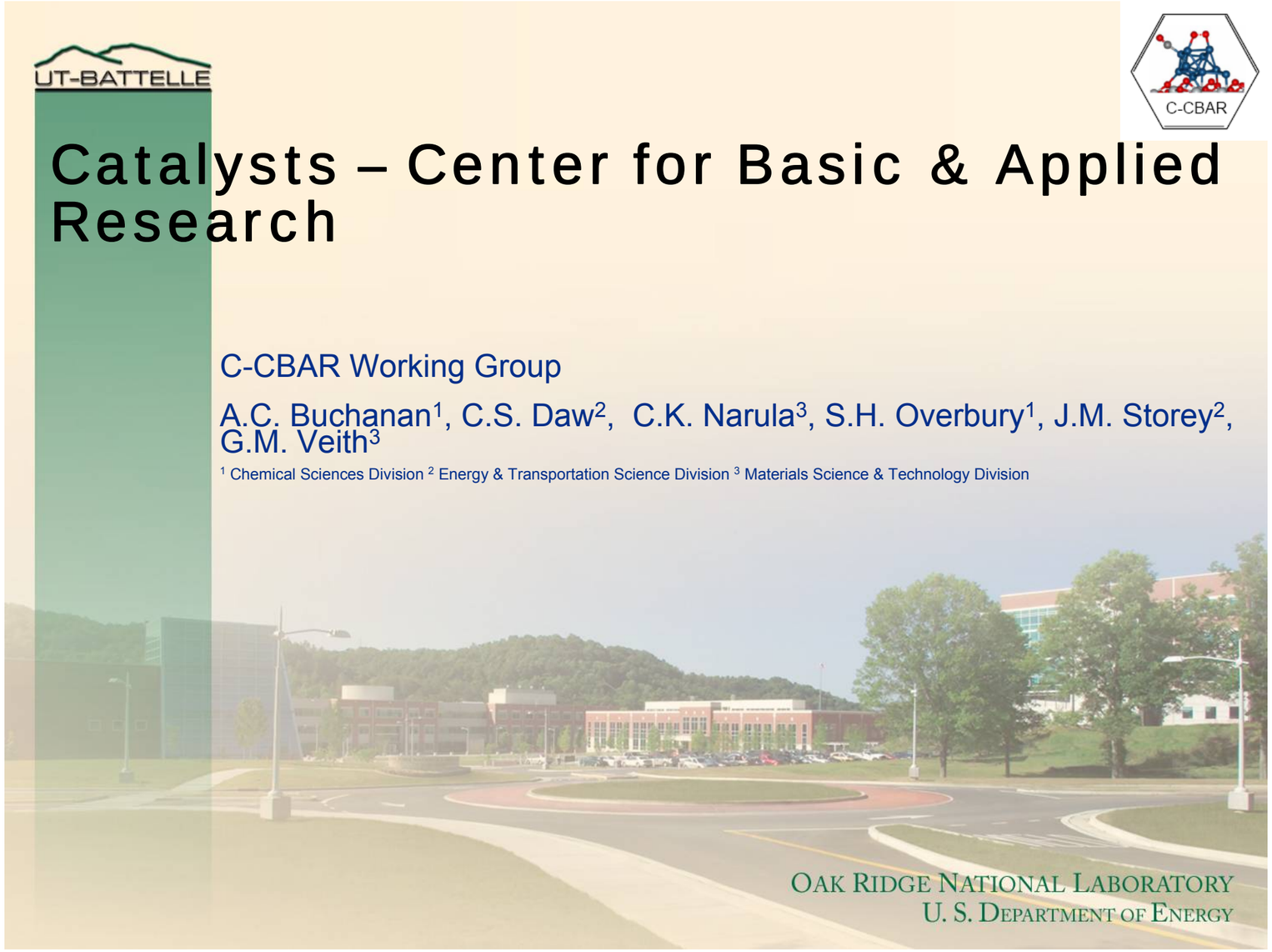
Catalysts – Center for Basic & Applied Research

C-CBAR Working Group

A.C. Buchanan[1], C.S. Daw[2], C.K. Narula[3], S.H. Overbury[1], J.M. Storey[2], G.M. Veith[3]

[1] Chemical Sciences Division [2] Energy & Transportation Science Division [3] Materials Science & Technology Division



ORNL has a long, distinguished history of catalysis research

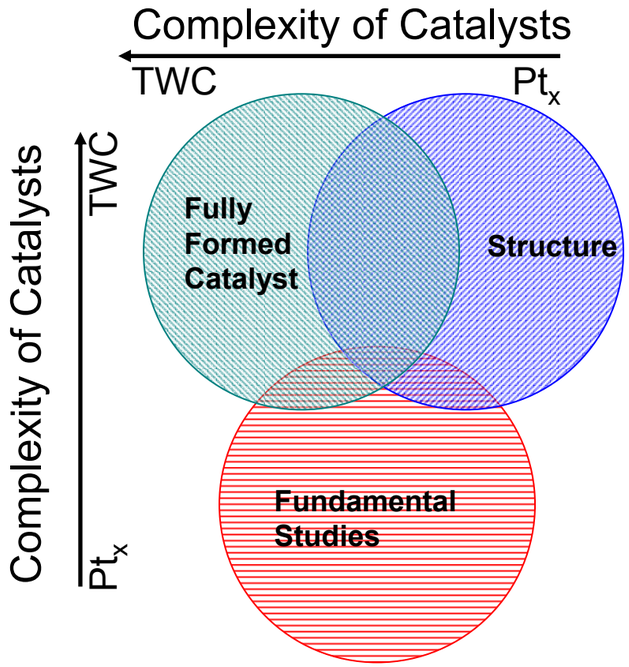
C-CBAR staff Comprise Many Disciplines

- **61 total staff, including post-doc, post-masters**
- **Chemistry, Chemical Engineering, Physics, Env. Chemistry, Materials/Ceramics Engr, Mechanical Engineering**

Catalysis is enabling technology to many industrial processes. The purposes of our R&D....

- **In pursuit of DOE major programmatic goals**
- **In response to research needs and data requirements from other Federal and State agencies**
- **In response to specific industry challenges**
- **High-risk, long range R&D from our own vision, to position us for future challenges and advancement of science and technology**

ORNL addresses all aspects of catalysis research from very fundamental studies to specific applications

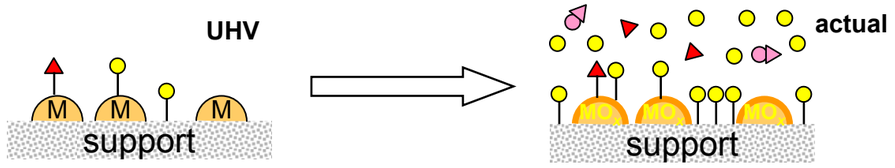


- **Design and synthesis of novel catalysts**
- **Fundamental surface science**
- **Automotive emission catalysts**
- **Theoretical modeling**
- **Characterization**

What can We Address with Theory?

