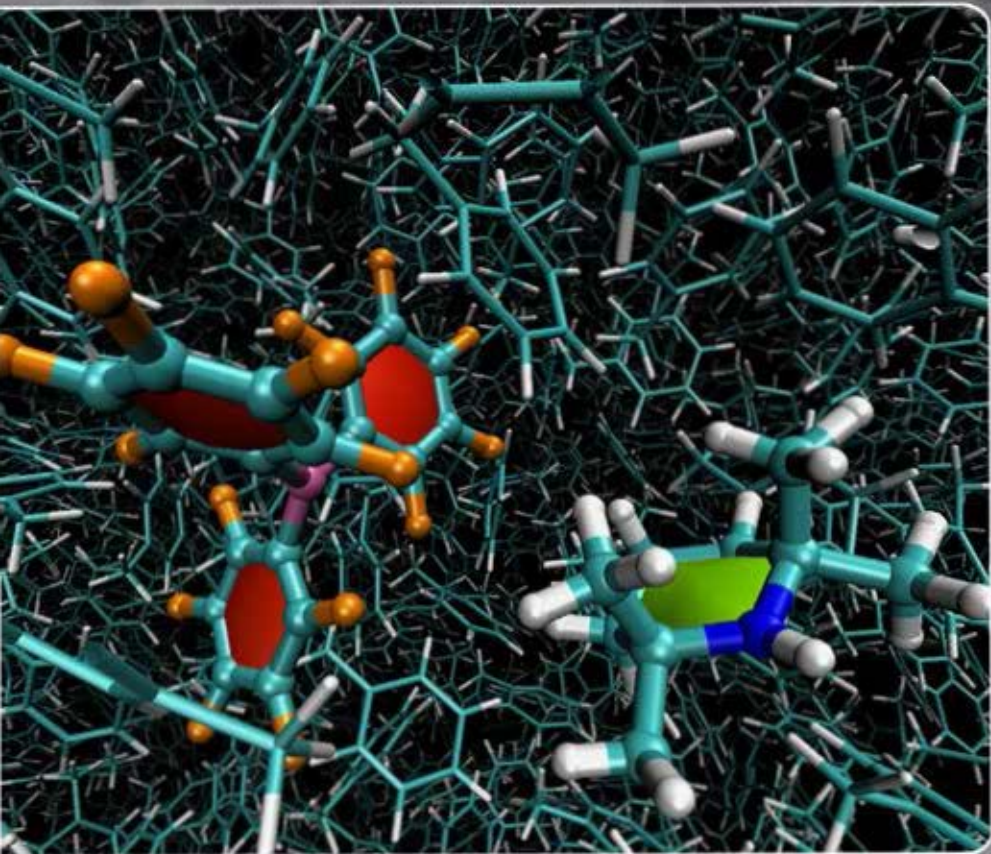


INSTITUTE FOR INTEGRATED CATALYSIS
2014 Program Briefing



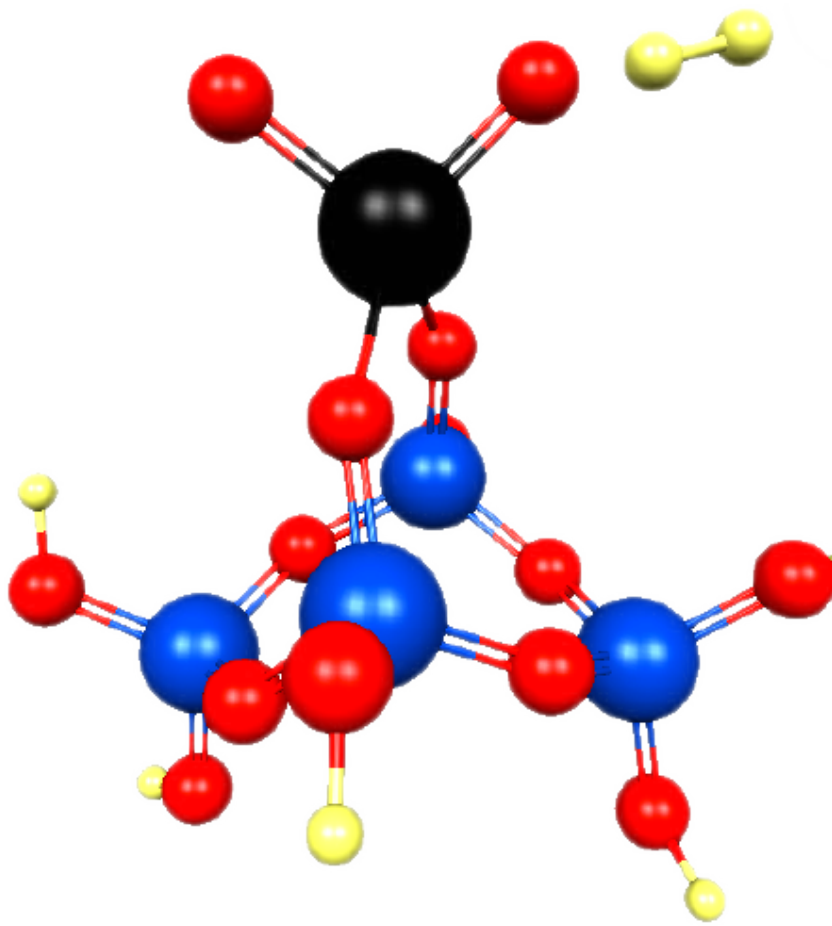
Pacific Northwest
NATIONAL LABORATORY

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U.S. DEPARTMENT OF
ENERGY

ABBREVIATIONS

AIMD	<i>Ab initio</i> molecular dynamic
BES	Basic Energy Sciences
DFT	Density functional theory
DOE	U.S. Department of Energy
EFRC	Energy Frontier Research Center
IIC	Institute for Integrated Catalysis
NH ₃ SCR	Selective catalytic reduction of NO _x with ammonia
NMR	Nuclear magnetic resonance
PNNL	Pacific Northwest National Laboratory
POSS	Polyhedral oligomeric silsesquioxane®
STM	Scanning tunneling microscopy
TMA	Trimethyl acetate
TMAA	Trimethyl acetic acid



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INTRODUCTION

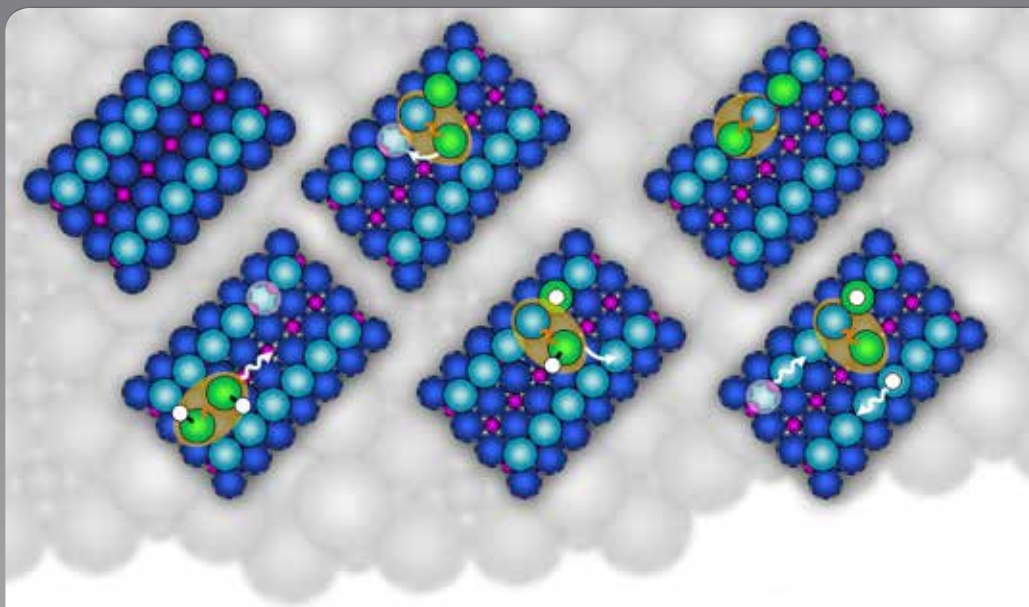
Catalysis is key to transitioning from fossil fuel-based energy to renewable energy, vital for a long-term sustainable society. Currently, 80% of all chemical products and energy carriers are made using catalysts in at least one of the processing steps. Scientific and engineering advances are required to design and synthesize more efficient and selective catalysts and to develop new routes that enable a more distributed production of energy carriers, partly for chemical storage of electricity. Fundamental catalysis research is being strengthened by advances in Pacific Northwest National Laboratory's (PNNL's) capabilities to measure chemical and physical properties under a wide variety of conditions and with unprecedented spatial and temporal resolution. Analysis of the resulting data is greatly aided by theoretical chemistry and computational methods. Advancing our understanding and using it to synthesize new catalysts and devise new approaches will address the challenge of more efficient energy production and use.

The IIC is the largest non-industrial catalysis research and development organization in the United States

Institute for Integrated Catalysis

The Institute for Integrated Catalysis (IIC) at PNNL is advancing the ability to control chemical transformations and chemical-electrical energy interconversions to reduce significantly the global energy system's carbon footprint. The IIC is the largest non-industrial catalysis research and development organization in the United States. The Institute has a critical mass of more than 150 permanent scientists and engineers contributing to catalysis research and development, working on projects totaling more than \$25 million/year.

The goals of the U.S. Department of Energy's (DOE's) Basic Energy Sciences (BES) funded programs are to provide a fundamental understanding of catalytic processes for the reductive conversion of biogenic resources and for the direct conversion of carbon dioxide to energy carriers. Using this knowledge, the IIC synthesizes new catalysts and designs new catalytic routes to energy carriers. Combining and sterically assembling multifunctional sites in solid and molecular



catalysts affords cascade strategies that impact complex transformations. The integration across multiple disciplines, including heterogeneous and homogeneous catalysis, surface science, and computational methods, forms the basis for new approaches in four areas:

1. Reductive conversion of biomass to fuels
2. Reductive conversion of carbon dioxide
3. Photochemical production of molecular hydrogen and the fundamentals of hydrogen activation with and without metal catalysts
4. Reduction of NO_x from the exhaust of automotive and truck engines operated under lean conditions.

These activities involve basic and applied research to understand the chemical aspects of catalysis and to use it to advance both science and practical applications. Our fundamental efforts, concentrated in the BES Catalysis Science program, benefit markedly from strong interactions with other basic and applied catalysis programs in the IIC and with other synergistic basic science programs funded by BES at PNNL.

Basic Energy Sciences Program

This booklet describes the current programs and capabilities that are the basis for realizing our vision and goals. Highlighted are core projects within the IIC that are currently supported by the BES Catalysis Science program, as well as affiliated projects funded by other BES program offices. The fundamental science projects are located in PNNL's Catalysis Sciences Group in the Physical Sciences Division in the Fundamental & Computational Sciences Directorate.

