as Preferential Nucleation Sites for BaO on γ -Al₂O₃." *Journal of Catalysis* 251(1):189-194.

Identifying Nucleation Sites for Catalytic Phase on γ -alumina

- Penta-coordinate Al^{3+} ions readily observable in $\gamma\text{-Al}_2\text{O}_3$ using ultra-high field ^{27}Al NMR.
- Via spin-lattice relaxation measurements, these species were determined to be located on the alumina surface.



$\text{Al}_{\text{pen}}??$



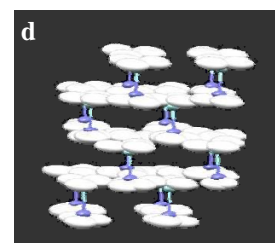
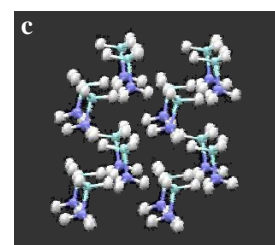
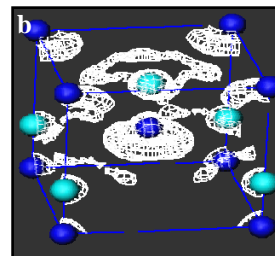
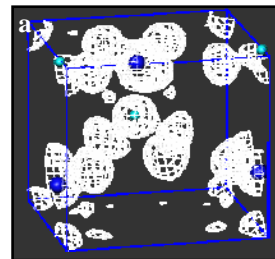
- Catalytic phases, e.g., BaO (at left), nucleate at these penta-coordinated sites.
- Results suggest strategies for improving dispersions in oxide-supported catalysts.

Neutron Spectroscopy to Study Dynamics in Hydrogen Storage Materials

The special *di-hydrogen* bonding interaction—attractive interaction between protonic and hydridic hydrogen—seen in ammonia borane has been proposed as an important feature in materials that release molecular hydrogen at moderate temperatures, required for fuel cell powered vehicles. However, little is understood about the details of these hydrogen-hydrogen interactions.

This study by Pacific Northwest National Laboratory and Los Alamos National Laboratory resolved the ambiguity over the directionality of the hydridic and protic hydrogen-bonding interactions. Combining theory and experiment, using neutron-scattering techniques, provides greater insight into the structure and dynamics of hydrogen-rich materials. By combining periodic density functional theory calculations with inelastic neutron-scattering methods, we assigned crystal normal modes of ammonia borane at 15 K. The low-frequency modes and lattice modes provide key insight into the di-hydrogen bonding interactions.

The figures show the spatial representations of the hydrogen derived from the Fourier transform of the experimental neutron-scattering intensity mapped onto the refined crystal structure obtained from neutron powder diffraction (NPD) experiments at a temperature above (a) and below (b) the phase transition. For comparison, the hydrogen positions were calculated using only the experimental lattice parameters from NPD for the lowest energy structures using periodic electronic structure combined with dynamics at the same temperatures above (c) and below (d) the phase transitions. Both theory and experiment show that the orthorhombic to tetragonal phase transition in ammonia borane catalyzes the motion of the hydrogen in the solid state. The hydrogen in the orthorhombic phase (180 K) is highly localized in contrast to the hydrogen in the tetragonal phase (275 K). The hydrogen is HIGHLY delocalized. The NPD experiment cannot even define a position, and theory concurs that the hydrogen is very mobile even though there is significant di-hydrogen bonding.



Principal Investigators:

Tom Autrey; Nancy Hess and Greg Schenter, coPI

Citations:

Feaver, AM, P Shamberger, G Cao, AC Stowe, and T Autrey. 2007. “Coherent Carbon Cryogel-Ammonia Borane Nanocomposites for Improved Hydrogen Storage.” *Journal of Physical Chemistry B* 111(26):7469-7472.

Gunaydin-Sen, O, R Achey, NS Dalal, AC Stowe, and T Autrey. 2007. “High Resolution ^{15}N NMR of the 225 K Phase Transition of Ammonia Borane.” *Journal of Physical Chemistry B* 111(4):677-681.

Stowe, AC, WJ Shaw, JC Linehan, B Schmid, and T Autrey. 2007. “In Situ Solid State B-11 MAS-NMR Studies of the Thermal Decomposition of Ammonia Borane.” *Physical Chemistry Chemical Physics* 9(15):1831-1836.

Neutron Spectroscopy to Study Dynamics in Hydrogen Storage Materials

Molecular Simulation

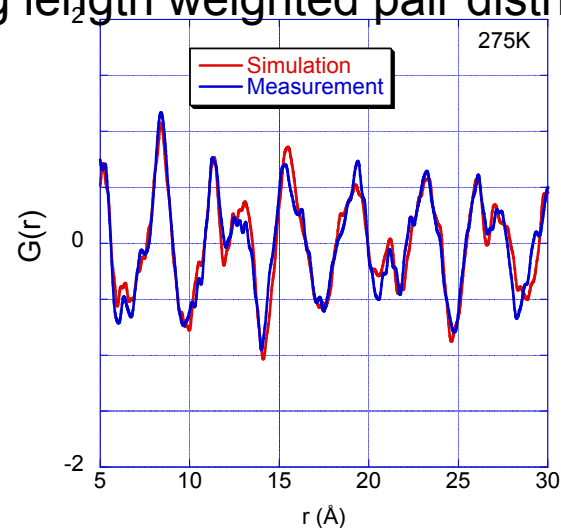
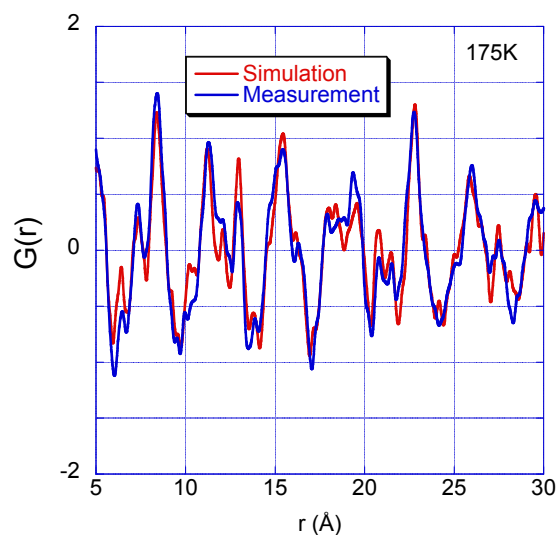
CP2K software
DFT electronic structure
PBE functional
TZVP basis set
Goedecker pseudopotential

and

Neutron Powder Diffraction Measurement

ND₃¹¹BD₃ synthesized at PNNL and LANL
Data collected at LANSCE Lujan Center
on NPDF diffractometer
PDFgetN data reduction software for extraction
of experimental PDF

Pair Distribution Function, $G(r)$ = Fourier transform of Structure Factor, $S(Q)$
= scattering length weighted pair distribution function



Excellent agreement between theory and experiment only occurs if correlated molecular motions are included!

Using XAFS to Understand Rhodium Catalysts for Releasing Hydrogen

A research team from Pacific Northwest National Laboratory, Argonne National Laboratory, and the University of Oregon used x-ray absorption fine structure (XAFS) spectroscopy to determine the structure of the rhodium cluster present during the catalyzed dehydrocoupling of amine boranes under operando conditions. The XAFS provides structural information on the resting state of the catalyst under operating conditions, comparable to the information gained regarding x-ray crystal structure when crystals cannot be isolated. The team showed how various XAFS strategies can be used with other analytical methods to differentiate homogeneous from heterogeneous systems. By analyzing the in situ XAFS spectra, the research team determined that the active catalyst species for releasing hydrogen from amine boranes is a homogeneous rhodium complex.