- **Supported catalyst systems**

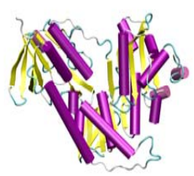
- **Activity of transition metal catalysts often depends on chemical environment**
  - **environment = fluid phase (*T*; *p*; *C*), support, surface species, …**
  - **effect of oxidizing environment: oxide as active phase: Ru/CO oxidation; Ag/epoxidation; Pt/CO oxidation**



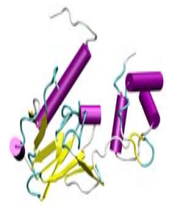
- **Heterogeneous catalysis research trending toward ever smaller particles, reduced precious metal loading (esp. important for Pt)**
  - **higher activity or selectivity? (e.g. Au)**

- **How are properties (structure, composition, reactivity) of nanoparticles…**
  - **affected by an oxidizing environment?**
  - **dependent on size?**

Theoretical Studies - Enzyme Catalysis

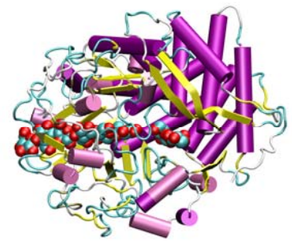


MerA

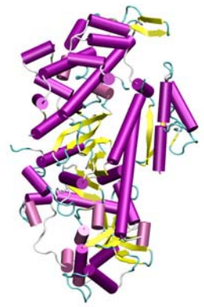


MerB

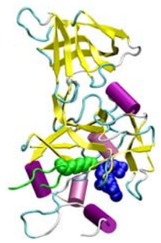
Enzymes for Environmental Bioremediation



Understanding catalytic mechanism of cellulases in deconstructing cellulosic biomass



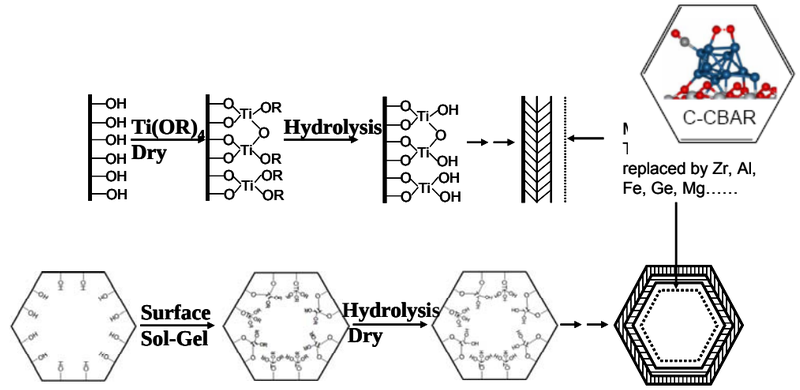
Molecular motor myosin and the mechanism of ATP hydrolysis



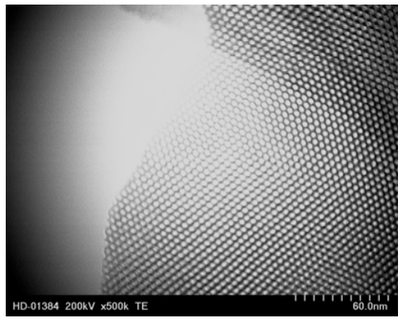
Specificities and mechanisms of Histone-modifying enzymes

Synthesis of catalysts

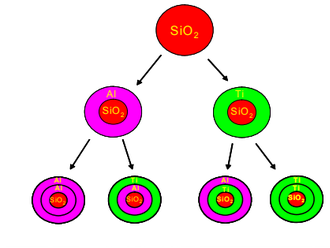
- **Classical impregnation and incipient wetness methods on commercial oxides**
- **Sol-gel synthesis of oxides**
- **Surface sol-gel for layer-by-layer growth**
- **templated co-synthesis of porous materials**
- **surface functionalization with oxides and organics**
- **Atomic layer deposition (ALD) for conformal functionalization of supports**
- **Various precursors for metal particle deposition**

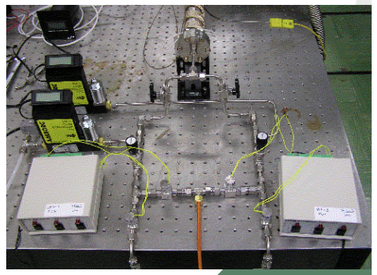


Layer-by-layer growth by surface sol gel process



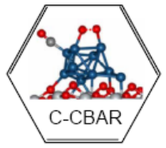
Diverse morphologies of silica based supports– fibers, ordered pores, 3-d pore networks, aligned pores, porous films and monoliths, control of pore diameter and spacing…





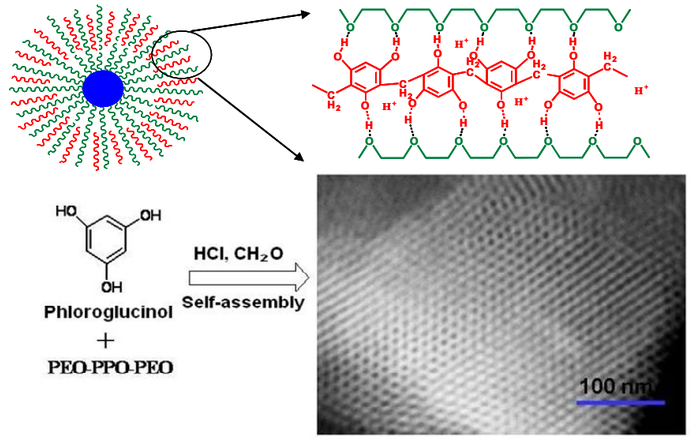
ALD for conformal layer growth

Carbon as nanostructured material for catalysis

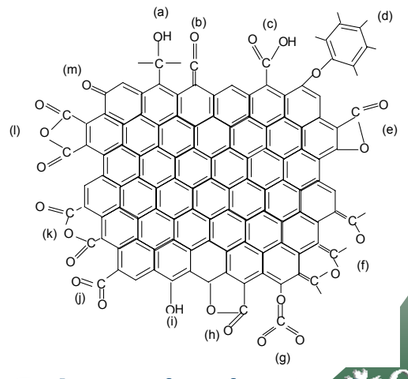


- **Synthetic carbon as route to understanding C catalysis**
  - **pore morphologies and surface functionality**
  - **Previous work based on “activated” carbons**
  - **support for metals, sulfides or carbides**
  - **catalyst for oxidation reactions, Oxidative dehydrogenation and chlorination**
- **Explore novel synthesis routes**
  - **Manipulate templates, hydrophobicity, block co-polymers to control of nanostructure**
  - **Introduce specific surface functionalities**
  - **Methods to attach highly dispersed metals or carbides on mesoporous carbons**
- **Explore catalytic properties of synthetic carbons**
  - **Selectivity in oxidation of H_2S, oxidative dehydrogenation**
  - **Metal carbide formation and activity**