The BES Catalysis Science core program, **Multifunctional Catalysis to Synthesize and Utilize Energy Carriers**, consists of three thrust areas, aimed at developing new catalytic chemistry from understanding these components:

Thrust 1: Conversion of Biogenic Molecules in the Presence and Absence of Water

Subtask 1.1: Multifunctional Solid Catalysts for Lignin to Hydrocarbons — Understanding and Controlling Scalable Catalytic Routes in the Aqueous Phase

Subtask 1.2: Well-Defined Metal Oxide Catalysts — Understanding Fundamental Chemical Transformations and the Role of Water for Catalyzed Reactions

Thrust 2: Conversion of Carbon Dioxide to Energy Carriers

Subtask 2.1: Multifunctional Catalysts for Carbon Dioxide Reduction

Subtask 2.2: An Energy-Based Approach to Bifunctional Molecular Catalysis for Carbon Dioxide Reduction and Fuel Utilization

Thrust 3: Generation and Conversion of Hydrogen

Subtask 3.1: Fundamental Studies of Water Splitting on Model Titanium Dioxide, Ruthenium Dioxide and Mixed Titanium Dioxide-Ruthenium Dioxide Catalysts

Subtask 3.2: Activation of Small Molecules with Bifunctional Ambiphilic Catalyst Complexes

Subtask 3.3: Heterogeneously Catalyzed Reactions in Condensed Media

These seven subtasks benefit from Wendy Shaw's DOE Early Career Award, which is entitled Catalyst Biomimics: A Novel Approach in Catalyst Design. They also benefit from the affiliated Center for Molecular Electrocatalysis (Energy Frontier Research Center [EFRC]). In addition, these subtasks benefit from collaborative discussions with our applied research into biomass-based fuels and vehicle emissions controls.

THRUST 1: CONVERSION OF BIOGENIC MOLECULES IN THE PRESENCE AND ABSENCE OF WATER

Our aim is to develop a better understanding of how complex, polar biogenic molecules interact with the metal and the acid-base components of a catalyst consisting of metals supported on oxide surfaces. We are studying surfaces that are well defined and that allow a bridge between single crystals and dispersed materials. The role of increasing concentrations of water is being explored via physicochemical characterization and kinetic analysis. Hydrodeoxygenation and hydroalkylation are the key reactions to help understand potential routes from lignocellulosic biomass to alkane energy carriers requiring several catalytic functions to occur sequentially. Because most the reactions involve water or occur in its presence, the direct and indirect effects on the catalytic transformations are explored. While competing for reaction sites, water also affects the adsorbed state of reactants and products as well as the transition states. The competition and relative stabilization between water and reactants drastically influences conversion rates and selectivities.

This thrust consists of two subtasks:

- ▶ Multifunctional Solid Catalysts for Lignin to Hydrocarbons — Understanding and Controlling Scalable Catalytic Routes in the Aqueous Phase
- ▶ Well-Defined Metal Oxide Catalysts — Understanding Fundamental Chemical Transformations and the Role of Water for Catalyzed Reactions

Subtask 1.1: Multifunctional Solid Catalysts for Lignin to Hydrocarbons — Understanding and Controlling Scalable Catalytic Routes in Aqueous Phase

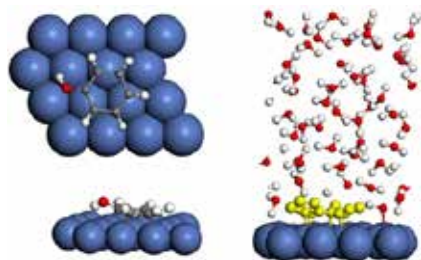
PI – Johannes Lercher

Co-PIs – Donald M. Camaioni, John Fulton, Jian Zhi Hu, Bernd Kabius, Donghai Mei, and Yong Wang

The catalyzed conversion of lignin to hydrocarbon energy carriers requires a cascade of reactions for deconstructing and reducing the polymeric, highly oxofunctionalized material. 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 fraction of lignocellulose. In the present phase, we are focused on understanding the properties of catalysts in an aqueous environment and the catalytic chemistry of lignin fragments in the aqueous environment as well as the biphasic oil-water environment. In particular, we are studying ether

hydrogenolysis and hydrolysis, the reduction of phenols, hydrodeoxygenation of alcohols, and the alkylation of (substituted) phenols in the aqueous phase using supported noble and base metals as well as zeolites. Hydrogenation, hydrogenolysis, and even hydrolysis were found to be effectively catalyzed by supported palladium and nickel catalysts allowing for higher reaction rates on these metal particles than observed previously by molecular catalysts.

The impact of water on the supported metal has been explored, using X-ray absorption spectroscopy. We followed the state of palladium and catalysts under reaction conditions. We have demonstrated that both metals were not oxidized and interacted only weakly with water in the presence of 30 bar H_2 . We showed that under typical operating conditions with temperatures up to $200^\circ C$, the metal surfaces were in equilibrium with H_2 . The high partial pressure of the H_2 kept the metals in a reduced state even in acidic solutions (0.5 wt% H_3PO_4 or 15 wt% CH_3CO_2H) at $200^\circ C$. In the case of palladium, water's lack of influence is best demonstrated in the palladium-palladium distances, indicating the presence of sorbed hydrogen and of palladium hydrides. It has also been shown that the concentration of hydrogen in palladium subtly depends on the presence organic reactants competing for H_2 . This demonstrates that neither the palladium particles nor the hydrogen/palladium ratio in the nanoparticle are influenced by water, but dynamically adapts to reaction conditions.



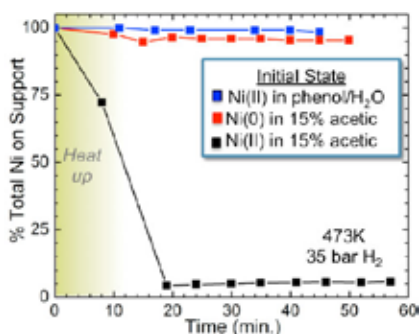
Snapshot of *ab initio* molecular dynamic simulation of phenol adsorption to Ni(III) surface in the absence and presence of water.

In support of these observations, density functional theory (DFT) *ab initio* molecular dynamic (AIMD) simulations have shown that palladium-water interactions are relatively weak for metallic palladium metal and that these interactions become even weaker in presence of H_2 and when hydrogen atoms are incorporated into the metal particles. We also modeled the effects of liquid water on metal-catalyzed hydrogenation of phenol. Our dynamic modeling results indicate that both the polarization of the metal induced by water molecules at the interface (changes in the work function) and phenol-water interactions (solvation effect) play important roles in stabilizing adsorbed phenol molecules and the transition states for the hydrogenation steps.

The effect of liquid water on the electronic structure of the metals is a repulsive interaction between the electrons of the water and the electron density emanating from the metal surface. The redistribution of electrons from the metal surface into the subsurface lowers the metal work function by approximately 1 eV and causes the metal to be a stronger chemical reducing agent. As a result, the phenol

adsorption energy is lowered, despite stabilizing interactions between adsorbed phenol and surrounding water molecules. The reaction barriers for adding surface-bound hydrogen atoms to phenol are lowered too, by the interaction of the polarized transition states with water. The liquid environment significantly influences the relative energetics of polarized surface-bound intermediates. For phenol hydrogenation, this enhanced solvation results in a shift towards the energetic preference to form ketones as a result of tautomerization of surface-bound enol-intermediates.

Catalysts with dual functions, consisting of highly dispersed nickel nanoparticles on acidic supports including sulfonated carbons and zeolites (HZSM5 and HBEA), have been synthesized and characterized. The catalysts efficiently convert liquid phase phenol to cyclohexane through cascade reactions, the nickel particles catalyzing hydrogenation of unsaturated C=C and C=O bonds and the acidic sites on the support catalyzing dehydration of cyclohexanol. Interestingly, nickel/sulfonated carbon catalysts were effective for hydrodeoxygenation of phenol in the hydrocarbon solvent but not in water. The presence of liquid water inhibited deoxygenation but not hydrogenation. Although we are only beginning to understand the phenomena at this time, it appears that the presence of liquid water slows dehydration of cyclohexanol, because we observed the formation of nickel particles during catalysis in liquid water using *in situ* X-ray absorption spectroscopy.



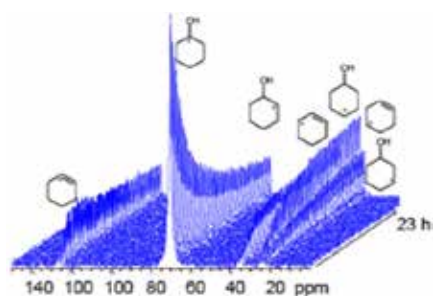
Ni⁰ nanoparticles supported on HZSM5 zeolite are stable relative to NiO during hydrodeoxygenation of phenol. Whereas NiO particles dissolve rapidly in 15 wt% acetic acid, pre-reduced nickel nanoparticles are stable.

Zelolites have been shown to be uniquely effective at cleaving carbon-oxygen bonds (dehydration catalyzed by zeolites had a 100-fold higher activity per proton than reactions catalyzed by mineral acids). Zeolites were also effective in forming carbon-carbon bonds (alkylation of phenol is only possible in sufficiently large zeolite pores). Using *in situ* ¹³C magic angle spinning nuclear magnetic resonance (NMR) spectroscopy, cyclohexanol dehydration was shown to be reversible and the protonation/deprotonation of cyclohexene was shown to be fast compared to the addition of water. To perform these experiments, we developed a micro-autoclave/solid-state NMR rotor capable of withstanding temperatures up to 200°C and pressures up to 20 bar. This capability will be invaluable for elucidating elementary steps in the hydrodeoxygenation and alkylation reactions. As an example, our ¹³C spectra show that the conversion

of cyclohexanol is accompanied by significant migration of the hydroxyl group in cyclohexanol and the double bond in cyclohexene with respect to the initial position of the labelled carbon.

A combination of spectroscopies, in particular NMR and extended X-ray absorption fine structure spectroscopy, as well as transmission electron microscopy, which was performed on both dry zeolite powder and a zeolite suspension in liquid, showed that water damaged the zeolite producing structural defect sites, *i.e.*, silicon-oxygen and aluminum-oxygen bond cleavage leading to a loss of lattice integrity. The effect of liquid pore water on the catalytic Brønsted acid sites has been explored through both experiment and theory. This exploration is leading to a better understanding of the processes occurring during acid-catalyzed reactions such as dehydration of cycloalkanol. Because zeolites have often been employed as palladium- and nickel-catalyst support material, an understanding of framework modifications is deemed crucial for further catalyst stability and performance enhancement. We are particularly interested in MFI- and BEA-type zeolites, because the large and medium pore size promotes alkylation reactions occurring during biomass conversion to liquid-fuel-range alkanes.

The degree of substitution of Si^{4+} by Al^{3+} in zeolite framework determines the concentration of Brønsted acid sites. As the location of these aluminum-tetrahedral sites will influence the subtle steric requirements for the catalyzed reactions, quantitative information about the location of aluminum T-sites in the framework is critical to rationalize catalytic properties and to design new catalysts. Using a combination of extended X-ray absorption fine structure analysis and ^{27}Al MAS NMR spectroscopy supported by DFT-based molecular dynamics simulations, a first quantitative distribution of Al^{3+} in the HBEA zeolite framework has been attained. The distribution of aluminum T-sites in samples of HBEA150 and HBEA25 differed markedly and in neither zeolite did the distribution follow the predicted thermodynamic stability of the aluminum T-sites. This strongly suggests that the incorporation of aluminum into the zeolite lattice during hydrothermal synthesis is controlled by kinetics and primarily determined by the templating constituent. As the HBEA150 was prepared by removing a significant fraction of aluminum from the lattice, the lack of population in highly populated sites of HBEA25 may be associated with the dealumination process. It helps to understand that some sites are more resilient

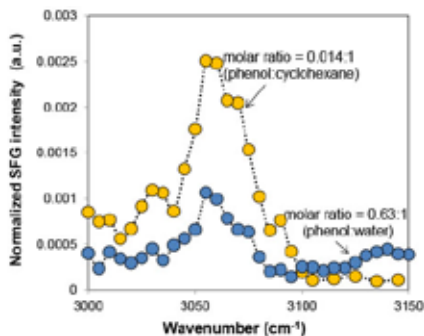


Stacked plot ^{13}C NMR spectra acquired during hydrolysis of cyclohexanol over HBEA150 at 130°C in liquid water. Using laboratory-fabricated magic angle spinning NMR autoclave/rotor.

towards removal of aluminum than others. While the details of this dealumination process are yet to be explored, the analysis using a combination of extended X-ray absorption fine structure, NMR, and theory demonstrates the potential to analyze zeolite active sites in a depth and detail, which were not available hitherto.