In the experiments, rhodium clusters containing four or six rhodium atoms bound to amine boranes were observed as the major rhodium-containing species during and after the catalyzed anaerobic dehydrocoupling. During the later stages of the reaction, a nonmetallic rhodium complex precipitates in which individual rhodium clusters likely form polymer chains ligated by the reaction products that have two or more ligating sites. The best fits of the XAFS data show that 80 percent of the rhodium species contain a rhodium atom directly bound to three rhodium atoms with an observed bond distance of 2.73 Å and to two boron atoms at 2.10 Å. Twenty percent of the rhodium species have each rhodium atom bound to four rhodium atoms with a bond distance of about 2.73 Å, and a single rhodium atom at a nonbonding distance of 3.88 Å. Metallic rhodium was not observed at any time during the anaerobic reaction.

Principal Investigators:

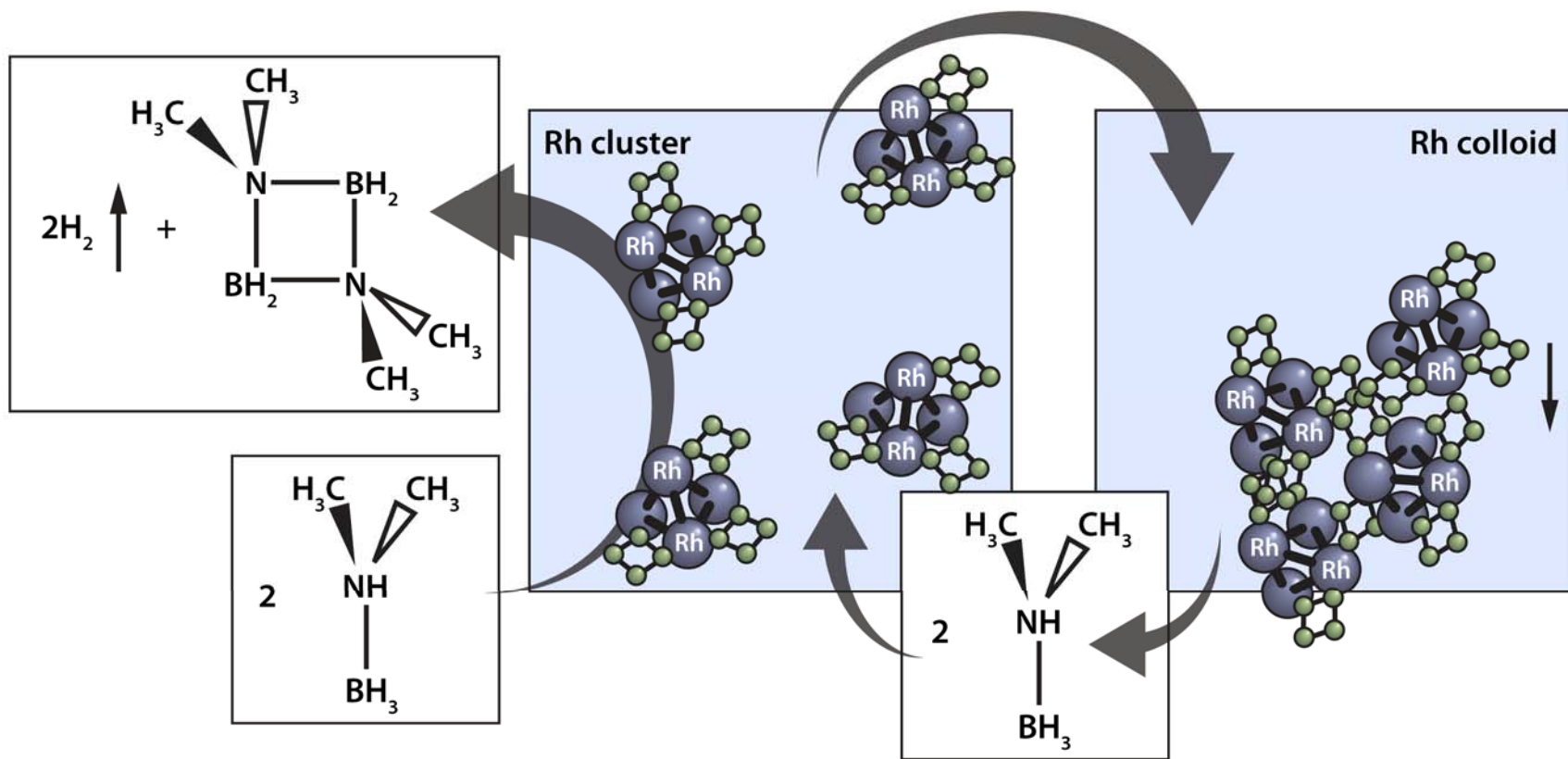
Tom Autrey, John L. Fulton, and John Linehan

Citations:

Fulton, JL, JC Linehan, T Autrey, M Balasubramanian, YS Chen, and NK Szymczak. 2007. "When Is a Nanoparticle a Cluster? An Operando EXAFS Study of Amine Borane Dehydrocoupling by Rh₄₋₆ Clusters." *Journal of the American Chemical Society* 129(39):11936-11949.

When is a Nanoparticle a Cluster?

Using XAFS to Understand Rhodium Catalysts for Releasing Hydrogen

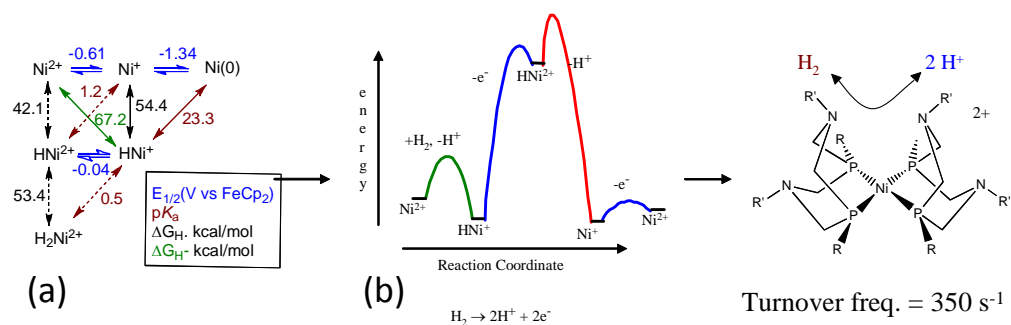


J. AM. CHEM. SOC. 2007, 129, 11936-11949

Design of Highly Active Ni-based Molecular Catalysts for H₂ Production/Oxidation

Recent studies of molecular catalysts in the laboratories at Pacific Northwest National Laboratory, the University of Colorado, and the National Renewable Energy Laboratory indicate that pendant bases incorporated in the second coordination sphere of the metal are critical for highly efficient catalytic processes. These relays facilitate the rapid and precise delivery of protons to the active metal site. The catalysts depicted in structure 1 are based on nickel, an inexpensive, first-row transition metal. Catalyst 1 (where R=R' = phenyl) produces H₂ at a turnover frequency of ~350 s⁻¹ at 22°C, approaching those of [NiFe] hydrogenase enzymes. Catalyst 1 is air stable and uninhibited by carbon monoxide, unlike commercial platinum catalysts and hydrogenase enzymes. Slight variations in the structure produce catalysts for H₂ oxidation.

The design of these catalysts proceeds as shown in the figure. Thermodynamic diagrams (a) are generated and used to construct reaction profiles (b) illustrating the relative energies of the intermediates for various possible mechanisms. This information is used to determine the optimal structural features of the first coordination sphere. Second, pendant bases of appropriate basicity are incorporated into the second coordination sphere to facilitate proton transfer reactions between the metal and solution.



Although these tools have been applied to the development of catalysts for H₂ production and oxidation, they are broadly applicable to for designing catalysts for reactions involving multiple electron and proton transfers.