Synthetic carbon materials are crucial for investigation of the factors that affect catalytic processes in carbon



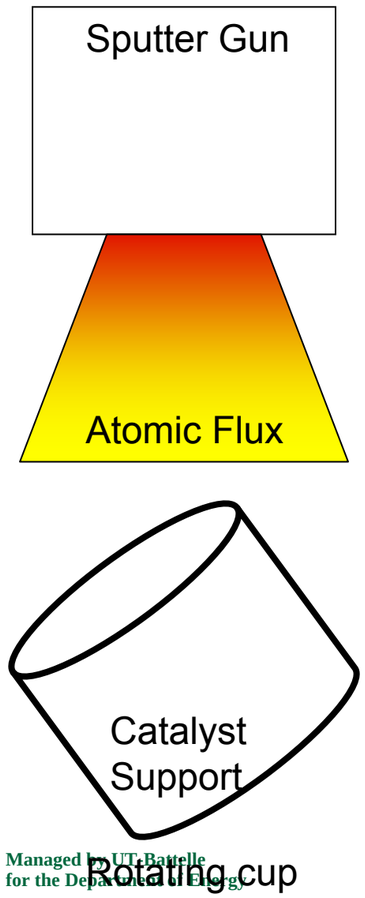
New routes to mesoporous carbon

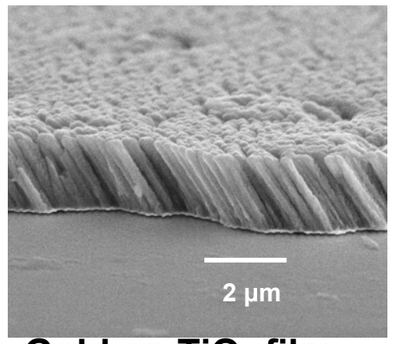


Carbon surface functionalities.
Where are the active sites?

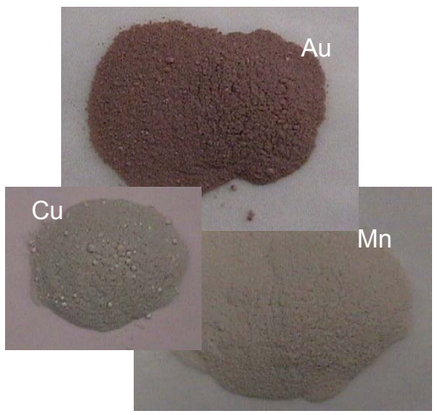
Vapor deposition technology to prepare supported metal catalysts.

- Both bulk powders and thin films
- No contamination from precursors
- Uniform nanoparticles
- Expands materials options
- Applicable to fuel cells, gas and liquid phase reactions

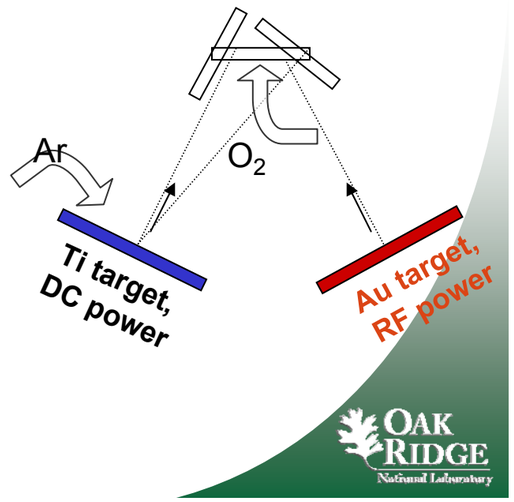




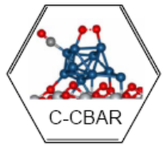
Gold on TiO_2 film



Various metals on Al_2O_3



Characterization of structure, transformations and surface species



- **What is surface area of the support? What is the dispersion of the metal particles? Did treatments collapse pores? What is the distribution of pore sizes ? How stable are the metal particles? Quantachrome Autosorb 1-C** for Volumetric gas adsorption
- **What is the structure of the materials? What is the aspect ratio and ordering of pores? What is morphology of particles? What is the size distribution of supported particles? HD-2000 STEM and AC-STEM** *for microscopic analysis*
- **What phases are present? Is the sample completely or partially crystalline? At what temperature does crystalization occur? What phases are present under reaction conditions? Powder XRD** *with controlled temperature and atmosphere.*
- **What temperature is required for reduction or oxidation of catalyst? How much of sample is oxidized/reduced? How much adsorbs on the sample? What are desorption products? Altamira AMI-200** *for TPR, TPO, TPD, pulsed chemisorption*
- **What is final composition of sample? What is metal loading? Are there impurities? Did we get the right component ratio? ICP-AE**
- **What is fate of functional ligands and template molecules? What temperature does dehydration, decomposition or condensation occur? What products are evolved from these reactions? What are the reaction energetics? TA Instruments 2010** *for TGA and DSC with mass spectrometric analysis*
- **What species are on the surface? What phases are present? FTIR spectroscopy, UV-visible and multi-wavelength Raman**