Preliminary results on phenol, alcohols, and water interacting with powdered catalyst materials at room temperature have been obtained from sum frequency generation spectroscopy. It is possible to monitor the adsorbed molecules as well as the water solvent over a broad spectral range, 1000-4000 cm^{-1} . The results indicate that at room temperature, the zeolite surface predominantly adsorbs water molecules and the competitive adsorption between the water and substrates molecules at different temperatures may be probed. Further experiments under controlled temperature and pressure, as well as controlled concentrations and pHs, are planned to determine the potential of sum frequency generation spectroscopy to contribute to understanding the processes and mechanisms of the surface interaction and reactivity of zeolite catalysts.

As these measurements and simulations have led the way to better catalysts for lignin conversion, we now also work to address the challenge of quantitatively and qualitatively exploring all individual steps of these reactions (adding calorimetry and sum frequency generation spectroscopy to the suite of analytical methods) to use this information to synthesize tailored catalysts that combine the functions in catalysts organized at a mesoscale level.



Sum frequency generation spectra of interface between HBEA25 and phenol-water solution (lower trace) and phenol-cyclohexane solution (upper trace) in the aromatic carbon-hydrogen stretch region.

Subtask 1.2: Well-Defined Metal Oxide Catalysts — Understanding Fundamental Chemical Transformations and the Role of Water for Catalyzed Reactions

PI – Charles H.F. Peden

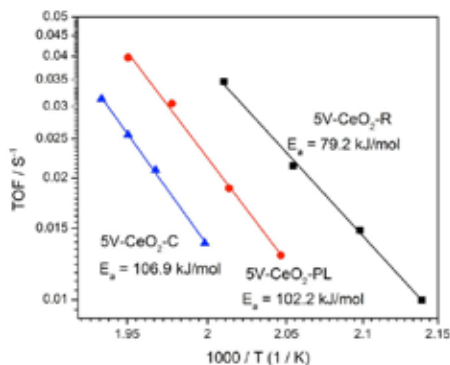
Co-PIs – Zdenek Dohánek, Jianzhi Hu, Bruce D. Kay, Jun Liu, Roger Rousseau, and Yong Wang

By employing an integrated experimental and theoretical approach, we are advancing our 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.

High Surface Area Model Catalysts. We are synthesizing dispersed transition metal oxides with controlled domain size and atomic connectivity supported on high surface area scaffolds with nominally inert and homogeneous surfaces and then providing a detailed characterization. With such materials, we are able to more precisely probe structure-function relations for supported transition metal oxides and reduce the ambiguity of the interpretation of results from ensemble-averaging spectroscopic techniques such as NMR, infrared, ultraviolet-visible, and X-ray absorption. Direct tests and comparisons with results from ultrahigh vacuum models and from high-level electronic structure calculations can be made much more rigorous.

Recently, we prepared CeO_2 supports including nanocubes, nanorods, and nanopolyhedras with dominating facets, *i.e.*, low index (100), (110) and (111) facets. We investigated the facet effects on the structure and catalytic performance of supported vanadium oxide catalysts using oxidative dehydrogenation of methanol as a model reaction. In the presence of mixed facets, infrared and Raman spectroscopic measurements demonstrate that surface vanadia species preferentially deposit on the (100) facet of CeO_2 , presumably because of its higher surface energy. At the same surface vanadium densities, VO_x species on (100) facets show better dispersion, followed by (110) and (111) facets. The VO_x species on CeO_2 nanorods with an approximately equal amount of (110) and (100) facets display higher oxidative dehydrogenation activity and lower apparent reaction activation energies compared to VO_x species on CeO_2 nanopolyhedras with dominating (111) facets and CeO_2 nanocubes with dominating (100) facets. The higher activity for $\text{VO}_x/\text{CeO}_2(110)$ might be related to the fact that more abundant oxygen vacancies are present on the (110) facets, evidenced from Raman spectroscopic measurements.



Arrhenius plots of 5V-CeO₂-R/C/PL catalysts in oxidative dehydrogenation of methanol.

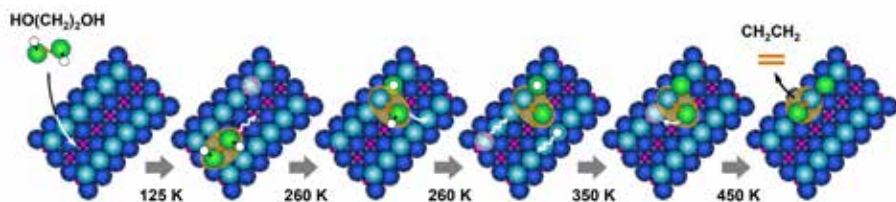
Planar Model Catalysts. Due to the vast number of simultaneous reaction pathways, the chemistry governing the deoxygenation of complex macromolecules contained in biomass (*e.g.*, cellulose, hemicellulose, lignin) is very difficult to decipher. Therefore, smaller building blocks containing prototypical functional

groups such as diols and polyols have to be employed to gain mechanistic understanding of the underlying chemical transformations and to provide insight into the role individual moieties play.

Experimental studies of polyols on titania surfaces. In our recent studies, we have followed a complete sequence of elemental steps in the reaction of both ethylene glycol and 1,3-propylene glycol on $\text{TiO}_2(110)$ at low coverages using variable temperature scanning tunneling microscopy (STM), temperature-programmed desorption measurements and DFT simulations. The use of ethylene glycol and 1,3-propylene glycol allowed us to compare and contrast the chemistries of two functionally similar molecules with different steric constraints and yielded information about how molecular geometry may influence the observed chemical reactivity. Our temperature-dependent studies provided evidence for

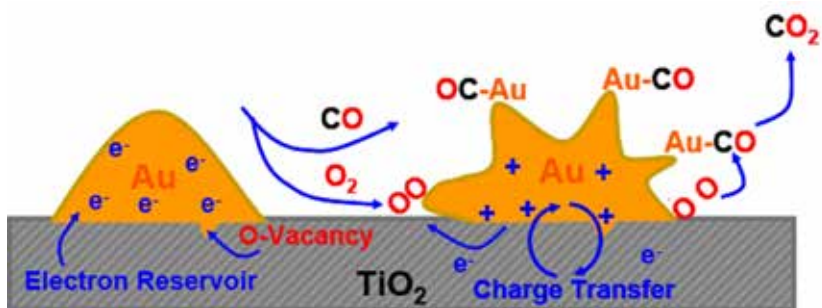
- ▶ Oxygen-hydrogen dissociation of titanium-row-bound diols at temperatures as low as 125 K
- ▶ Diol diffusion to and dissociation in bridging oxygen vacancy sites via both carbon-oxygen and oxygen-hydrogen bond cleavage above ~ 230 K.

In addition, the studies illustrated the dissociation dynamics of the second titanium-row-bound OH group at 300 K and revealed the formation of a new high-temperature intermediate above ~ 400 K. Coverage-dependent temperature-programmed desorption studies further showed that alkenes and aldehydes are the major carbon-containing products formed from ethylene glycol and 1,3-propylene glycol. While the alkenes are observed from the lowest coverages, aldehydes form primarily at high coverages. This study represents a first attempt to gain a detailed mechanistic understanding of chemical transformations of diols on model single crystalline transition metal oxide surfaces.



A sequence of elemental steps in the conversion of diols on $\text{TiO}_2(110)$ determined from combined scanning tunneling microscopy, temperature-programmed desorption, and density functional theory studies.

Theoretical studies of strong metal support interactions. Reducible oxides, such as titanium dioxide and cerium dioxide, can play a critical role in catalysis either directly taking part in reactivity or by modulating the reactivity of metal particles supported on these oxides. We have undertaken ambitious theoretical studies to clarify the role of reducible oxides in catalysis with a specific goal of understanding how excess charge carriers, generated by defects such as oxygen vacancies, impact surface reactivity. In a recent study,⁴ we probed metal particle/reducible oxide interactions, by employing DFT-based AIMDs on a prototypical metal cluster (Au_{20}) supported on a reducible oxide (rutile $\text{TiO}_2(110)$) to explicitly account for finite temperature effects and the role of excess surface charge in the metal oxide. We found that in a reducing chemical environment, the charge state of the gold particle is negative, whereas in the presence of oxidizing species co-adsorbed to the oxide surface, the cluster obtains a net positive charge. In the context of the well-known carbon monoxide oxidation reaction, charge transfer facilitates the plasticization of Au_{20} , which allows for a strong adsorbate-induced surface reconstruction upon addition of carbon monoxide, leading to the formation of mobile gold-carbon monoxide species on the surface. The charging/discharging of the cluster during the catalytic cycle of carbon monoxide oxidation enhances and controls the amount of O_2 adsorbed at oxide surface/cluster interfaces and strongly influences the energetics of all redox steps in catalytic conversions. Contrary to the ubiquitous picture of a statically charged metal cluster performing catalysis with the oxide being only a spectator, we find charge transfer occurs dynamically throughout the catalytic cycle with electrons shuttling back and forth between the metal and the support. We are currently extending and generalizing these findings to obtain a more comprehensive picture of support/metal interactions and their impact upon catalytic reactivity.



A schematic representation of the dynamic exchange of electrons between the metal cluster and the support during the carbon monoxide (CO) oxidation reaction catalyzed by gold (Au) clusters supported on titanium dioxide (TiO₂).

THRUST 2: CONVERSION OF CARBON DIOXIDE TO ENERGY CARRIERS

The use of carbon dioxide as a renewable resource in a carbon-neutral economy is highly desirable due to the range of possible fuels. Research in this thrust focuses on solving scientific challenges that hinder conversion of carbon dioxide to energy carriers such as methanol and methane. The primary objective is to develop a fundamental understanding of homogeneous and heterogeneous catalytic processes on structurally well-defined catalytic systems and to design novel catalysts that take synergistic advantage of the acquired mechanistic insights. The thrust consists of two subtasks:

- ▶ Multifunctional Catalysts for Carbon Dioxide Reduction
- ▶ An Energy-Based Approach to Bifunctional Molecular Catalysis for Carbon Dioxide Reduction and Fuel Utilization.

The unifying theme of this thrust is the study of the catalytic activity of single metal centers in the presence of a second functionality for both heterogeneous and homogeneous catalysts. The overall aim compares and contrasts thermal and electrocatalytic carbon dioxide reduction in each environment.