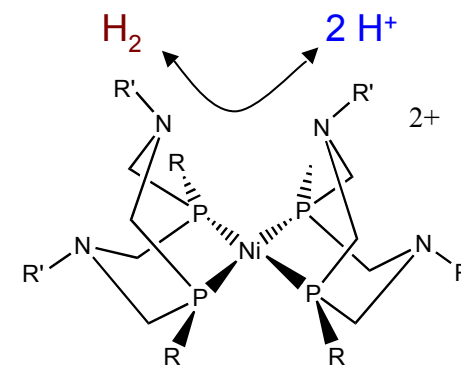
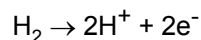
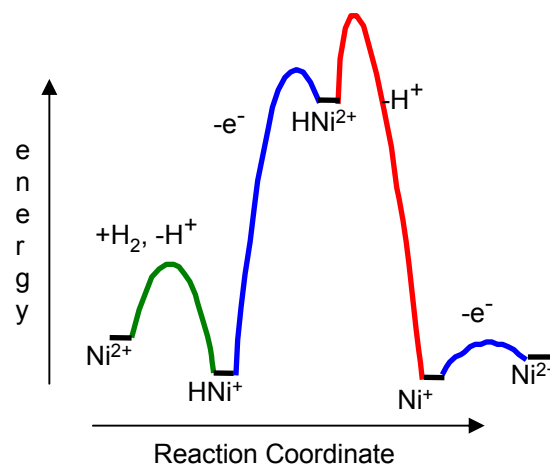
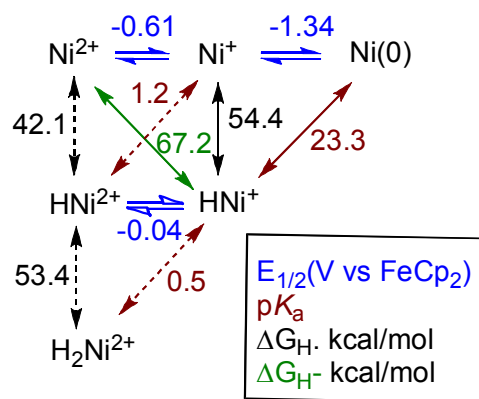
Principal Investigator:

Dan DuBois

Citations:

Wilson, AD, RK Shoemaker, A Meidaner, JT Muckerman, M Rakowski DuBois, and DL DuBois. 2007. "Coordination Chemistry of Saturated Molecules Special Feature." *Proceedings of the National Academy of Sciences* 104:6951-6956.

Design of Highly Active Ni-based Molecular Electrocatalysts for H₂ Production/Oxidation



Turnover freq. = 350 s⁻¹

Quantitative determination of thermodynamic relationships from models or experiment

→ Determine reaction profiles

→ Design first and second coordination spheres of catalyst

Behavior of Hydrogen on Catalyst's Surface Reveals Intriguing Details

Researchers at Pacific Northwest National Laboratory and the University of Texas at Austin discovered that a single hydrogen atom moves after it splits from a water molecule on the surface of the catalyst rutile titanium oxide. The hydrogen atom hopscoches across the oxygen atoms that stud the surface of the catalyst, while the hydrogen on what is left from water remains fixed, suggesting that the electronic structure of this popular catalyst is not entirely as it seems.

By understanding how water's atoms behave on this catalyst's surface, scientists and engineers may be able to develop more efficient solar cells, corrosion-resistant materials, and technologies that split water to generate hydrogen gas.

Using a scanning tunneling microscope, the researchers examined the atoms on the catalyst's surface before and after water adsorption. The surface's topographical map looks like a washboard on a dirt road with ridges and valleys repeating indefinitely. Here the ridges are rows of oxygen atoms and the valleys are rows of titanium atoms. When one of the oxygen atoms is removed it exposes the underlying titanium and creates the reactive pocket on the catalyst.

When water reaches the surface, at room temperature, the water molecule discards one of its two hydrogen atoms. What remains of the water molecule, an oxygen bonded to a hydrogen, settles into one of the reactive pockets, and the discarded hydrogen binds to the nearest oxygen.

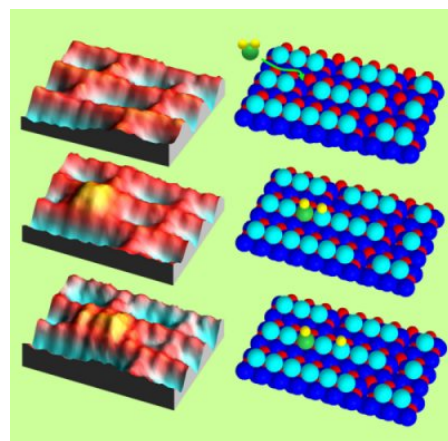
The discarded hydrogen then begins to move down the row of oxygen atoms. This hydrogen is roughly 10 times more likely to move than the other hydrogen from the same water molecule. This research points to an underlying difference in the atomic structure near the catalyst's active sites.

Principal Investigators:

Zdenek Dohnálek

Citations:

Zhang, Z, O Bondarchuk, BD Kay, JM White, and Z Dohnálek. 2006. "Imaging Water Dissociation on TiO₂(110): Evidence for Inequivalent Geminate OH Groups." *Journal of Physical Chemistry B* 110:21840-21845.



A scanning tunneling microscope (left) shows the atoms on the catalyst's surface before (top), during and after (bottom) water adsorption. The red ridges are oxygen atoms; the light blue valleys, titanium atoms. The yellow is the hydrogen atoms from the water molecule. On the right is a model showing water splitting.

Behavior of Hydrogen on Catalyst's Surface Reveals Intriguing Details

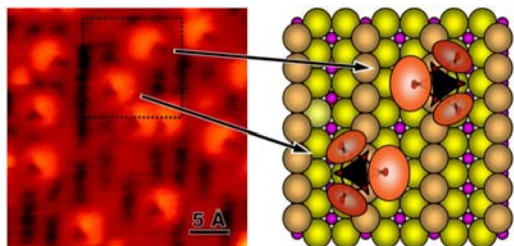
- ▶ Water dissociation on $\text{TiO}_2(110)$ imaged using scanning tunneling microscopy before and after water adsorption
- ▶ Evidence found for inequivalent geminate OH groups from dissociation at an oxygen vacancy
- ▶ Hydrogen on what is left from water remains fixed suggesting an unexpected twist on the electronic structure of this popular catalyst



New Model System Offers Insight into Catalyst Structure and Behavior

Developed by researchers from Pacific Northwest National Laboratory, the University of Texas-Austin, and Washington State University, the formation of a new model system of cyclic $(\text{WO}_3)_3$ clusters, which line up molecule-by-molecule on TiO_2 , may offer a platform for fundamental reactivity studies of metal oxides used as catalysts in converting hydrocarbons into fuels and value-added chemicals.

There is a striking difference between commercial catalysts and the new model system. Variability in commercial catalyst size and chemical composition makes it difficult to accurately understand or describe the



Images from the scanning tunneling microscope show the first-ever imaging of monodisperse oxide clusters on another oxide. The dark triangles show the center of the tungsten trioxide trimer, while the brighter side of the triangle indicates the raised tungsten atom. Consistent orientation of the atoms is shown in the graphic.

reactions taking place at a molecular level. The model system—where all the molecular clusters are the same size, are evenly dispersed, and are oriented in one of two directions on a single layer of TiO_2 crystals—holds promise as a platform for studying the behavior of early-transition metal oxides.

Though it appears simple, the model system was very challenging to develop. The collaborators employed specialized instruments available from the U.S. Department of Energy's Environmental Molecular Sciences Laboratory, a national scientific user facility located at PNNL, to prepare and characterize the platform as well as the clusters. Using a unique approach that changed the tungsten oxide directly from a solid to a gas, the collaborators successfully stabilized the trimers of tungsten on the titania platform.

A scanning tunneling microscope imaged not only the trimers but also their consistent alignment with the single-crystal structure of the platform. In addition to scanning tunneling microscopy, the collaborators characterized the cluster mass, determined the stoichiometry, and identified the tungsten oxidation state using x-ray photoelectron spectroscopy.

For the first time, researchers have created and imaged monodisperse oxide clusters on another oxide.