Catalytic performance and mechanistic studies

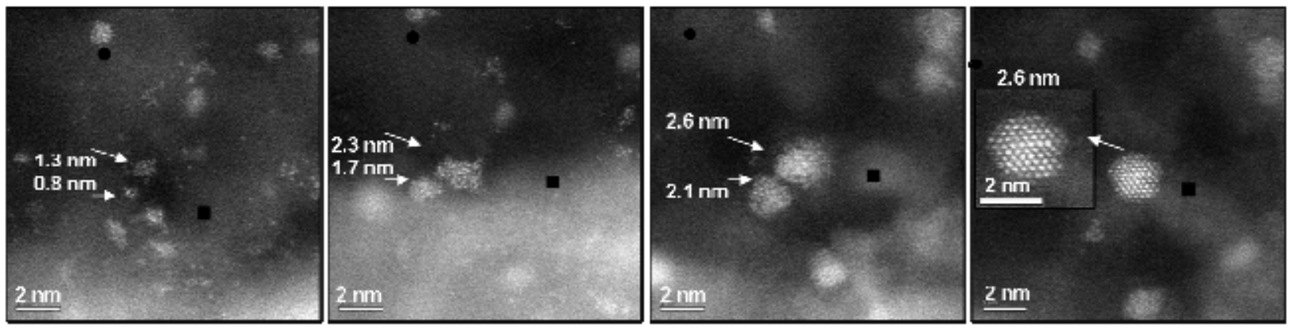
- **Steady state plug flow - GC and QMS product detection; TPO, TPR and TPD and pulsed chemisorption**
- **Pulsed catalytic reactor – ultra low dead volume reactor, transmission FTIR on 0.5 s time scale, continuous product analysis. Pulse and gas switching**
- **High pressure flow reactor- Liquid injection, hot box reactor, GC and QMS product analysis, P up to 30 bar**
- **Plug flow reactor – ambient pressure. Operation currently optimized for studies of desulfurization and H_2S reduction reactions, product detection by dedicated gas chromatograph and/or FTIR**
- **High-Pressure Flow Reactor – upto 1450 psi and 650ºC. Liquid or gas input, GC product analysis. Operation optimized of Oxydehydrogenation reactions**
- **Benchtop Flow Reactor – setup for catalyst testing under simulated vehicle exhaust (lean, rich, stoichiometric, and lean-rich cycle)**
- **Ex-Situ Reactor – to study nanostructural changes by exposing catalyst sample on a TEM grid to catalyst operating conditions**

Monitoring Nanostructural Changes

Ex-situ reactor for exposing catalyst on a TEM sample grid to operating conditions

Rapid screening tool for monitoring nanostructural change in a catalyst under operating conditions

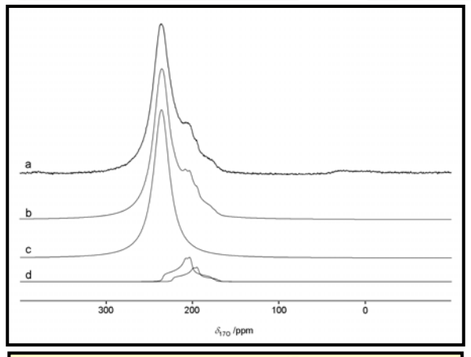
$Pt/\gamma\text{-}Al_2O_3$



Pt nano-particle growth in alumina supported catalyst under CO oxidation conditions, from left, fresh, CO oxidation initiation, 2 cycles -, and 3 cycles of quantitative CO oxidation

NMR Investigations of Catalyst Structure and Substrate Interactions

- **NMR of quadrupolar nuclei in solids (^{17}O, ^{51}V, ^{47}Ti, ^{27}Al, etc.) requires high field strengths provided by our new 700 MHz NMR**
- **Multiple Quantum Magic Angle Spinning NMR (MQ/MAS NMR): untangles isotropic chemical shift and quadrupole coupling tensors, permitting recognition of the number of unique resonances in the sample, e.g., reaction centers on catalysts**
- **Determination of site specific quadrupole coupling constant and asymmetry parameter allow the description of bonding at each site (oxidation state, coordination number, geometry)**
- **Combining MQ/MAS and Rotational Echo Double Resonance (REDOR) permits measurement of select inter-nuclear bond distances, e.g. establishing bonding arrangements in oxo-bridged bimetallic supported catalysts**

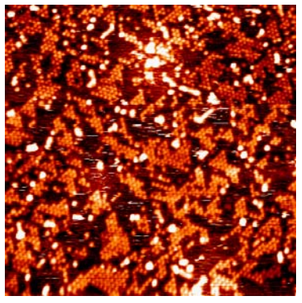


^{17}O-NMR spectra of carboxyl-^{17}O-enriched benzoic acid adsorbed on SBA-15 silica. (a) experimental, (b) full spectrum simulated, (c) motion averaged component simulated, (d) benzoic acid dimer simulated.

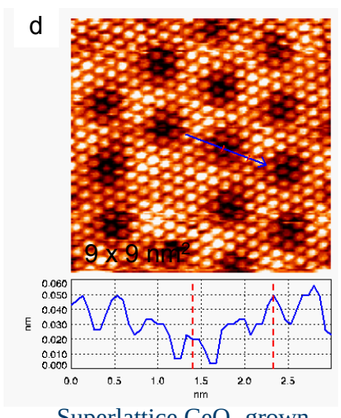
Imaging Surfaces: Scanned probes

- **Structures of surfaces used in surface adsorption and reactions stuc**
  - **Growth morphology and atomic structure of thin oxide films**
  - **Growth of metal particles on oxide surface**
  - **imaging molecules on surfaces by scanned probe techniques**
- **Computational modeling of adsorption and tip interactions**

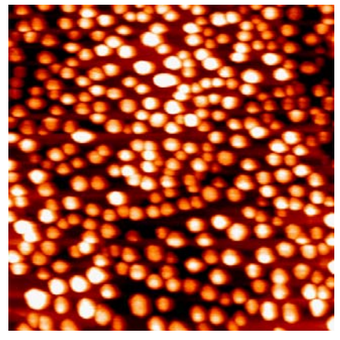
What are structure of model surface used for adsorption studies? How does reduction, oxidation or thermal treatment affect structure? How are metal clusters affected by oxidation state of oxide support? How are molecules adsorbed and distributed between the phases? Which phase is responsible for which surface reactivity?



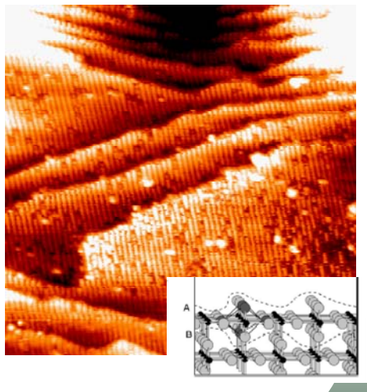
Oxygen adsorbed on Ru(0001)



Superlattice CeO_2 grown on Ru(0001)



Rh cluster on CeO_2(111)



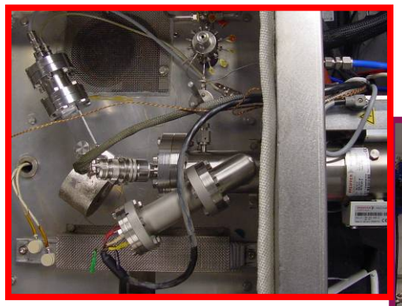
Step structure on TiO_2(110)

National lab capabilities with industrial and academic collaborations to address critical issues in applied catalysis

C-CBAR

Objectives:

- Kinetic mechanism identification
- Device modeling
- System optimization



SpaciMS

- capillary inlet mass spec.
- concentration profiles inside monoliths
- magnetic sector detector: H_2

Microreactor

- powders
- surface areas
- TPR/TPO
- performance eval.