Subtask 2.1: Multifunctional Catalysts for Carbon Dioxide Reduction

PI – Roger Rousseau

Co-PIs – Zdenek Dohnálek, Dave Heldebrant, Abhi Karkamkar, and Janos Szanyi

By combining experimental and theoretical capabilities, we are quantifying the mechanistic chemistry of catalytic carbon dioxide conversion to fuels (methane, methanol, and C₂ oxygenated hydrocarbons) by well-characterized multifunctional catalysts in media including vapor phase, liquid phase, and ionic liquid environments. This project will

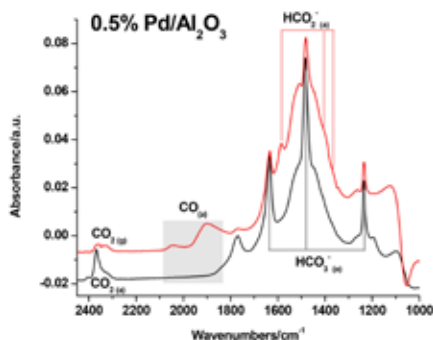
- ▶ Identify the chemical functionalities required by a catalyst to perform the desired transformations of carbon dioxide
- ▶ Determine how these functionalities can be tuned by change of catalyst structure or support to optimize catalyst activity and selectivity
- ▶ Evaluate the role of the chemical environment on the mechanistic pathway
- ▶ Systematically build catalysts using this information and test them towards carbon dioxide conversion.

High Surface Area Model Catalysts: Synthesis, Characterization, and Kinetics Studies. Although sub-nanometer-sized metal particles are frequently present in

supported heterogeneous catalysts, their contribution to the overall reactivity and selectivity is not understood. To test catalytic activity as a function of the size and shape of metal particles, it is critical to understand how metal particles interact with the support material and how these interactions vary with changing reaction conditions (temperature, reducing/oxidizing environment, *etc.*).

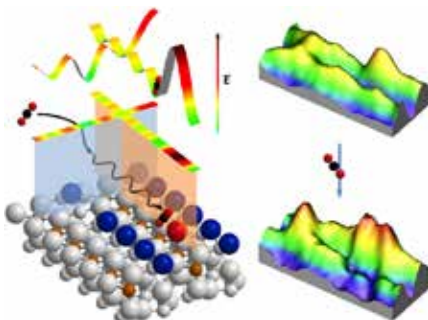
We have prepared active metals (palladium and ruthenium) in geometries ranging from atomically dispersed metals to two-dimensional rafts and three-dimensional metal particles and tested their activity for carbon dioxide reduction with hydrogen. Both atomically dispersed palladium and ruthenium supported on $\gamma\text{-Al}_2\text{O}_3$ are able to activate carbon dioxide and produce carbon monoxide with high selectivity. The three-dimensional clusters on the other hand yield primarily methane. Our work has also substantiated the critical role oxides play in providing a Lewis acidic site for the activation of carbon dioxide. For instance, atomically dispersed palladium supported on $\gamma\text{-Al}_2\text{O}_3$ is highly active in the reduction of carbon dioxide, but it is completely inactive when supported on carbon multiwall nanotubes. Doping atomically dispersed palladium on carbon nanotubes with a small amount of lanthanum oxide produced a catalyst with activity and selectivity comparable to that of atomically dispersed palladium on $\gamma\text{-Al}_2\text{O}_3$. Kinetics studies yield similar apparent activation energies for carbon monoxide formation on both catalysts suggesting a common mechanism. Intriguingly, we have recently observed the formation of bi-carbonates under catalytic operating conditions, suggesting that these species may be intermediates in the overall reduction mechanism.

Ultrahigh Vacuum Studies of Carbon Dioxide. Here, we synthesize and study well-defined planar models of mono- and bifunctional catalytic structures for carbon dioxide reduction to mimic high surface area catalysts. We use atomically resolved imaging and ensemble-averaging spectroscopies, together with theoretical calculations to develop a detailed description of catalyst structure, binding, thermal stability, and electronic properties. Elementary steps taking place during carbon dioxide reduction and hydrogenation, such as adsorption, bond dissociation and formation, diffusion, and desorption, can be revealed in great detail and provide a mechanistic understanding of the reaction pathways leading to desired products on model high surface area catalysts.



In situ Fourier-transform infrared spectroscopy measurements on Pd/Al₂O₃ samples during carbon dioxide hydrogenation at 473 K. As the concentrations of CO_{2(ads)} and HCO_{3(ads)} species formed on the alumina surface decrease, CO_(ads) on palladium appears, together with HCO_{2(ads)} on alumina.

Our work to date has focused on the detailed understanding of carbon dioxide adsorption, diffusion, binding, and dissociation on reduced and oxidized $\text{TiO}_2(110)$ surfaces (funded within Subtask 3.1). The combined experimental and theoretical studies have shown that oxygen vacancies can act as active sites that facilitate kinetically hindered carbon dioxide reduction to carbon monoxide. Further, an extremely low-barrier rotation-tumbling mechanism for carbon dioxide diffusion was found on titanium rows and a number of dynamic high coverage structures were observed. We are currently preparing alternate planar model surfaces (specifically, graphene oxide and $\text{RuO}_2[110]$) to serve as models for our high surface area studies.



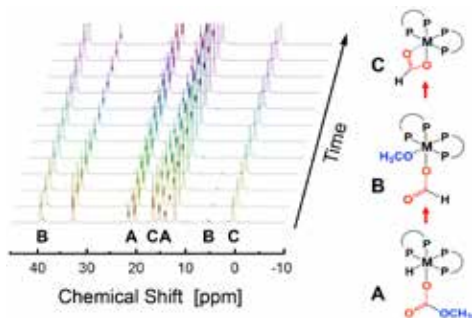
Schematic view and scanning tunneling microscopy images illustrating interaction of carbon dioxide with titanium sites and oxygen vacancies and adatoms.

Homotopic Polyoligomeric Silesquioxane (POSS) Clusters. Synthesis, Catalysis and Kinetics. The POSS framework allows us to make homotopic catalysts (via wet synthetic organometallic chemical routes) that can be used as a bridge between homogeneous and heterogeneous catalysts. A series of ruthenium-supported POSS catalysts have been synthesized and deployed in either homogeneous solution and/or supported on surfaces to function as heterogeneous catalysts. We have demonstrated that homogeneous catalysts can be tethered to POSS without loss of reactivity. Moreover, catalysts where ruthenium is directly integrated into the POSS framework can reduce carbon dioxide to formate in solution as well and carbon dioxide to carbon monoxide when supported on alumina. Indeed, we found the reactivity of the ruthenium-supported POSS sites is equal to that of the monoatomic sites employed in the high surface area studies. However, catalysts formed by supported POSS units allow us to obtain a higher weight loading of monodispersed metal atom sites than can be achieved with catalysts prepared by incipient wetness.

We have synthesized and tested POSS-based catalysts in homogeneous (condensed phase, heterogeneous (gas) phase, and ionic liquids (polar media) to compare and contrast mechanistic pathways. We are synthesizing and performing kinetic measurements on analogs of binuclear and multinuclear metal clusters and testing their activity towards carbon dioxide reduction.

Catalytic Reactivity in Switchable Ionic Liquids. Switchable ionic liquids are under development at PNNL for carbon dioxide separation from emission sources. These liquids are composed of an alcohol and an organic base that chemically bind

carbon dioxide to form an ionic liquid containing an alkylcarbonate anion. The aim of this research is to utilize the base/alcohol moieties in the liquid for a combined capture and concentration to aid the catalytic conversion of the carbon dioxide into higher value chemicals. We have successfully demonstrated combined carbon dioxide capture and conversion to methyl formate catalytically in the ionic liquid in the absence of a carbon dioxide overpressure at 129°C. *In operando* ^{13}C NMR studies suggest the reaction proceeds, by hydrogenation of the alkyl carbonate salt to a formate salt and the liberated alcohol. Then, the formate salt and the alcohol are esterified to produce a formate ester. We have yet to observe the subsequent hydrogenation to produce methanol and regenerate the switchable ionic liquid, likely due to competition with a water-gas shift equilibrium. Studies to overcome this limitation are in progress. The overall target process in its entirety is catalytic in alcohol and base with the only byproduct being water. To date, this complete cycle has been demonstrated with homogeneous catalysts based on iron and ruthenium (provided by Subtask 2.2) as well as POSS- and zeolite-based catalysts. Preliminary mechanistic studies based on *in operando* NMR and infrared (IR) spectroscopy and kinetic measurements are currently underway. Testing of this approach with heterogeneous catalysts is also underway.



In situ nuclear magnetic resonance spectroscopy studies of carbon dioxide hydrogenation by homogeneous catalysts in switchable ionic liquids suggests that alkylcarbonate hydrogenation is a critical mechanistic step for combined capture and conversion.

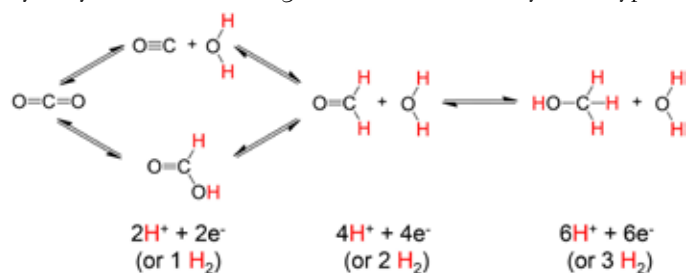
Subtask 2.2: An Energy-Based Approach to Bifunctional Molecular Catalysis for Carbon Dioxide Reduction and Fuel Utilization

PI – Aaron M. Appel

Co-PIs – John C. Linehan, Eric S. Wiedner, Wendy J. Shaw, R. Morris Bullock, and Donald M. Camaioni

In this subtask, the goal is to learn how to rationally design catalysts for the interconversion of energy and fuels, specifically for the reduction of carbon dioxide to C1 species, including carbon monoxide, formic acid, formaldehyde, and methanol. Two approaches are used here to design molecular catalysts for these C1 transformations. Our first approach is to consider the reaction energetics for each step of a catalytic transformation. By controlling the energies of the catalytic intermediates,

artificial barriers in the overall transformation can be avoided by stepping smoothly in energy from the reactants to the products. Our second approach is to use multiple catalyst-substrate interactions, as is ubiquitously observed in reactions catalyzed by enzymes. The resulting multifunctional catalysts are typically more active than



Subtask 2.2 is focused on molecular catalysis for efficiently producing and utilizing fuels from carbon dioxide.

their monofunctional analogs, and therefore, the extension of this feature to new catalytic transformations is expected to be beneficial.

Hydrogenation of Carbon Dioxide to Formic Acid. Carbon dioxide hydrogenation typically requires moderate temperatures and pressures as well as catalysts that are complexes of precious metals. The first step in this transformation is the transfer of a hydride from the catalyst to carbon dioxide. The feasibility of this step can be determined from the relative hydride donor abilities of formate and the metal-hydride catalyst. Based on thermochemical data, we have designed an active catalyst system utilizing a molecular cobalt complex that efficiently operates at 1 atm and 21°C.



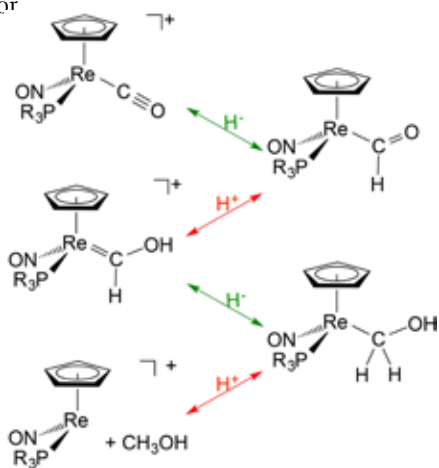
Thermodynamic data has been used to design effective molecular catalysts for the hydrogenation of carbon dioxide using first-row transition metals.