Principal Investigators:

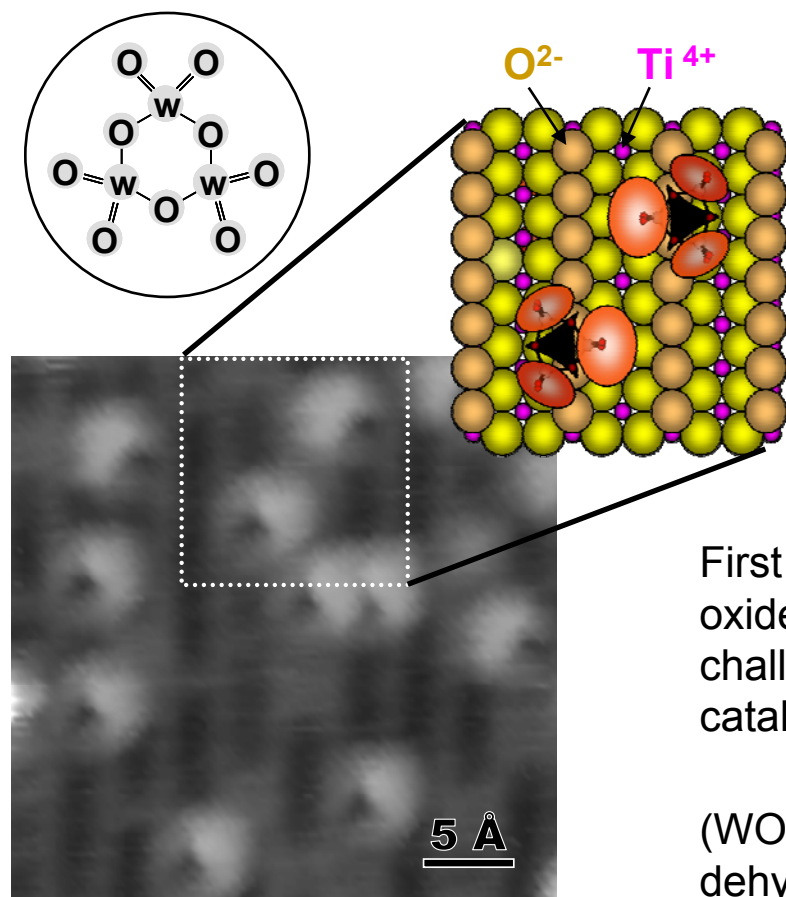
Zdenek Dohnálek and Bruce Kay

Citations:

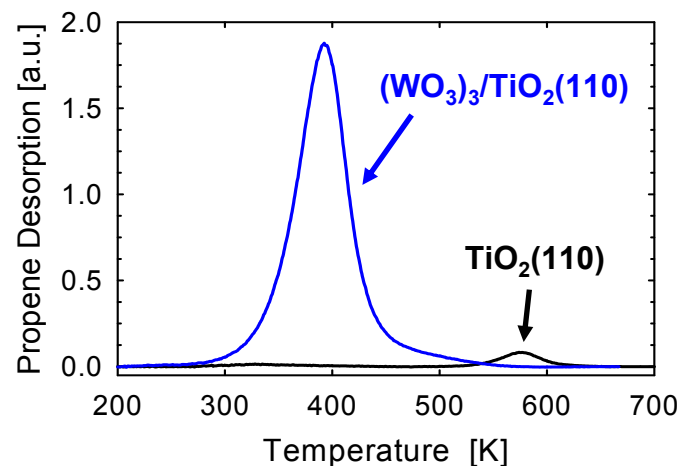
Bondarchuk, O, X Huang, J Kim, BD Kay, LS Wang, JM White, and Z Dohnálek. 2006. "Formation of Monodisperse $(\text{WO}_3)_3$ Clusters on $\text{TiO}_2(110)$." *Angewandte Chemie International Edition* 45(29):4786-4789.

New Model System Offers Insight into Catalyst Structure and Behavior

Scanning Tunneling Microscopy of Monodispersed $(\text{WO}_3)_3$ on $\text{TiO}_2(110)$



Alcohol Dehydration on $(\text{WO}_3)_3 / \text{TiO}_2(110)$



First successful attempt to form monodispersed oxide clusters on an oxide support: a significant challenge for nanoscience and for creating model catalysts

$(\text{WO}_3)_3$ clusters efficiently catalyze alcohol dehydration reducing temperature (~ 175 K) and increasing yield compared to $\text{TiO}_2(110)$ substrate

The First Experimental Confirmation of Cooperative NO₂ Adsorption on BaO

As potential NO_x storage materials in lean automotive pollution abatement catalysis, supported alkali and alkaline earth oxides have been studied extensively. However, the initial adsorption of NO₂ over these materials is still poorly understood. Theoretical studies unambiguously support a pair-wise (cooperative) adsorption of NO₂ on alkaline earth oxides, resulting in the formation of nitrite-nitrate ion pairs. At high NO₂ exposures or at elevated temperatures, the initially formed nitrites are oxidized to nitrates by NO₂, resulting in the conversion of all the oxide material to nitrates. In contrast, previous experimental studies concluded that no direct nitrate formation occurred upon the exposure of BaO to NO₂.

These controversial results between theory and experimental work prompted Pacific Northwest National Laboratory to revisit the problem of the initial interaction of BaO with NO₂. Using a reactive-layer-assisted deposition method, we prepared a pure, greater-than-30-monolayer BaO film on an Al₂O₃/NiAl(110) substrate. The adsorption and reaction of NO₂ on the BaO film were then studied at temperatures up to 300 K using temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), and reflection absorption infrared spectroscopy (RAIRS). The TPD results revealed that both nitrite and nitrate species formed on BaO even at the lowest NO₂ exposure at 90 K. In addition, no weakly held physisorbed NO₂/N₂O₄ was seen on the sample until the strongly held NO_x species reached saturation coverage. The result of the XPS and RAIRS experiments substantiated this observation and confirmed the simultaneous formation of nitrites and nitrates in comparable quantities.

The results of our study unambiguously show that NO₂ adsorbs cooperatively on BaO, and nitrite-nitrate ion pairs form in equal quantities until the first layer of NO_x forms on the BaO surface under ultra-high vacuum conditions. Our study also revealed that the nitrite species formed during the initial stage of NO₂ adsorption can be oxidized by another NO₂ to form nitrates. This process, however, is activated, and only takes place at elevated temperatures (>300 K) or at high NO₂ pressures. The reason that the cooperative adsorption of NO₂ on BaO in previous studies was not observed is that the thin BaO films used were always contaminated by the support material due to the high reactivity of BaO towards the supports. In our control experiments, we also observed nitrite formation only in the initial stages of NO₂ adsorption and the subsequent conversion (oxidation) of these nitrites to nitrates by NO₂.

Principal Investigators:

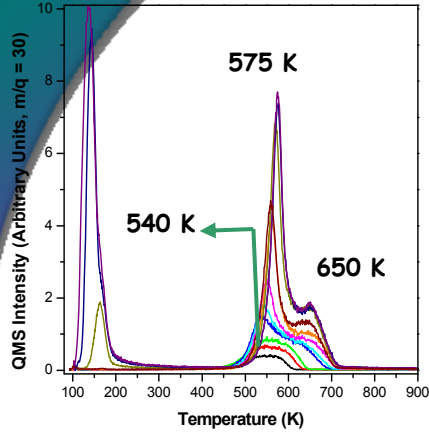
Cheol-Woo Yi and Janos Szanyi

Citations:

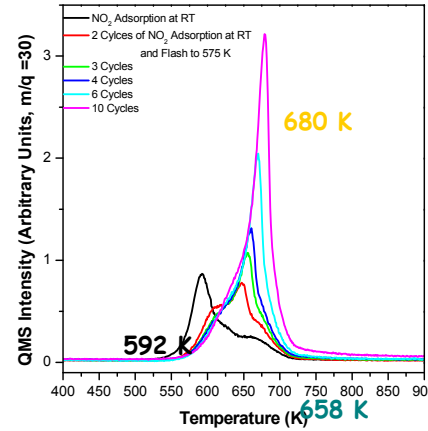
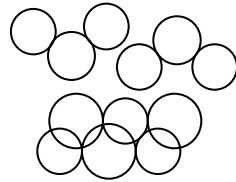
Yi, C, J Kwak, CHF Peden, CM Wang, and J Szanyi. 2007. "Understanding Practical Catalysts Using a Surface Science Approach: The Importance of Strong Interaction between BaO and Al₂O₃ in NO_x Storage Materials." *Journal of Physical Chemistry C* 111(41):14942-14944.