DRIFTS reactor

- powders, washcoated wafers
- quantify adsorbates
- identify intermed.

Bench reactor

- monolith cores
- performance eval.
- SpaciMS

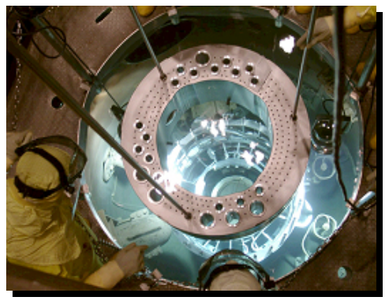
Other capabilities

- microscopy, XRD
- engine dynamometers

OAK RIDGE National Laboratory

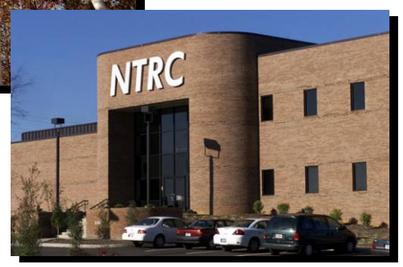
C-CBAR has access to ORNL's major facilities for research

High Temperature
Materials Laboratory



High Flux
Isotope Reactor

National
Environmental
Research Park



National Transportation
Research Center

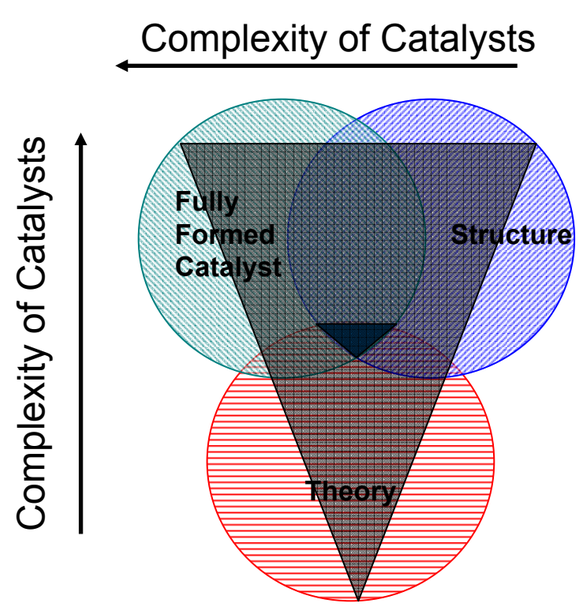
Center for Nanophase Materials Sciences

Center for Computational Sciences

OAK RIDGE National Laboratory

Catalyst by Design

Supported clusters (Pt, Rh) are integral part of vehicle emission treatment catalysts such as oxidation catalyst, three-way catalyst, lean NO_x traps, diesel particulate filters. We have carried out an extensive study of supported Pt clusters, their oxidation behavior, and their activity as CO, HC, and NO_x oxidation catalyst.

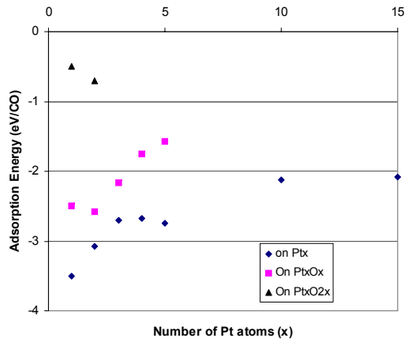


- Theoretical Modeling
  - Density functional theory calculations. Generalized gradient approximation (PW91 functional).
  - Optimization of Pt clusters on oxide supports
  - Interaction of CO, NO_x, and HC with catalysts
- Experimental System
  - Synthesis of Pt Nanoclusters on morphologically diverse oxide supports
  - Interaction of CO, NO_x, and HC with catalysts
- Structure
  - Nano-structural characterization

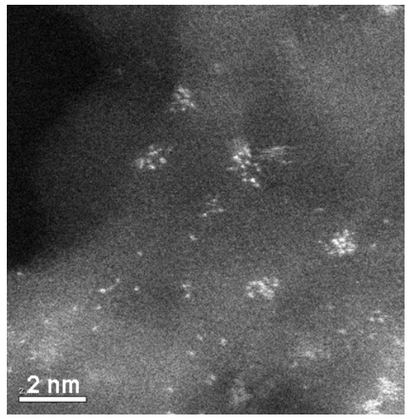
This approach can also be extended to zeolite based catalysts

Catalyst by Design

We have demonstrated that the iterative application of theory, experimental studies, and nanostructural characterization can advance catalyst discovery process

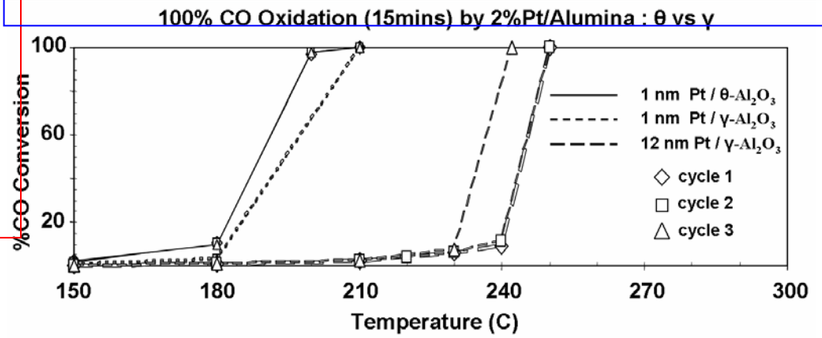


Theory predicts that oxidized Pt nanoclusters are better CO oxidation catalysts than Pt-particles



➢HAADF-STEM mode clearly shows that Pt/γ-Al_2O_3 comprises isolated atoms, 2-3 atom clusters, nano-clusters of between 10-20 atoms