At elevated pressure, this complex of a first-row transition metal has comparable catalytic performance to the fastest precious metal-based molecular catalysts for carbon dioxide hydrogenation. We are currently designing a catalyst by using thermodynamic data for even less expensive metal complexes, such as those of iron and nickel.

Reduction of Formate to Methanol. Converting carbon dioxide to high energy density fuels will require reduction past the initial products: carbon monoxide and formic acid. The reduction of formate using molecular electrocatalysts is underexplored and is one focus within this subtask. Initial studies are focused on designing stable metal-formate complexes able to accept a hydride at the formate ligand.

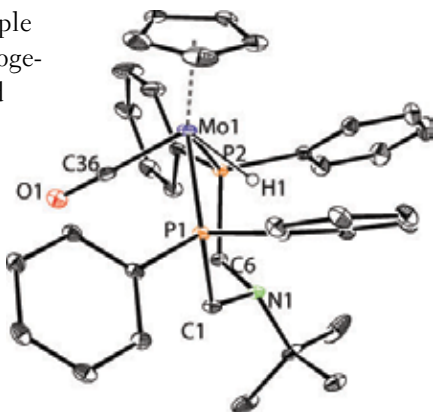
Reduction of Carbon Monoxide to Methanol.

The development of molecular catalysts for carbon monoxide reduction has been a long-standing challenge. In particular, molecular electrocatalysts for this transformation are not yet known. We have focused a new effort on developing a thermochemical understanding of the potential catalytic intermediates for this process, so that viable electrocatalysts can be designed. In initial work, the energetics of a series of possible catalytic intermediates have been characterized, revealing that the classic rhenium complexes that have been studied for this transformation will always be energetically unfavorable. These results have also provided guidance on how to proceed toward electrocatalytic systems.



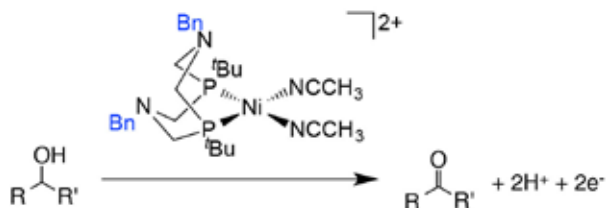
Thermochemical studies have been performed to understand how to design molecular catalysts for the reduction of carbon monoxide to methanol.

Ketone Hydrogenation. Reduction of carbon dioxide to a liquid fuel will require multiple catalytic transformations, including hydrogenation of the carbon-oxygen double bond in formaldehyde to produce methanol. To understand the requirements for the reduction of carbon-oxygen double bonds, we are examining the use of molybdenum and tungsten complexes as catalysts for hydrogenation of ketones and aldehydes to alcohols. We are currently investigating the effects of incorporating bifunctionality into these catalysts for ionic hydrogenations, so that the catalytic activity can be improved by independently tuning both the hydride donor ability and acidity.



Bifunctional molecular complexes have been prepared to allow independent tuning of the hydricity and acidity for these ionic hydrogenation catalysts.

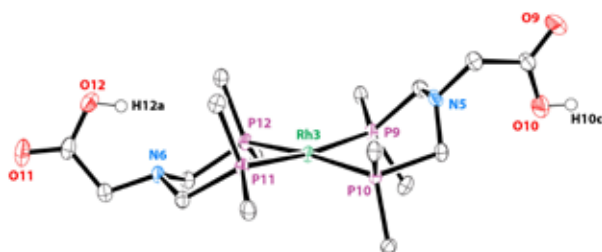
Oxidation of Alcohols. Energy efficient use of fuels will be aided by the development of electrocatalysts for use in fuel cells; however, the electrocatalytic oxidation of alcohols typically requires catalysts that contain precious metals. Based on the previous discovery that bifunctional nickel complexes containing a pendant base are capable of electrocatalytic oxidation of formate, we are investigating the oxidation



Nickel complexes can drive electrocatalytic oxidation of alcohols and are the first non-precious metal molecular catalysts for this transformation.

of alcohols using similar nickel complexes. Initial mechanistic studies have been performed using chemical oxidants, and electrocatalytic studies are in progress, both of which have yielded promising results.

Dynamic Control of Catalysts. Dynamic control over catalytically active species uses an external trigger to change the molecular structure, ligation, or other physical attribute of the catalyst. The dynamic control could have many forms and provide opportunities for advancing catalysis, from relatively simplistic functions, such as recovery of homogeneous catalysts, to the more elegant control over reactivity exerted in enzymatic systems. Current efforts in this area are focused on the incorporation of dynamically light-switchable peptides into carbon dioxide hydrogenation catalysts, to provide a foundation for regulating catalytic activity



Amino acid substituents have been incorporated into active molecular catalysts as an anchoring point for stimulus responsive functionality.

with remote regions of the catalyst. Effective carbon dioxide reduction catalysts with peptide side chains have been synthesized and tested, and the synthesis of complexes that have active switchable sites is currently underway.

Relationship to Other Projects. This effort is directly linked to the subtask on heterogeneous catalysis for carbon dioxide reduction, led by Roger Rousseau (2.1), and is synergistic with the subtask on hydrogen activation, led by Tom Autrey (3.2). Additionally, this subtask has a close working relationship with the Center for Molecular Electrocatalysis, a BES-funded EFRC led by PNNL, which focuses on the electrocatalytic production and utilization of hydrogen and the reduction of oxygen and nitrogen.

THRUST 3: GENERATION AND CONVERSION OF HYDROGEN

The efficient production and utilization of molecular hydrogen is crucial to all aspects of the chemical storage of energy: H_2 is an energy carrier itself and it is a reductant in the synthesis and upgrading of other chemical energy carriers, *e.g.*, biomass (thrust 1) and carbon dioxide (thrust 2). Ideally, the hydrogen would be made or transferred directly from renewable sources, *e.g.*, water, using renewable energy resources, *e.g.*, wind, solar by electrical and/or thermal processes. Current processes, however, exhibit low energy efficiencies (quantum yields of hydrogen in the photolysis of water <5%) and low chemoselectivities (*e.g.*, hydrogenolysis of carbon-oxygen bonds without breaking a carbon-carbon bond). In thrust 3, by separating functionalities (light absorption and energy transfer) and promoting heterolytic bond cleavage, we seek to enhance the desired conversions, particularly in polarizable media that accompany the processing of biomass and the use of water as a reactant.

The three subtasks in this thrust address the formation and activation of molecular hydrogen by multifunctional catalysts. All the tasks focus on obtaining a fundamental understanding of the properties and chemistry at polar interfaces. We seek an understanding of the collective nature of catalysis, *i.e.*, the role of bonding and conformational and environmental effects on reactive sites in the production and utilization of hydrogen.

Subtask 3.1: Fundamental Studies of Water Splitting on Model Titanium Dioxide, Ruthenium Dioxide and Mixed Titanium Dioxide-Ruthenium Dioxide Catalysts

PI — Michael A. Henderson

Co-PIs — Zdenek Dohnálek, Greg Kimmel, Igor Lyubinetzky, and Janos Szanyi

The objective of this subtask is to provide fundamental insight into catalytic and photocatalytic water-splitting reactions using model titanium dioxide, ruthenium dioxide and mixed titanium dioxide-ruthenium dioxide materials. We concentrate on obtaining a better fundamental understanding of the role of supported ruthenium dioxide as a co-catalyst in the photocatalytic splitting of water to hydrogen and oxygen. Co-catalysts are widely employed in many water-splitting photocatalysts. Ruthenium dioxide has emerged as an important material in promoting hydrogen-hydrogen and oxygen-oxygen bond formation reactions during water splitting. The details of how ruthenium dioxide functions in these capacities are

poorly understood. We will employ simple probe photochemical and chemical reactions to examine how ruthenium dioxide films, nanoparticles, and clusters enhance the catalytic and photocatalytic properties of titanium dioxide. The outcome of this research will be a better understanding specifically of ruthenium dioxide as a co-catalyst in water splitting on titanium dioxide, and in general of the properties of co-catalysts in heterogeneous catalytic and photocatalytic processes.

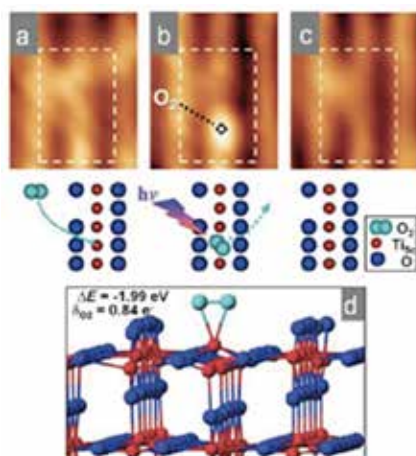
Site-Specific Surface Photochemistry. One of the many challenges facing heterogeneous catalytic researchers is identifying the surface sites responsible for specific catalytic reactions. Having the ability to determine the active sites is key to designing catalysts for maximum specificity and reactivity. This challenge is amplified in the arena of heterogeneous photocatalysis because multiple processes (*e.g.*, non-thermal charge transfer and thermal chemistry) come into play. Scanning probe microscopy offers the unique ability to interrogate photochemical reactions occurring at model surfaces on a site-by-site basis. We recently demonstrated this ability of scanning probe microscopy by providing the first definitive proof of the sites involved in oxygen photochemistry on the $\text{TiO}_2(110)$ surface. The figures show STM images that identify the surface sites on $\text{TiO}_2(110)$ involved in oxygen phodesorption and photodissociation, respectively.

An oxygen molecule adsorbs near an oxygen vacancy site at a typical five-coordinate Ti^{4+} site (Ti^{5c}). Ultraviolet irradiation removes this oxygen species through desorption without affecting the surface. In contrast, the second figure reveals the site for oxygen photodissociation on $\text{TiO}_2(110)$. When an oxygen molecule adsorbs in an oxygen vacancy site, the charge associated with the site (*i.e.*, Ti^{3+}) is transferred to the oxygen molecule removing the contrast in STM and making the oxygen vacancy appear normal. However, ultraviolet irradiation reveals where the oxygen/oxygen vacancy species are by initiating dissociation, leading to oxygen adatoms at adjacent sites. We have also shown that these two processes occur on very different timescales, with phodesorption proceeding photodissociation.

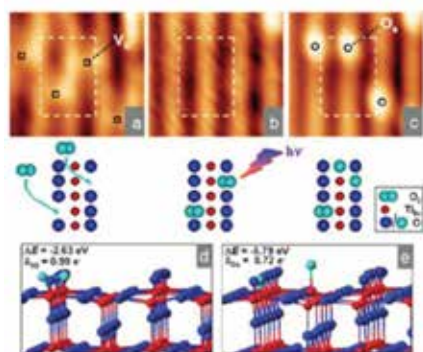
Insights into why specific oxygen photochemistry occurs at these sites comes from DFT calculations, performed in collaboration with Aaron Deskins at Worcester Polytechnic Institute. These calculations show that there is a strong thermodynamic driving force for “healing” the vacancy through oxygen photodissociation. Insights into the electronic structure of oxygen on $\text{TiO}_2(110)$ from electron energy loss spectroscopy confirms the binding geometry for oxygen at Ti^{5c} sites (*i.e.*, side-on) from DFT and also suggest that this species is more like a peroxy form (O_2^{2-}) than a superoxy form (O_2^-) of adsorbed oxygen.