Yi, CW, JH Kwak, and J Szanyi. 2007. "Interaction of NO₂ with BaO: From Cooperative Adsorption to Ba(NO₃)₂ Formation." *Journal of Physical Chemistry C (Letter)* 111(42):15299-15305.

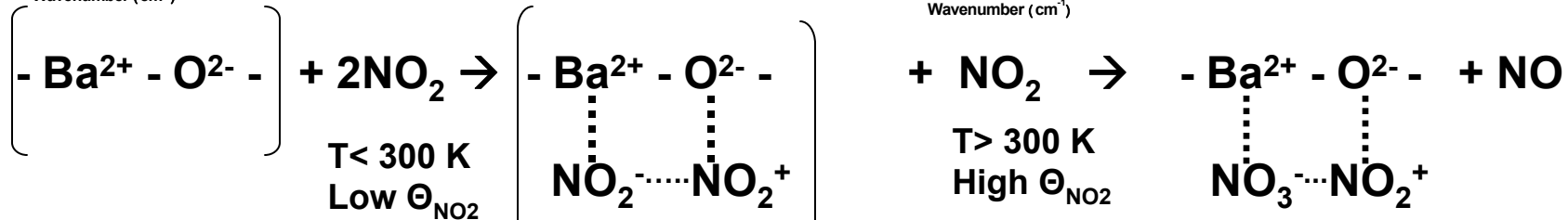
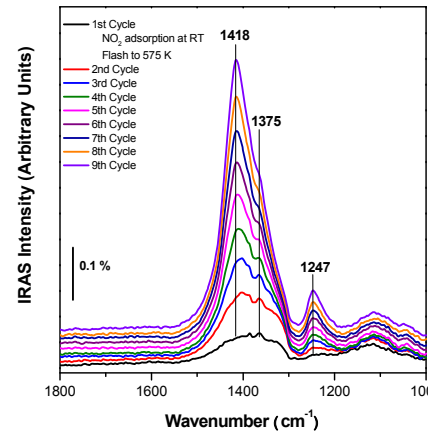
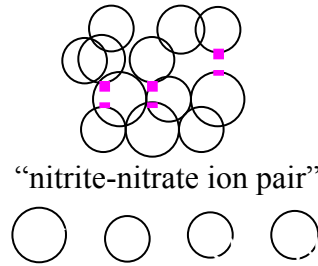
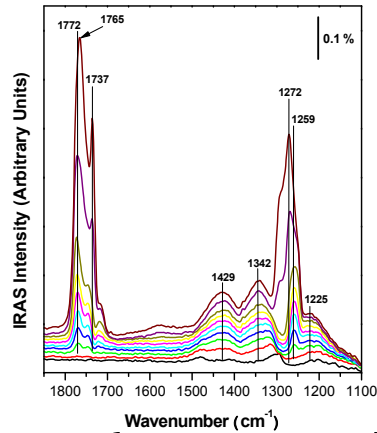
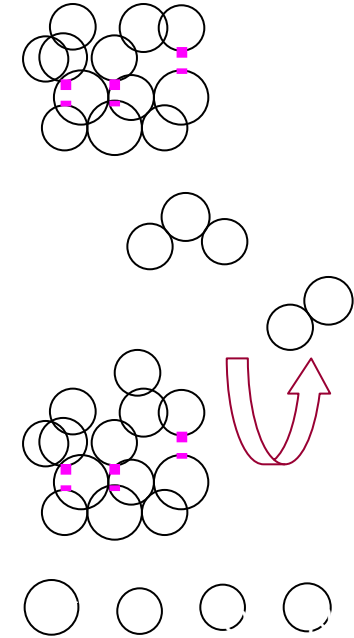
First Experimental Confirmation of Cooperative NO₂ Adsorption on BaO



Cooperative NO₂ Adsorption on BaO



Oxidation of NO₂⁻ to NO₃⁻ by NO₂



First Principles Modeling of e-/h+ Polaron Transport in TiO₂

The ability of photoexcited charges to diffuse from the bulk to the surface critically affects photocatalytic performance in TiO₂. Unfortunately, a large percentage of the energy dissipates as it moves from the bulk to the surface in a poorly understood process. Determining the inherent rates of charge-hopping in the absence of bulk defects or impurities is experimentally difficult. Employing the Marcus theory, Pacific Northwest National Laboratory researchers modeled the movement of electrons and the corresponding holes from the bulk to the surface in TiO₂. As part of this effort, we calculated the point charge hopping rates in both rutile and anatase TiO₂. The investigation showed that non-adiabatic activation energies for electron hopping have similar magnitudes in rutile and anatase.

Principal Investigator:

Michel Dupuis

Citations:

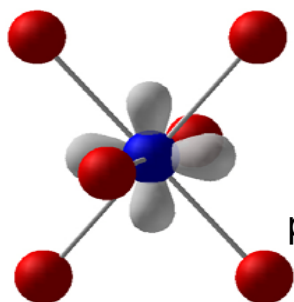
Dupuis, M. 2006. "Charge Transport in Metal Oxides: Theoretical Studies." International Congress of Quantum Chemistry (ICQC), Kyoto, Japan.

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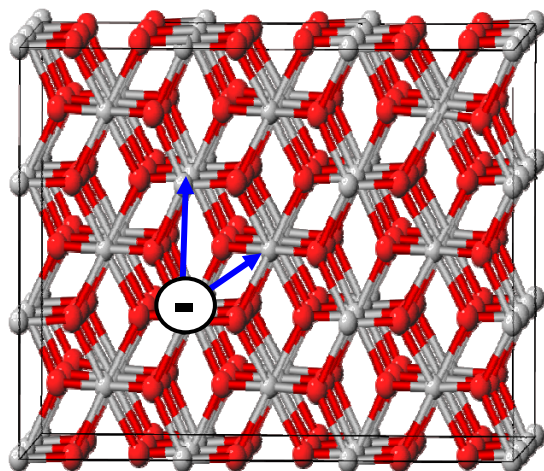
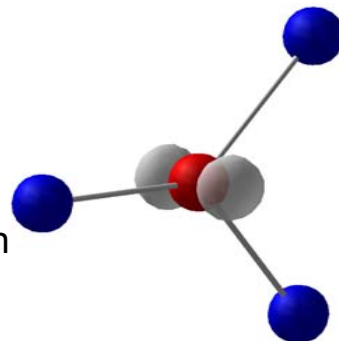
Deskins, NA. 2006. "Charge Transport in TiO₂: Theoretical Studies." ACS National Meeting, San Francisco, California.

Dupuis, M. 2007. "Charge Transport in Metal Oxides: Theoretical Studies." International Workshop on Oxide Surfaces (IWOX V), Lake Tahoe, California.

First Principles Modeling of e-/h+ Polaron Transport in TiO₂



Charge density difference plots of a Ti 3d T_{2g} electron polaron and O 2p hole polaron.



Hopping of an electron to adjacent Ti⁴⁺ site.

Results

- Non-adiabatic activation energies (ΔG^*) for electron hopping have similar magnitudes in rutile and anatase (~ 0.3 eV).
- Electronic coupling matrix element (V_{ab}) largest for electron polaron hopping parallel to $\langle 001 \rangle$ in rutile and indicative of adiabatic transfer (thermal hopping mechanism) with a value of 0.20 eV.
- Other directions investigated in both rutile and anatase gave V_{ab} values $\sim 1/10^{\text{th}}$ smaller, indicative of diabatic transfer (tunneling mechanism) in anatase.
- Hole polaron hopping has ΔG^* of 0.5-0.6 eV in rutile, and 0.4-0.6 eV in anatase.
- Hole localization on the (110) rutile surface.