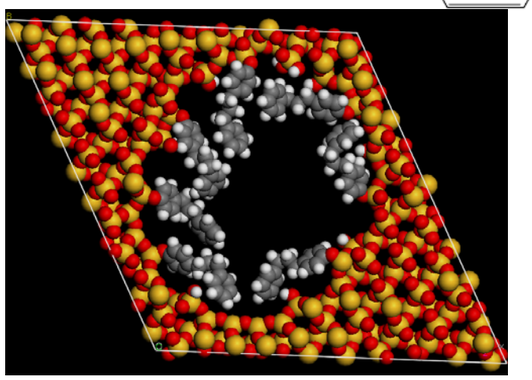
➢Only a 3-atom cluster has been observed previously



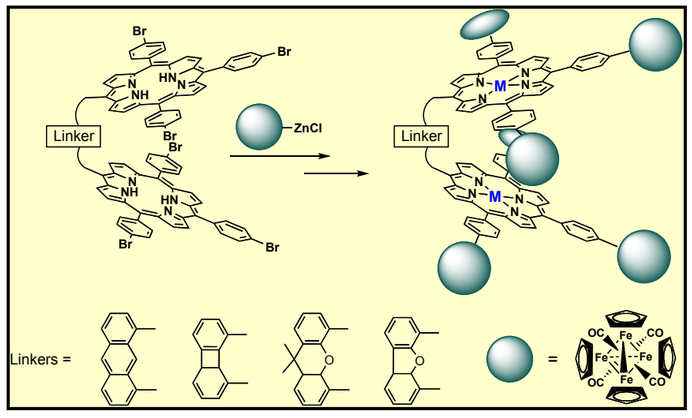
Pt nanoclusters are better CO oxidation catalysts than large Pt particles

Organic and Organometallic Chemistry

- **Supported organometallics for multi-electron redox processes**
- **Mesoporous metal oxides and organic hybrids**
- **Electrochemistry and electrocatalysis**
- **Photochemistry and photocatalysis**
- **Multi-step chemical synthesis**
- **Steady-state and time-resolved optical spectroscopy**



Model of pore in mesoporous silica with surface-confined organic molecules

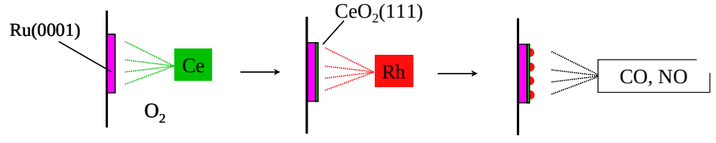


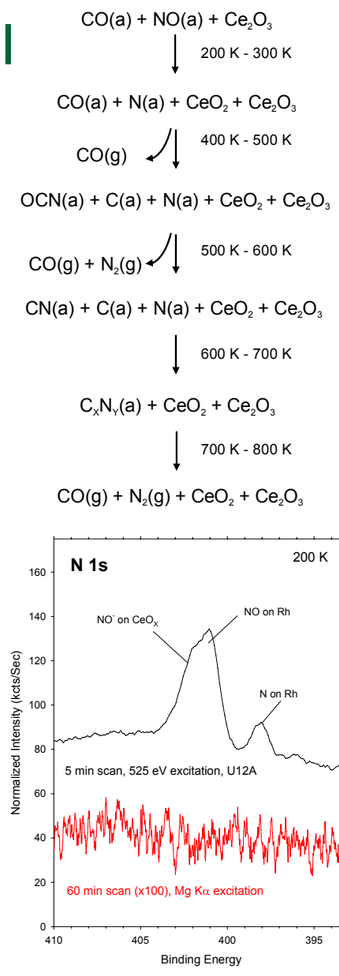
Prototype co-facial metalloporphyrin with electron exchange catalyst for the 4e- reduction of oxygen to water

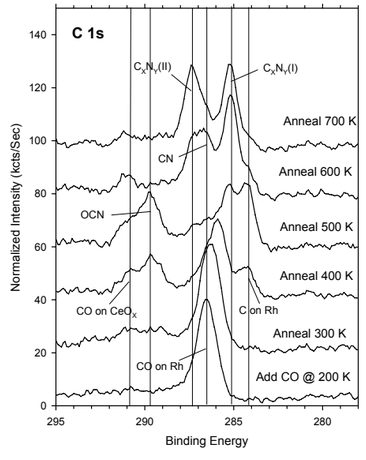
Time correlated single photon counting spectrometer

Chemistry on Model Catalyst surfaces

- **Surface chemistry on model catalytic surfaces by UHV techniques**
  - **Rh supported on oxidized / reduced cerium oxide films**
  - **Redox reactions**
  - **Lab and synchrotron based research**

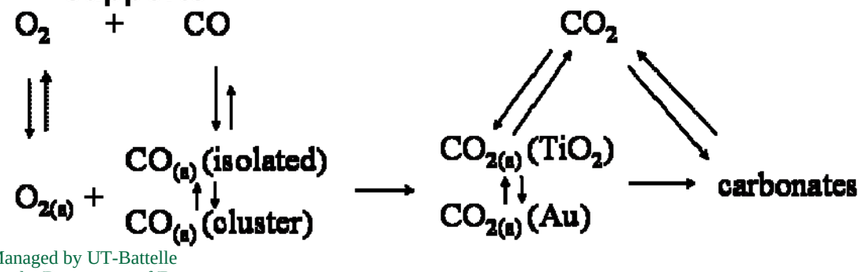


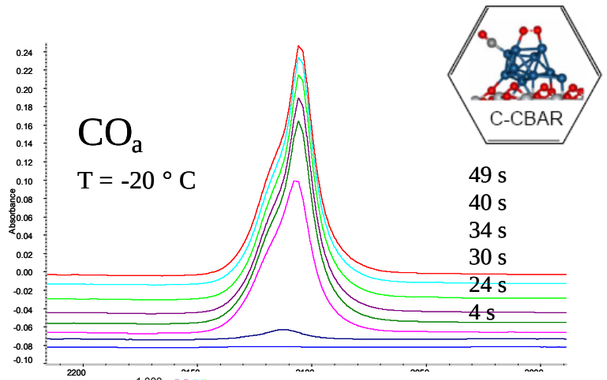


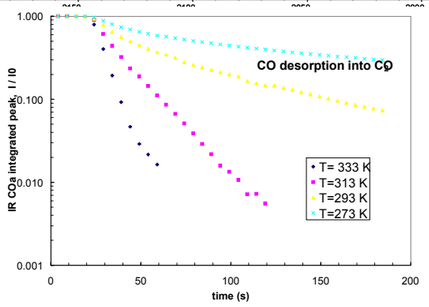


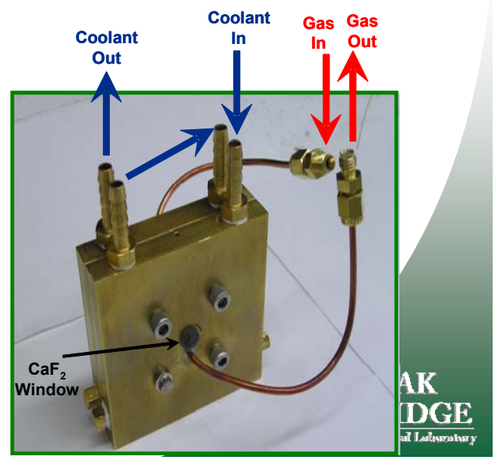
Probing surface reactions under steady-state or transient reaction conditions