Continuing on the theme of examining site specificity in photocatalysis, we further illustrate the sensitivity of STM to probe local effects during surface photochemistry with the example of trimethyl acetic acid (TMAA) photodecomposition in the vicinity of oxygen vacancy sites on $\text{TiO}_2(110)$. Adsorption of TMAA on this surface generates two types of trimethyl acetate (TMA) groups: those bound at oxygen vacancy sites (squares) and those bound at Ti^{5c} sites (circles). Panel c clearly shows that ultraviolet irradiation photodecomposes TMA groups at Ti^{5c} sites but does not for those at oxygen vacancy sites. These results indicate that holes arriving at the surface show a strong preference for where the TMA group resides.

These results represent more than just the first observations of site specificity in the cases of oxygen and TMA photochemistry on titanium dioxide—they illustrate the potential for following charge transfer processes at interfaces on a site-by-site and molecule-by-molecule basis. Determining photoactive site specificity will allow researchers to directly test the performances of designed sites and the influences of poisons, promoters, and co-adsorbates. This exciting potential of combining STM and photochemistry is highlighted in an invited article in *Chemical Review* co-authored by Henderson and Lyubinetsky.

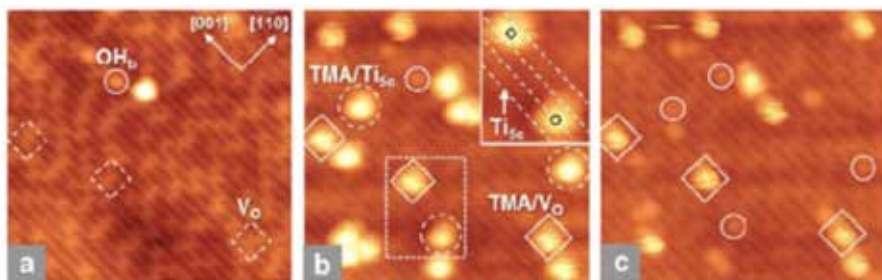


Scanning tunneling microscopy images (a) before and (b) after oxygen adsorption at a Ti^{5c} site on $\text{TiO}_2(110)$ at 50 K, and (c) after ultraviolet irradiation. Ball models are included of the rectangular areas. (d) Density functional theory calculated bonding configuration, adsorption energy, and Bader charge for oxygen chemisorbed at a Ti^{5c} site.



Scanning tunneling microscopy images (a) before and (b) after oxygen adsorption at a Ti^{5c} site on $\text{TiO}_2(110)$ at 50 K, and (c) after ultraviolet irradiation. Ball models are included of the rectangular areas. (d) Density functional theory calculated bonding configuration, adsorption energy, and Bader charge for oxygen chemisorbed at a Ti^{5c} site.

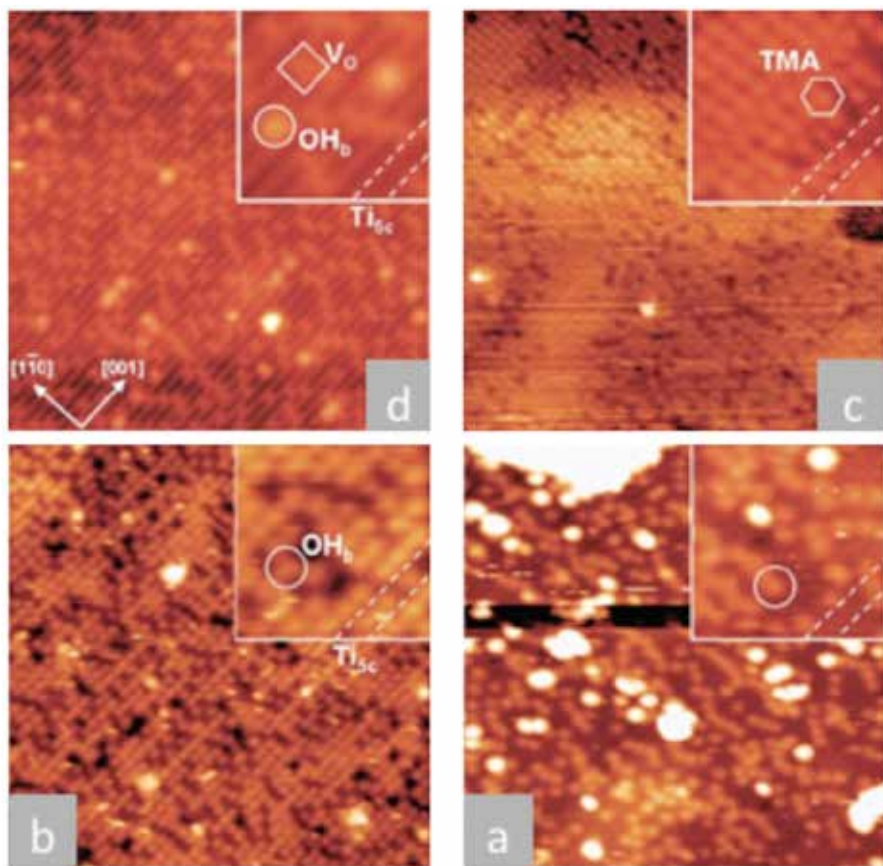
A Photochemical Pathway to a Highly Hydroxylated $\text{TiO}_2(110)$ Surface. In a novel surface preparation approach, a TMAA-covered surface was used to photochemically prepare a highly hydroxylated $\text{TiO}_2(110)$ surface. The extent of surface hydroxylation that can be achieved on $\text{TiO}_2(110)$ under ultrahigh vacuum conditions is limited to about double the surface coverage of the oxygen vacancy sites, the latter of which is typically below 0.1 ML. Because TMAA thermally decomposes on the $\text{TiO}_2(110)$ surface to TMA groups and a bridging OH group, a bridging OH group coverage of ~ 0.5 ML can easily be generated, but with a complementary coverage of TMA (see panel b). We show that ultraviolet irradiation can photodecompose virtually all the adsorbed TMA groups leaving only the bridging OH group groups (see panel c). Repeated TMA adsorption and photolysis cycles can increase the bridging OH group coverage to near saturation (not shown). The resulting OH-covered surface is shown to be reactive to subsequent oxygen exposure (see panel d). This work illustrates how photochemistry can be used to prepare metastable surfaces that are difficult to otherwise produce through thermal pathways.



Scanning tunneling microscopy images (at 250 K) of the same $\text{TiO}_2(110)$ surface area: (a) before and (b) after trimethyl acetic acid exposure, and (c) after ultraviolet irradiation. Inset in panel b displays the magnified area marked by a rectangle, with positions of trimethyl acetate and Ti_{5c} rows indicated.

The Importance of Diffusion in Photocatalysis on Titanium Dioxide. Using methanol photochemistry on $\text{TiO}_2(110)$, we have shown that thermal processes can be as important in photocatalysis as those associated with charge transfer. We previously demonstrated that adsorbed molecular methanol by itself is fairly photoinactive on $\text{TiO}_2(110)$ but that methoxy groups are highly photoactive, being converted to adsorbed formaldehyde through a direct reaction with a valence band hole. Methanol, however, does not readily dissociate to methoxy on this surface without the participation of defects (vacancies or steps) or co-adsorbed oxygen atoms, and even then methanol molecules must be able to diffuse to these sites first. Under conditions in which diffusion is hindered (such as at low temperature and coverage or when the surface is packed with competing species), the rate of

methanol dissociation to methoxy, and hence the rate of methanol photodecomposition, will depend on the thermally activated process of diffusion. We have recently illustrated the importance of diffusional limitations to photochemistry in a combined temperature-programmed desorption and STM study. Our study provided data for the yields of unreacted methanol and the photoproduct formaldehyde from ultraviolet irradiation of a low coverage of methanol co-adsorbed with oxygen adatoms on $\text{TiO}_2(110)$ at 100 K. Before ultraviolet irradiation, the co-adsorbed adlayer is preheated to various temperatures and then recooled. The amount of photoreaction is fairly limited for preheating temperatures below ~ 200 K. As the surface is preheated above 200 K, the yield of the photoreaction significantly increased.

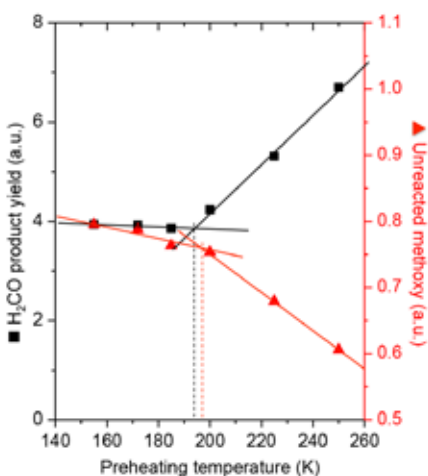


Scanning tunneling microscopy images of $\text{TiO}_2(110)$: (a) before and (b) after a near-saturation trimethyl acetic acid exposure at 300 K, followed by (c) ultraviolet irradiation and (d) subsequent oxygen exposure. Insets display magnified views of the surface with labeled species.

The origin of the enhanced ultraviolet reactivity after preheating above 200 K becomes obvious from STM data. Our research shows a low coverage of methanol adsorbed on the clean $\text{TiO}_2(110)$ surface at 110 K. The bright (red) spots residing on the Ti^{5c} rows in panel a are due to molecular methanol molecules, whereas the fainter spot located on an oxygen row is a methanol molecule (dissociated) at an oxygen vacancy site. Both features are immobile on the surface below ~ 220 K; however, the former species diffuse along the Ti^{5c} rows at 230 K. These STM results indicate that methanol molecules are able to diffuse on $\text{TiO}_2(110)$ and find reaction sites at temperatures above 200 K. The photoactivity seen in the earlier figure below ~ 200 K was therefore due to the low probability of a methanol initially landing next to an oxygen adatom at 100 K. These data also illustrate the importance of addressing both thermal and non-thermal processes to fully understand a photocatalytic process.

Preparation of Well-Defined $\text{RuO}_2(110)$ Surfaces. Ruthenium dioxide is a promising oxide-based co-catalyst in many catalytic and photocatalytic processes. For example, it is commonly used to promote hydrogen formation during water splitting. We have proposed to examine the role of ruthenium dioxide as a photochemical co-catalyst on $\text{TiO}_2(110)$.

The first step in this process is to prepare well-characterized ruthenium dioxide surfaces and understand how small probe molecules interact with these surfaces. As it turns out, ruthenium dioxide is stable in the rutile bulk structure and its (110) surface is thermodynamically stable, resembling the $\text{TiO}_2(110)$ surface. The figure illustrates our initial success in preparing the $\text{RuO}_2(110)$ surface through oxidation of the $\text{Ru}(0001)$ surface. Oxidation of $\text{Ru}(0001)$ at 550 K in $\sim 10^{-5}$ Torr oxygen resulted in large (110) terraces with atomically well-defined structures. We are now in the process of examining how these surfaces interact with simple probe molecules using STM and other surface science techniques.



Temperature-programmed desorption yields following ultraviolet irradiation of ~ 0.1 ML methanol co-adsorbed with ~ 0.03 ML oxygen adatoms at 100 K on $\text{TiO}_2(110)$ after preheating to various temperatures.