Organic Radical Ejection During Photocatalysis on TiO₂(110)

Little is known about the detailed molecular mechanisms of organic photooxidation processes on TiO₂, so experts at Pacific Northwest National Laboratory, the University of California-Santa Barbara, the University of Alabama, and the Dalian Institute in China examined the photodecomposition of a series of ketones and aldehydes on TiO₂(110) using temperature-programmed desorption and photon-stimulated desorption. The research showed that the photoactivity of ketones and aldehydes requires prior thermal reaction between the organic and co-adsorbed oxygen to form a diolate species ((R1-)(R2-)COO). The diolates photodecompose by ejecting the more stable gas-phase radical from the surface as an organic radical. The companion fragment is left behind as a carboxylate species. The ejection of the organic radicals during ultraviolet irradiation may be a major mechanistic pathway in the photooxidizing organic compounds.

Principal Investigator:

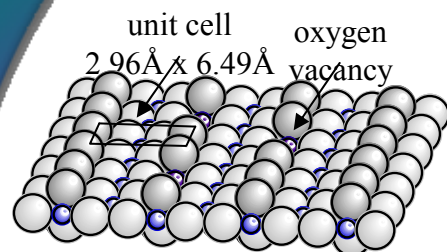
Mike Henderson

Citations:

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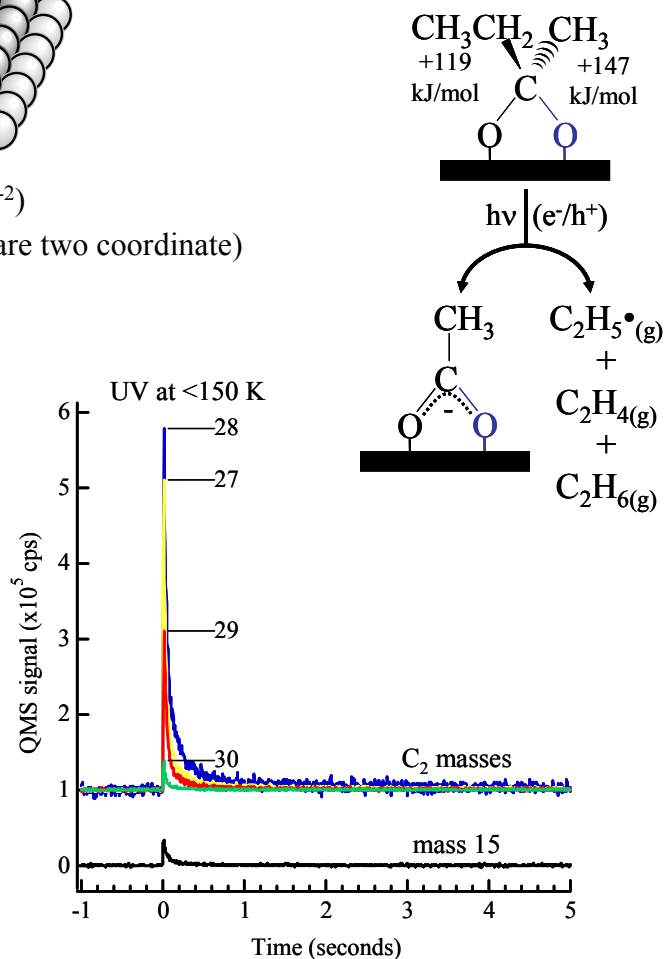
Henderson, MA. 2007. "Photon Stimulated Desorption of Organic Radicals During UV Photocatalysis on TiO₂(110)." Eleventh International Desorption Induced by Electron Transitions (DIET XI) Conference, Berlin, Germany.

Organic Radical Ejection During Photocatalysis on TiO₂(110)



- Ti cations ($5.2 \times 10^{14} \text{ cm}^{-2}$)
- O anions (shaded atoms are two coordinate)

UV irradiation of butanone adsorbed on O₂-predosed TiO₂(110)



Results

- Photoactivity of ketones and aldehydes requires prior thermal reaction between the organic and co-adsorbed oxygen to form a diolate species ((R₁-)(R₂-)COO).
- Diolates photodecompose by ejection of either R₁ or R₂ from the surface as an organic radical, leaving behind the companion fragment as a carboxylate species.
- More stable gas phase radical is preferentially ejected.
- Ejection of organic radicals during UV irradiation on TiO₂ surfaces may be a major mechanistic pathway in the photooxidation of organics such as ketones and aldehydes.

Adsorbate Ordering on the TiO₂(110) Surface

Intermolecular interactions play important roles in catalysis and photocatalysis. Researchers at Pacific Northwest National Laboratory explored the adsorption structure of trimethyl acetic acid (TMAA) on the same surface region on TiO₂(110) during TMAA adsorption. No significant surface diffusion was seen at room temperature. The initial adsorption involves isolated TMAA groups. Pairing occurs orthogonal to cation rows, suggesting an attractive interaction, most likely through influence of acid protons on bridging oxygen rows. This implies that TMAA photocatalysis selectivity change is initiated by TMAA pairing.

Principal Investigators:

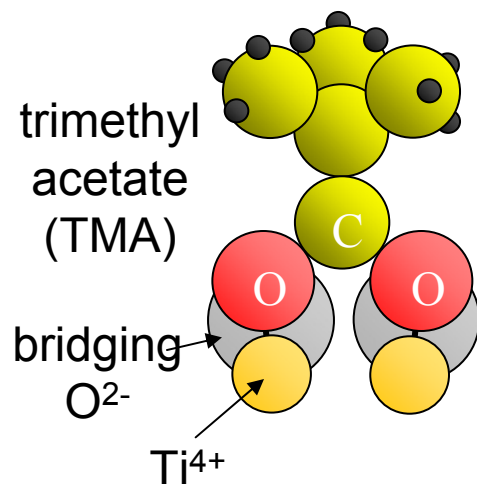
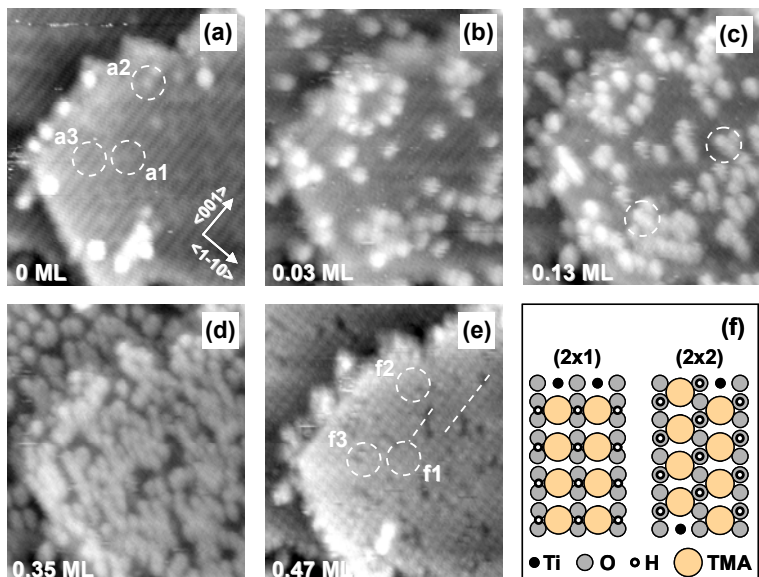
Igor Lyubinetsky and Mike Henderson

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Lyubinetsky, I, ZQ Yu, and MA Henderson. 2007. "Direct Observation of Adsorption Evolution and Bonding Configuration of TMAA on TiO₂(110)." *Journal of Physical Chemistry C* 111:4342.