- **Dynamic FTIR provides reaction pathways**
  - **Gas switching/pulsing**
  - **DRIFTS (-25 < T< 500 °C) or transmission FTIR (-25 < T< 80 °C)**
  - **Simultaneous product gas analysis**
- **Evolution of FTIR peaks**
  - **Desorption energetics**
  - **Coverage effects**
  - **Operando surface species**
- **Role of water and hydroxyls**
- **Role of carbonates during reaction**
- **Compare reaction mechanism on different supports**



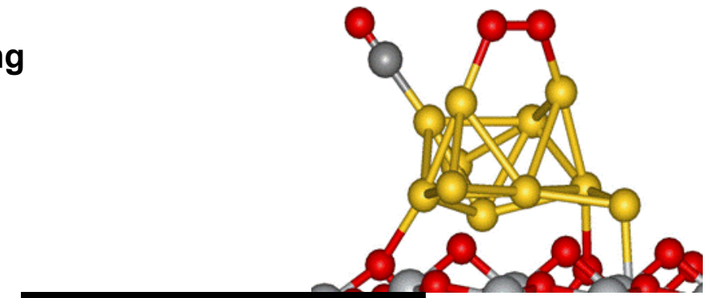




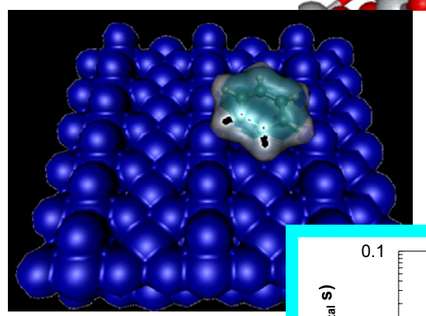


Computational modeling of surfaces and surface reactions

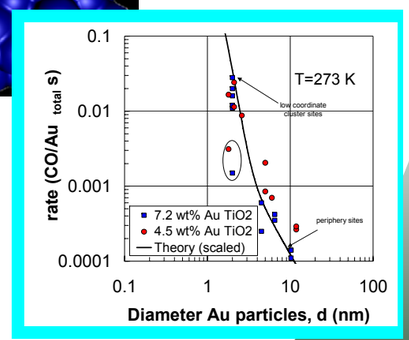
- **Current activities**
  - **first principles computations of bonding energetics**
    - **Structure of metal clusters on oxide supports**
      - **Au on TiO_2**
      - **Rh on CeO_2**
    - **Reaction pathways and energetics**
      - **CO oxidation over Au catalysts**
      - **Cluster size dependent reaction rates**
    - **modeling of oxide structure**
      - **Modeling STM images**
    - **metal- support interactions**
    - **Molecular adsorption on CeO_2**
      - **Methanol adsorption**
- **close interactions between experimental and computational effort**



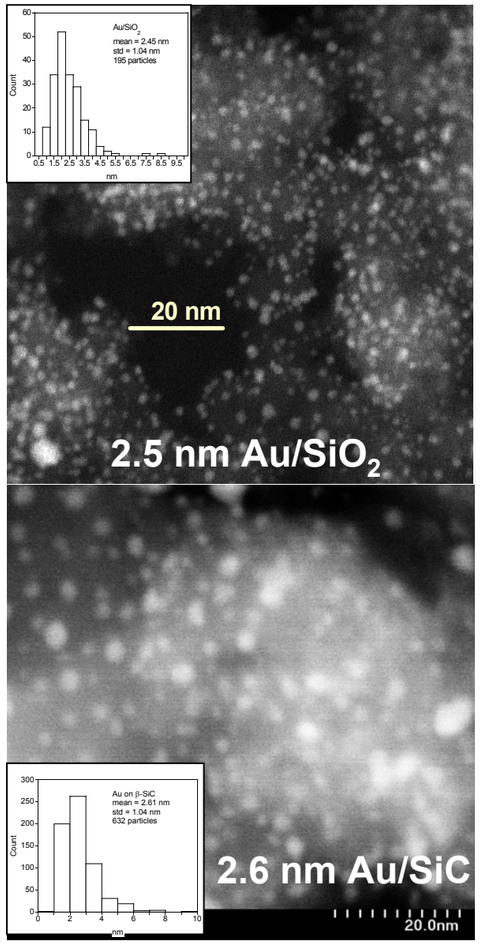
CO and O_2 adsorbed on a Au cluster on TiO_2



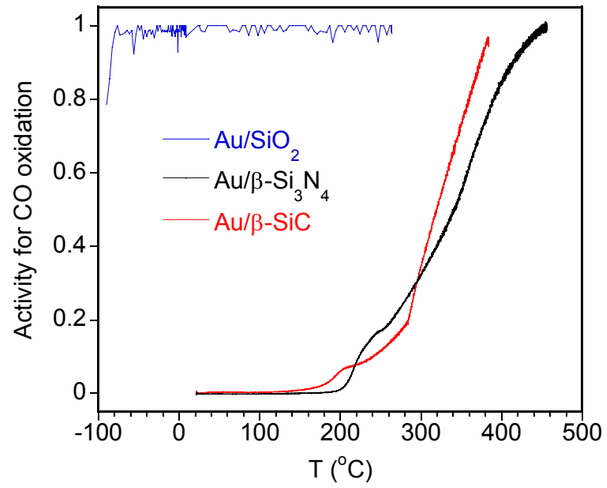
Computed structures of adsorbed benzene on TiO_2



Comparison of computed and experimental size dependence in catalytic reaction rates



Goal is to understand how metal support interactions mediate catalytic properties by exploring traditional and non-traditional support materials as well as thin films



For example why to the same sized catalysts clusters behave differently on different supports?