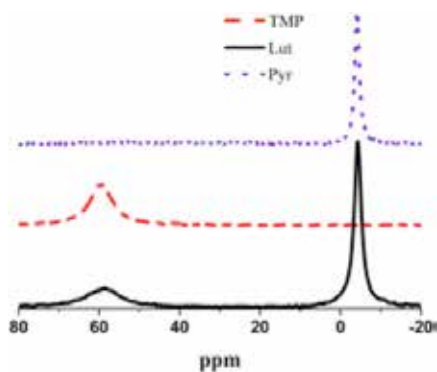
Subtask 3.2: Activation of Small Molecules with Bifunctional Ambiphilic Catalyst Complexes

PI — Tom Autrey

Co-PIs — Donald Camaioni, Abhi Karkamkar, Greg Schenter, Shawn Kathmann, Bojana Ginovska-Pangovska, Sean Whittemore, and Herman Cho

We are studying the chemical and physical properties of bifunctional ambiphilic molecular complexes with a goal of providing the fundamental insight required to rationally develop novel approaches to activate molecules for catalytic transformations. Current research uses a combination of experiment and theory to study the relationship between structure and reactivity in Lewis acid-Lewis base pairs involved in the catalytic reduction of polar substrates.

Sterics, electronics, and the properties of solvents define the kinetic barriers and thermodynamic driving force for the catalytic cycle. Our research is designed to understand how these tunable factors set the energy landscape that limit or enhances molecular transformations in catalytic reaction pathways. Our group is using spectroscopic methods (NMR and Raman) and developing reaction calorimetry methods to directly measure reaction rates and the enthalpic driving force of chemical transformations. We benefit from the use of computational methods (AIMDs) to help us understand complex reaction phenomena and guide the development of experimental design.



¹¹B nuclear magnetic resonance spectra of three distinct Lewis acid-base equilibrium conditions: (1) tris(pentafluorophenyl)borane (BCF) with pyridine, (2) BCF with 2,2,6,6-tetramethylpiperidine or TMP, and (3) BCF with 2,6-lutidine or Lut. (<http://pubs.rsc.org/en/content/articlehtml/2013/dt/c2dt31628e>).

Fundamental insight into the properties of ambiphilic 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 studying the quantum effects in hydrogen-bonding and hydrogen-activation reactions, the role of large amplitude motions and anharmonics in strained molecular complexes, and how weak interactions, such as van der Waals, and electrostatic interactions affect the structure and dynamics in the ionic salts of Lewis acid-Lewis base pair complexes. We are developing new reaction calorimetry techniques and approaches to provide a direct measure of kinetics and thermodynamics simultaneously. These approaches are providing the first detailed experimental insights

into the energy landscape describing the catalytic reduction of polar substrates by frustrated Lewis pairs. This insight is invaluable to benchmark theoretical predictions and provide guidance for future research directions. These new techniques, which are continually being improved, are not specific to frustrated Lewis pair chemistry and are beneficial to understanding catalytic reactions in general.

Our BES research is unique in that it is the only work to date that provides an experimental measure of both the rates and driving force for these catalytic reactions. Specifically, using a unique approach to reaction calorimetry, we have shown that the activation of hydrogen by the inter-molecular frustrated Lewis pairs is well described by a termolecular reaction between the Lewis acid, Lewis base, and molecular hydrogen with a very low activation barrier, $E_a \approx 20\text{-}25$ kJ/mol. We have also studied the catalytic reduction of t-butylbenzylimine (imine) using the linked frustrated Lewis pair $(\text{Mes})_2\text{P}(\text{CH}_2\text{CH}_2)\text{B}(\text{C}_6\text{F}_5)_2$. The rate constants for hydrogen activation, k_2 , and hydrogen transfer, k_3 , are readily obtained from a least-squares fit of the kinetic model to the experimental data obtained from the mixing reaction calorimeter. The overall reaction enthalpy for the reduction of the imine, ΔH , is ca. -75 kJ/mol. This example shows the remarkable utility of calorimetry to provide both kinetic and thermodynamic data simultaneously. It is also notable that hydrogen activation is rate limiting. This suggests that the disappearance of the imine will appear linear as a function of time. Our initial measurement of the catalytic reduction of the imine using *in situ* NMR is consistent with this prediction.

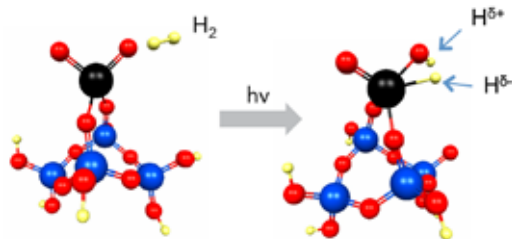
In summary, our progress to date has provided a novel experimental approach to measure both the kinetics and thermodynamics of catalytic reaction pathways. With this new methodology, we have gained insight into the reaction mechanism, *i.e.*, a termolecular reaction pathway for inter-molecular frustrated Lewis pairs, 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 turnover frequency for the full catalytic cycle. Our computational results suggest that the hydrogen-activation step is asynchronous with a side-on Lewis acid and head-on Lewis base interaction leading to heterolytic scission of hydrogen. Finally, we are using new computational methods that we developed and continue to improve to investigate the role of solvent viscosity and polarity on the catalytic reduction of polar substrates using frustrated Lewis pairs.

Subtask 3.3: Heterogeneously Catalyzed Reactions in Condensed Media

PI — Robert Weber

Co-PIs – Lelia Cosimbescu, Abhi Karkamkar, Birgit Schwenzer, Yongsoon Shin, and Zheming Wang

We are creating and characterizing frustrated, surface-supported donor-acceptor complexes and modeling the kinetics of the reactions they catalyze. The frustration affords heterolytic activation of the species 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 created using photo-activation of a ligand-to-metal-charge-transfer band of a transition metal chromophore and 2) a family in which an acid-base pair is formed from a strong supported Lewis acid and a sterically hindered base.



Temporally frustrated donor-acceptor complex formed by photo-excitation of a ligand-to-metal charge transfer complex.



Cartoon showing hydrogen complexed in the pocket of frustrated Lewis pair formed from a solid Lewis acid and a “juggled” Lewis base.

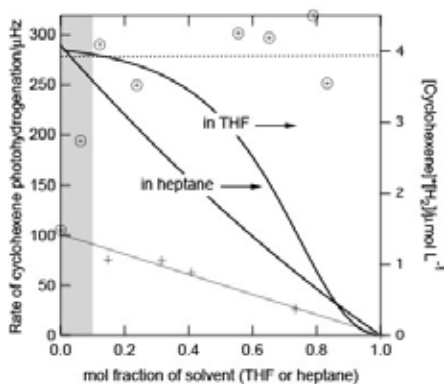
The first variant (which we call “temporally frustrated”) was prepared by grafting dioxo transition metal center (M=vanadium, chromium, molybdenum, or tungsten) to lacunary POSS[®] monomers. In the course of the synthesis of the dioxo transition metal clusters, we found that the chromophores exhibited significant solvatochromism. Moreover, the solvatochromism revealed a surprising structuring of the solvent mixtures around the chromophores, inferred from the plateau in Stokes shift as the concentration of chloroform increased. We have found evidence that such structuring of reaction media can occur in

the fluid phases encountered in the upgrading of biogenic fuel precursors that report to the aqueous phase during hydroprocessing of pyrolysis oils.

The photo-activated variant creates temporally frustrated donor-acceptor complexes that have lifetimes ($\sim 1 \mu\text{s}$) that are long compared to the timescales of diffusion and reaction. To test the effects of the structuring of the reaction media on reaction rates we used photo-activated hydrogenation of cyclohexene promoted by these complexes. The reaction rate constant exhibits a very strong solvent effect that is consistent with heterolytic addition of H_2 to the olefin.

In ongoing experiments we are testing the second variant, a spatially frustrated Lewis pair (analogous to those being studied in Subtask 3.2 led by Tom Autrey). In these experiments we elute a sterically hindered base through a gas chromatograph column packed with the solid acid using either helium or H_2 as the carrier gas. If the base and acid sites do form spatially frustrated Lewis pairs, we expect to see longer retention time when the carrier is hydrogen.

In parallel with these experimental syntheses and kinetics measurements, we are building capabilities to formulate microkinetic rate expressions that account for the targeted reactions, namely hydro-upgrading of biogenic precursors of renewable fuels. The experiments and the analyses capture variations in the local activity of the reactants and products under reaction conditions, *i.e.*, not equilibrated.



Rate of O2WPOSS-promoted, photo-activated hydrogenation of cyclohexene in polar and non-polar solvents. The rate law is first order in the local concentrations of cyclohexene and H_2 so it appears that the rate constant itself increases when the solvent is polar.

Center for Molecular Electrocatalysis

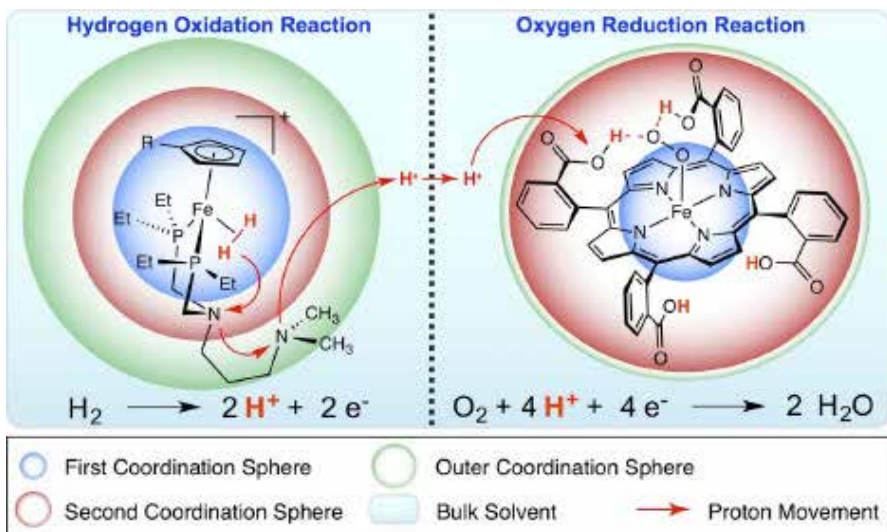
Director – R. Morris Bullock

Deputy Director – Monte Helm

Theory/Computational Leader – Michel Dupuis

Co-PIs – Michael Mock, John Roberts, Simone Raugei, Molly O'Hagan, Eric Wiedner, Aaron Appel, Roger Rousseau, and Wendy Shaw

The vision of the Center for Molecular Electrocatalysis is to develop a comprehensive understanding and spearhead a unique approach to the design of molecular electrocatalysts that efficiently convert electrical energy into chemical bonds in fuels, or the reverse, converting chemical energy from fuels into electrical energy. The approach relies on proton relays as powerful chemical functionalities designed into the catalysts and enabling facile proton delivery in these conversions. We believe this research will lead to transformational changes in the design of molecular electrocatalysts in energy research and beyond. Electrocatalytic processes involving multi-proton and -electron reactions are pervasive in energy science, and in particular play a vital role in future energy storage and energy delivery systems. We seek to understand, predict, and control the intramolecular and inter-molecular flow of protons in electrocatalytic processes of critical importance



In addition to being important for energy applications, the three reaction types studied at the Center for Molecular Electrocatalysis are prototypical systems for exploring how electrocatalysts must evolve to perform increasingly complex processes, moving from 2 to 4 to 6 protons. Controlling the transfer of protons across multiple coordination spheres for oxidation of hydrogen (left) and reduction of oxygen (right) is illustrated for iron catalysts developed in recent work by the Center.

to energy transformation reactions: the production of hydrogen, the oxidation of hydrogen, the reduction of oxygen, and the reduction of nitrogen. To achieve this goal, we focus on fundamental experimental and computational studies that address how proton relays regulate the movement of protons and electrons within and between molecules to enhance rate and efficiency of electrocatalysts.