Adsorbate Ordering on the $\text{TiO}_2(110)$ Surface

- (a) clean surface
- (b-e) increasing TMAA coverage
- (f) TMAA adsorption model



Results

- No significant surface diffusion at RT.
- Initial adsorption stage involves isolated TMA groups; pairing occurs for coverages above ~ 0.1 - 0.15 ML.
- Pairing occurs orthogonal to cation rows; suggests an attractive interaction, most likely through influence of acid protons on bridging O rows.
- Selectivity change in TMAA photocatalysis initiated by TMA pairing.

Molecular Dynamics Simulations of Rutile/Anatase Interfaces

The interfaces between rutile and anatase are important in photocatalysis with mixed-phase materials. These interfaces are important for understanding mixed-phase catalysts and a necessary first step toward characterizing electron/hole transport in these photo-active materials; for example, in mixed-phase TiO₂. Pacific Northwest National Laboratory researchers showed that adhesion energies for the most stable interfaces typically near -2 J/m². Interfaces are disordered but limited to a narrow region, in agreement with microscopy data. Formation of rutile octahedral structures is observed at the anatase side of the interface as a beginning of anatase to rutile phase transition. Simulations show promise for interpreting the complex interfaces resulting from mixed polymorphic materials.

The research team showed that adhesion energies for the most stable interfaces typically near -2 J/m². Interfaces are disordered, but single-phase regions are ordered, in agreement with microscopy data. We observed the formation of rutile octahedral structures at the anatase side of the interface and at the beginning of anatase to rutile phase transition.

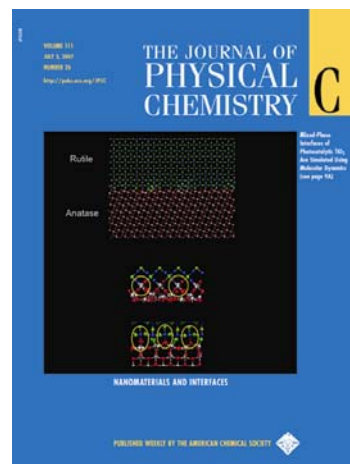
With the results of this investigation, scientists are now able to see the interface between the two materials and provide theorists with the structure at the interface, allowing theorists to model it for the first time. Researchers are now seeing that the whole of the combined rutile and anatase is greater than the sum of its parts.

Principal Investigator:

Mike Henderson

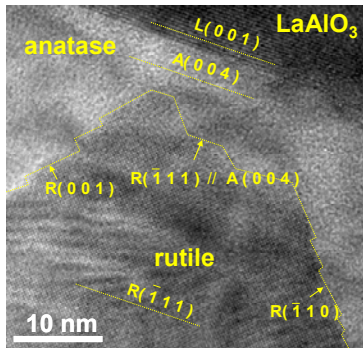
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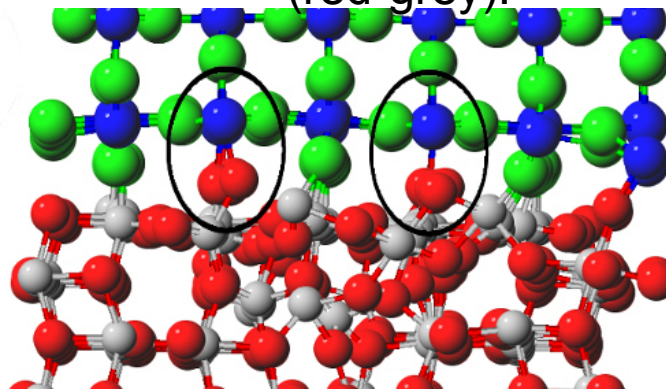


Molecular Dynamics Simulations of Rutile/Anatase Interfaces

TEM of an rutile-anatase interface



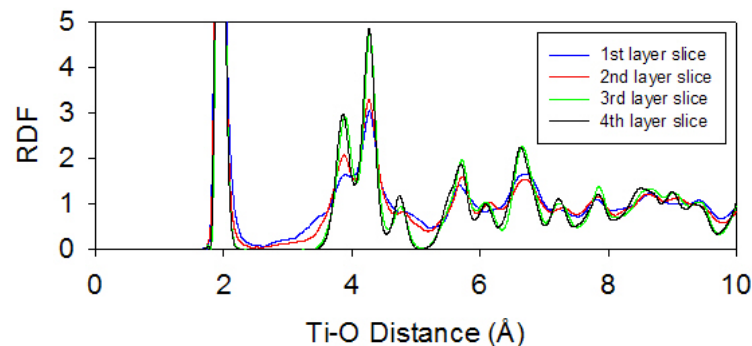
Interface between rutile (green-blue) and anatase (red-grey).



Results

- Adhesion energies for the most stable interfaces typically near -2 J/m^2 .
- Interfaces are disordered, but single phase regions are ordered, in agreement with TEM data.
- Formation of rutile octahedral structures observed at the anatase side of the interface; beginning of anatase to rutile phase transition.
- Simulations show promise for interpreting the complex interfaces resulting from mixed polymorphic TiO_2 materials.

RDF plot showing disorder as a function of distance from interface



Controlled Preparation of Mixed Rutile and Anatase on TiO₂ Surfaces

Mixed rutile-anatase composites show great promise as photocatalysts. However, well-defined model systems of the two polymorphs of TiO₂ have not been easy to synthesize, making it difficult to understand the relationship between chemistry, structure, and morphology. Researchers at Pacific Northwest National Laboratory have grown well-ordered mixed rutile-anatase films on LaAlO₃(001) using molecular beam epitaxy. The results of this research show that growth conditions dictate whether rutile, anatase, or a mixture of the two nucleates is formed. A complex but structurally well-defined interface between anatase and rutile forms over a narrow range of growth rates. Being able to synthesize these structures creates new opportunities to study their photochemistry in a controllable way.

Principal Investigators:

Scott Chambers and Mike Henderson

Citations:

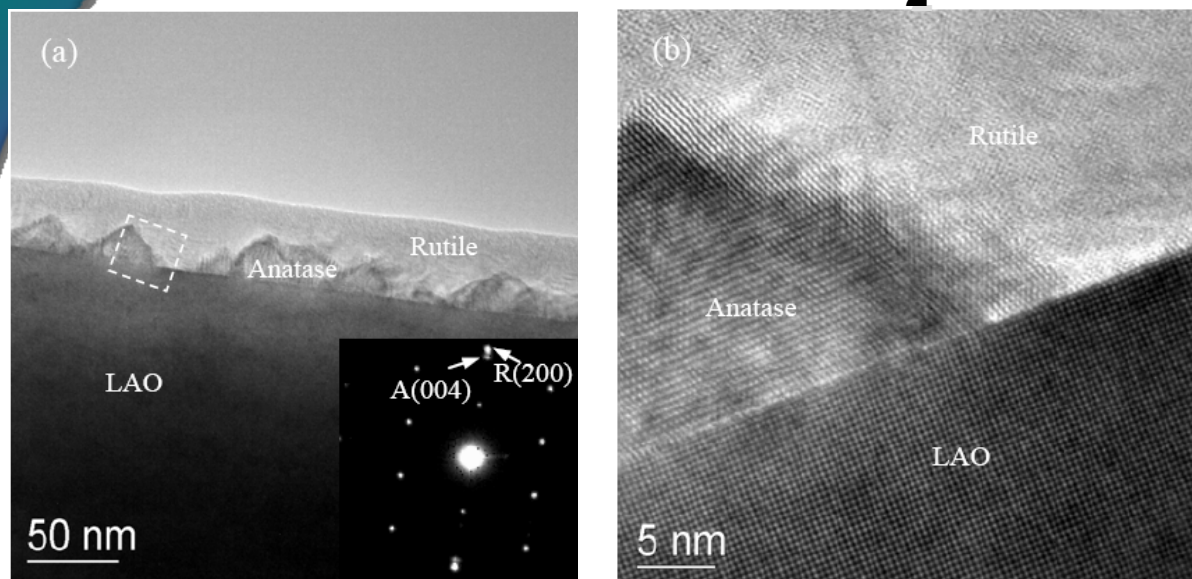
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Chambers, SA. 2007. "The Role of Substrate Surface Structure and Growth Rate on Metal Oxide Heteroepitaxy." 54th International Symposium of the AVS, Seattle, Washington, November 2007.