Emissions Research .... a comprehensive laboratory for internal combustion engine technology

- **A DOE National User Facility in the NTRC**
- **Emphasis on unique or extraordinary diagnostic and analytical tools for engine/emission control R&D**
- **R&D from bench-scale to vehicle**
  - **Chemical/analytical labs**
  - **6 dynamometer stands: 25-600 hp**
  - **Full-pass engine controls support research**
  - **Emissions analysis with high resolution of time and species**
  - **Non-invasive optical and mass-spec diagnostics**
  - **Modelling & simulation**

Example of project supporting major programmatic goal: Lean NOx Trap & natural gas engine research for ARES

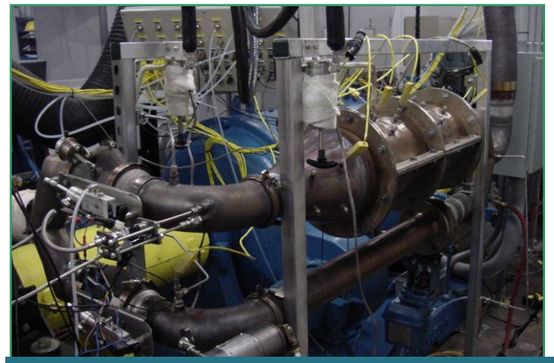
ARES goal

Achieve and Demonstrate

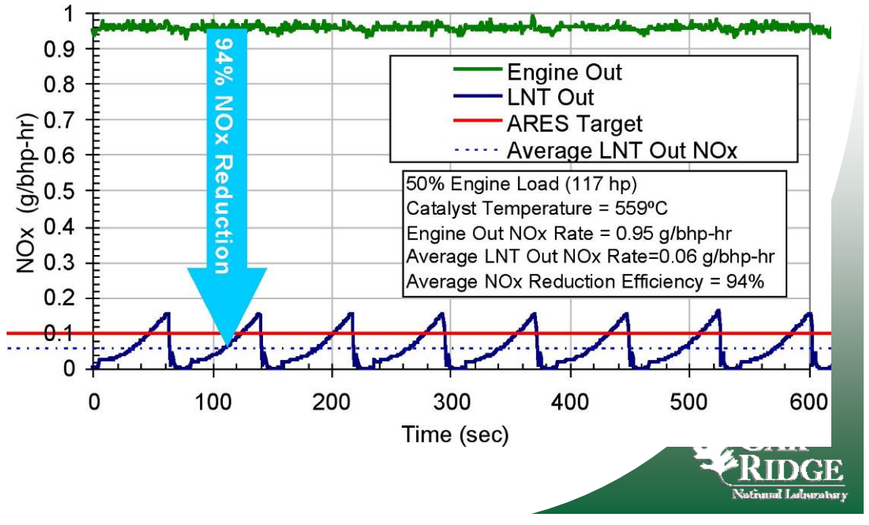
<0.1 g/bhp-hr NOx

Tasks:

- ✓ **Select engine, LNT and reformer**
- ✓ **Baseline emissions**
- ✓ **Integrate LNT, reformer and engine -**
- ✓ **Demonstrate low emissions**
- ✓ **Characterize unregulated emissions**
- ✓ **Characterize operation of LNT catalyst -**



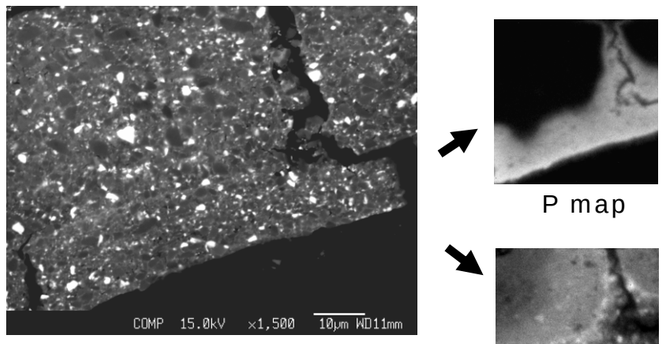
Cummins CNG 8.3+ at ORNL-NTRC



A project requested by another agency: Research team responded to EPA need for data to support low-sulfur diesel fuel rulemaking

- **Provided early evidence that full diesel engine + aftertreatment system could achieve Tier2 emission levels**
- **Mercedes A-170 CIDI with exhaust gas recirculation and modern fuel system**
- **Prototype NOx adsorber catalyst and lab-constrained regeneration system**
- **Catalyzed soot filter**
- **Diesel fuel with 3 ppm sulfur**
- **Results cited in EPA diesel sulfur rulemaking**

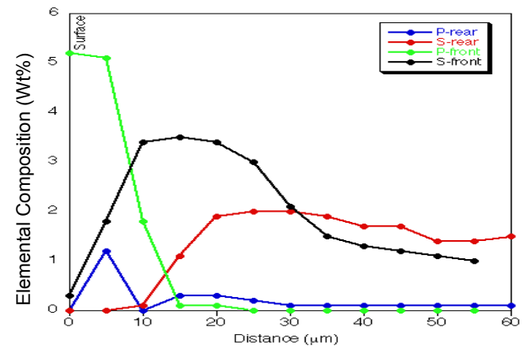
Catalyst poisoning by lube phosphorous studied as part of accelerated aging method development



CROSS SECTION
OF WASHCOAT

P map

S map



Depth into Washcoat (µm)

Unique sample preparation and high resolution Transmission Electron Microscopy (TEM) enable the depth profiling of elements

Importance –

Phosphorous poisoning by Zinc dialkyl dithio phosphate (ZDDP) lubricant additives negatively impacts the durability of diesel aftertreatment systems.

Accomplishments/findings:

Form of phosphorous reaching catalyst depends on oil leakage pathway

- Detailed exhaust analysis found various forms of phosphorus (phosphates, not P_2O_5)
- Lube into air intake: P high on catalyst surface, S in lower strata. No Zn present
- Lube directly to exhaust: Zn high on catalyst surface. P and S are still bound together
- Exhaust introduction produces hard glaze formation; prevents access to catalytic sites

- **Thus, C-CBAR offers a unique combination of world-class researchers, comprehensive experimental facilities, and state of the science instrumentation to address a variety of catalysis issues in support of DOE programs**

Working with us

- **There are several mechanisms for accessing C-CBAR experimental facilities and expertise.**
- **The main partnering mechanisms are User Agreements and Sponsored Research. Either mechanism can provide protection for proprietary information and data.**
- **User Agreements are aimed at customers who want to come to the CNMS, HTML, SNS and actively participate in their project.**
- **Sponsored Research is a more traditional arrangement where a work scope, schedule, and budget are defined collaboratively, with ORNL performing all work for the customer.**