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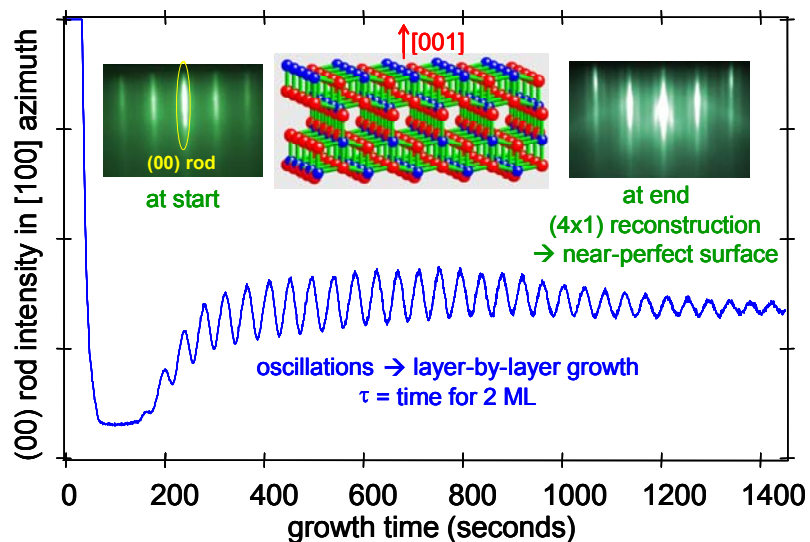
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Controlled Preparation of Mixed Rutile and Anatase on TiO₂ Surfaces



Results

- Growth conditions dictate whether rutile nucleates in anatase.
- Mixed film consists of top layer of rutile and bottom, anatase that serves as an interfacial layer between the substrate and rutile.
- Amorphous regions are not present away from interfaces.
- Mixed rutile-anatase films constitute model systems for studying how photochemistry is affected by the rutile-anatase interface.



Staff Accomplishments

Three Staff Elected AAAS Fellows

At Pacific Northwest National Laboratory, a number of our staff were elected as Fellows to the American Association for the Advancement of Science. Jun Liu, a Laboratory Fellow at Pacific Northwest National Laboratory, is being recognized for "distinguished contributions to the development, understanding and commercialization of self-assembled functional nanoporous materials, and to the development of environmentally friendly solution approaches for oriented nanostructures."

Lai-Sheng Wang is a professor of physics at Washington State University Tri-Cities and is an affiliate chief senior scientist at PNNL. He is being recognized for "distinguished and innovative contributions to the field of atomic clusters and for pioneering work on gaseous multiply-charged anions."

Richard Kouzes is a Laboratory Fellow being recognized "for distinguished contributions to defining the technical basis and implementation of nuclear radiation detection systems for applications to homeland security, nuclear structure, and neutrino physics."

Greg Exarhos to Lead Prestigious Professional Society



Pacific Northwest National Laboratory's Greg Exarhos was elected President of the AVS: Science and Technology of Materials, Interfaces, and Processing. Founded in 1953, this not-for-profit society was focused on vacuum science and technology, critical in the early development of vacuum tubes, enabling radio broadcasting, radar, and other technologies. Today, the society has broadened its scope to include such technologically relevant areas as surface science, electronic and magnetic materials, nanoscience, and biomaterials.

Exarhos joined the society because it provided the best forum for his work in materials science and engineering. He is also actively involved in the operations side of the society. An AVS Fellow, he has been elected to the Board of Directors, served as Chair of the Long Range Planning Committee, and has served as Chair of numerous society-sponsored meetings. He currently serves as the Publications Chair and oversees several journals, including the new open access journal, *Biointerphases*, which he launched for the society in 2006.

Chuck Peden to Chair National Catalysis and Surface Science Secretariat



Pacific Northwest National Laboratory's Chuck Peden was elected the 2008 Chair of the American Chemical Society's (ACS's) Catalysis Secretariat. The secretariat regularly organizes and cosponsors symposia at the national meetings of the ACS, but equally important is the Secretariat's role in integrating ACS divisions' activities concerned with catalysis and surface science to encourage comprehensive coverage of these subjects at ACS national meetings.

Bruce Kay Chaired Physical Chemistry Division of American Chemical Society



Pacific Northwest National Laboratory Fellow Bruce Kay is completing a five-year term leading the American Chemical Society's Physical Chemistry Division, which has approximately 6,000 members. In this leadership role, Kay developed and executes programs and symposia around action dynamics relevant to heterogeneous and homogeneous catalysis.

Tom Autrey to Serve as International Hydrogen Storage Materials Panel Expert



Pacific Northwest National Laboratory's Tom Autrey was selected to serve on the International Energy Agency's Hydrogen Storage Materials Panel. Autrey joins 42 other experimental, engineering, theoretical and safety experts from 15 different countries.

Researchers Serve on Editorial Boards of Key Scientific Journals

Pacific Northwest National Laboratory's János Szanyi was appointed to the Editorial Advisory Board of *Catalysis Letters*, a widely circulated journal that publishes rapid communications in the broad field of catalysis for the international community.

PNNL's Morris Bullock is finishing the final year of his term on the Editorial Advisory Board of *Inorganic Chemistry*, an often-cited, peer-reviewed journal published by the American Chemical Society (ACS).

PNNL's Bruce D. Kay is serving as a member of the Editorial Advisory Board of the *Journal of Physical Chemistry*, a peer-reviewed journal published by the ACS. Bruce was appointed to the board in 2005. In addition, Lai-Sheng Wang, an Affiliate Senior Chief Scientist at PNNL and a professor at Washington State University Tri-Cities was appointed to the journal's editorial advisory board.

Lai-Sheng Wang Accepted Research Award from University



Lai-Sheng Wang won the Sahlin Faculty Excellence Award for Research, Scholarship and Arts. Washington State University annually presents three Sahlin awards, recognizing excellence in teaching, public service, and research. An Affiliate Senior Chief Scientist at Pacific Northwest National Laboratory and a professor at Washington State University Tri-Cities, Lai-Sheng Wang is a world leader in nanoclusters research. For example, Lai-Sheng and his colleagues created hollow nanoscale cages of gold atoms, the first known metallic equivalent of the buckyball.

Morris Bullock Named to Second Term on Advisory Board of the Petroleum Research Fund

Pacific Northwest National Laboratory's Morris Bullock was re-appointed to another three-year term on the Advisory Board of the Petroleum Research Fund. This is an endowed fund, managed by the American Chemical Society, that supports basic research directly related to petroleum or alternative energy at nonprofit institutions in the United States and around world. Since the first grants from the fund were approved in 1954, several grant programs have evolved to serve segments of the scientific community. As a member of the board, Bullock reviews the proposals and the peer-reviewed comments provided and makes recommendations regarding which proposals should be funded and which should not.

A Laboratory Fellow, Bullock is known for his research into the behavior of hydrogen with metal complexes that may lead to replacement of precious metals in catalytic processes for energy production and energy utilization. Bullock was asked to take on a second term based on his outstanding work during his last term and his strong expertise in inorganic chemistry.

Staff Elected to Leadership Roles at Prestigious Gordon Conference

Several staff at Pacific Northwest National Laboratory have been elected to serve in leadership roles at the Gordon Research Conferences, which provide an international forum for the presentation and discussion of frontier research in the biological, chemical, and physical sciences, and their related technologies. PNNL's Michael Henderson was elected vice-chair of the 2009 Gordon Research Conference on Chemical Reaction on Surfaces and chair for the 2011 conference. Lai-Sheng Wang was elected chair of the conference on clusters, nanocrystals and nanostructures. Wang is a professor of physics at Washington State University Tri-Cities and is an affiliate chief senior scientist at PNNL.