University Collaborators. Scientists at PNNL and at four universities provide the expertise in experimental and theory/computational research required for a comprehensive approach to the problem. Jim Mayer (University of Washington; moving to Yale University in the summer of 2014) and Shannon Stahl (University of Wisconsin) focus on the development of new electrocatalysts for reduction of oxygen to water. Bruce Parkinson (University of Wyoming) is developing interdigitated electrode arrays that offer the electrochemical study of short-lived intermediates in the catalytic cycle. Sharon Hammes-Schiffer (University of Illinois) pioneered the theory of proton-coupled electron transfer. Her research focuses on characterizing proton-coupled electron transfer steps in the catalytic cycles of the hydrogen oxidation/production reactions and on developing computational methods to analyze electrochemical processes.

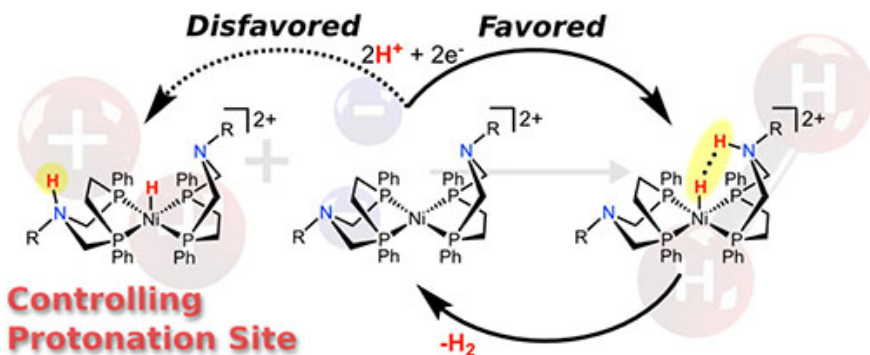
Goals and Approach. The Center for Molecular Electrocatalysis addresses fundamental challenges in understanding how molecular electrocatalysts function, and is using this knowledge to rationally design new classes of molecular electrocatalysts for energy storage and utilization. Closely coupled experimental and theoretical studies include inorganic synthesis, ligand design, mechanistic studies, electrochemical measurements, determination of thermochemical values, and evaluation of catalytic activity. These experimental approaches are synergistic with high-level theory/computational studies that provide unique insights into details of reactivity and structure. As indicated above, the unique design approach in this Center involve proton relays, *e.g.*, amine bases or carboxylic acids, in the coordination spheres that play a crucial role in the delivery of protons to (or from) the active site of molecular catalysts. The prevalence in energy science of reactions that require controlled movement of protons and electrons presages an immense scope for the roles of proton relays.

Accomplishments and Future Directions. Our comprehensive experimental and theoretical approach to understanding and controlling the movement of protons has led to the development of new catalysts based on inexpensive, abundant metals for oxidation and production of hydrogen. Nickel catalysts prepared in our laboratory are the fastest molecular electrocatalysts for production of hydrogen, although at a high overpotential. Cobalt electrocatalysts for production of hydrogen and iron catalysts for electrocatalytic oxidation of hydrogen have been developed using the concepts from the more extensive studies on nickel catalysts. NMR,

computations, and electrochemical studies are providing a deeper understanding of the roles of proton relays that advance the rational design of these complexes. Efforts are underway to lower the overpotentials with catalysts that retain high turnover frequencies.

Redox potentials, metal atom hydricities, and pKa values are quantities associated with molecular catalysts and proton relays (usually measured or derived through thermodynamic cycles) that are essential to construct free energy maps of catalytic cycles. Our efforts have established reliable computational protocols for the calculation and prediction of the above thermodynamic properties and have led to characterization of the reaction energy profiles for our highly reactive catalysts.

Efforts in developing electrocatalysts for reduction of oxygen have led to the synthesis of iron porphyrin complexes that function as selective electrocatalysts for reduction of oxygen to water in acidic solutions. Our strategy in nitrogen reduction focuses on the synthesis of complexes of molybdenum- and tungsten-containing ligands with proton relays, and has recently expanded to studies on chromium and iron complexes with nitrogen ligands. Recent results have shown that reduced nitrogen products (hydrazine and ammonia) result from adding acid to a chromium complex containing proton relays.



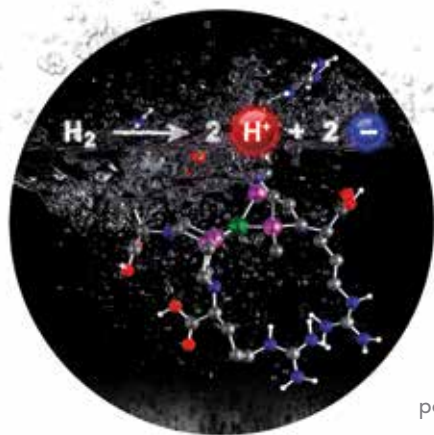
Delivery of protons to the correct position on the pendant amine (endo to the metal, rather than exo) leads to fast catalysis. Copyright: 2013. American Chemical Society

Relationship to Other Projects. The research in the Center for Molecular Electrocatalysis complements the studies of molecular catalysis carried out in the BES core program. Fundamental studies on reduction of carbon dioxide and carbon monoxide in the core BES program complement the work on hydrogen, oxygen, and nitrogen in the EFRC. The goals are distinct, although the techniques and approaches are related, allowing for substantial synergy between the projects, as well as beneficial interactions among the postdoctoral fellows and staff members.

Early Career: Catalyst Biomimics: A Novel Approach in Catalyst Design

PI: Wendy Shaw

The objective of this early career research effort is to incorporate a rationally designed proton channel into a series of homogeneous catalysts using advanced enzyme design and superior molecular catalyst design. Proton channels, which consist of a series of proton relays, are essential for the rapid rates of proton reduction or hydrogen oxidation observed in enzymes such as hydrogenase—enzymes which are widely studied for their potential impact on energy and fuel storage. By placing a fixed proton relay in a small synthetic hydrogenase mimic, such as $\text{Ni}[\text{P}^{\text{R}}_2\text{N}^{\text{R}}_2]_2$, scientists have shown rate enhancements of three to four orders of magnitude for hydrogen production and oxidation. However, these mimics still fall far short of the enzyme in overall activity. *Thus, the focus of our project is to design synthetic catalysts with an enzyme-like proton channel, exploiting the superior structure/function attributes that peptide chains demonstrate in enzymes while maintaining a relatively small catalyst (1,000-9,000 Da).*



Including an arginine in the ligand of a hydrogen oxidation catalyst results in water solubility, enhances proton movement through the COOH groups, and alters that active site structure through intramolecular guanidinium:guanidinium interactions. This results in a rate of 210 s^{-1} (overpotential of 180 mV) at 1 atm hydrogen pressure, and a rate of $140,000 \text{ s}^{-1}$ (overpotential of 460 mV) at 133 atm hydrogen.

Accomplishments. Using the amine of amino acids in the ring of a P_2N_2 ligand, we have added a second proton relay, either glycine or arginine, to create a two-relay proton channel in a hydrogen oxidation catalyst, $Ni(P^{Cy}_2N^{amino\ acid}_2)_2$. These complexes are soluble in water, performing bidirectional catalysis under nearly all pH conditions. Maximum catalytic activity is observed under low pH conditions, with rates ($33\ s^{-1}$ to $210\ s^{-1}$) similar to or faster than the currently reported fastest hydrogen oxidation catalyst ($60\ s^{-1}$). In addition to fast rates, these complexes operate at overpotentials as low as 150 mV, depending on pH, approaching that of the enzyme. The low overpotentials are thought to be related to the COOH group on the amino acid acting as a proton shuttle. The arginine-containing complex achieved a six-fold increase in rate over that of the glycine-containing complex at 1 atm hydrogen, and under 133 atm hydrogen, the complex achieved turnovers of $140,000\ s^{-1}$, an order of magnitude faster than the hydrogenase enzyme, though at higher overpotentials. The enhancements are not due to the addition of the guanidinium as a third proton shuttle. Rather, these enhancements are most consistent with a structural modification in the active site due to a quasi-aromatic interaction between the guanidinium groups, an interaction that is a common feature in enzymes.

Future Directions. These two amino-acid-based complexes represent a foundation upon which we can begin to systematically test the role of the outer coordination sphere to influence proton transfer, electron transfer, and catalytic bias. These aspects are being evaluated both experimentally and computationally. Another essential component of proton channels is proper positioning, something that structured peptides would provide. We will continue our work in this area for both hydrogen production and the two amino-acid-based oxidation catalysts.

CONNECTION TO APPLIED CATALYSIS RESEARCH

Important linkages to applied catalysis programs administered in other PNNL directorates are promoted by the IIC, all combining to attack “the Grand Challenge for catalysis science in the 21st century ... to understand how to design catalyst structures to control activity and selectivity,” and to put this understanding to use in addressing a secure energy future for our nation.

Catalyst Development for Efficient Biomass Conversion to Fuels

John Holladay, Roger Rousseau, Vanda Glezakou, Donghai Mei, and Robert Weber

Overview. In the past 5 years, researchers in PNNL’s fundamental sciences catalysis group (responding to the DOE BES program in catalysis science) have been actively interacting with researchers in PNNL’s applied programs (responding to the DOE Energy Efficiency and Renewable Energy Bioenergy Technologies Office) to provide fundamental insights based on advanced characterization techniques (performed at the Environmental Molecular Sciences Laboratory) and computational studies to accelerate the development of novel catalysts for biomass conversions into fuels.

Research Highlights. Ongoing integration of fundamental and applied programs has led to recent advancements on multiple projects. In the context of biomass-derived syngas conversion to higher alcohols, the team has recently demonstrated that iridium doping of silica and carbon-supported rhodium-manganese catalysts can result in long-lived (>100 days) catalysts with enhanced performance. Iridium doping can lead to increased selectivity towards oxygenated hydrocarbons in excess of 75% (up from the selectivity of 10-25% of the parent material) without loss of activity. The team has also contributed to development of lanthanum oxide promoted carbon-supported cobalt catalysts, and potassium-promoted molybdenum disulfide both for higher alcohol synthesis from syngas. Most recently, the team’s studies of coke-tolerant catalysts for steam reforming of benzene have been selected to appear on the cover of an upcoming issue of *ACS Catalysis*. We are now continuing and expanding these interdisciplinary collaborations in the areas of both metal- and acid-catalyzed, liquid phase, upgrading of bio-oil into refinery-blendable fuel feedstocks.

Future Directions. We have recently begun a project titled “Microkinetics of Aqueous Phase Reforming of Bio-oil,” which is part of a multi-laboratory consortium directed at advancing the modeling of the thermolytic conversion of biomass into renewable fuels. We are collaborating with the research group of Dion Vlachos

(University of Delaware) to create detailed rate models of catalyzed reactions that upgrade the aqueous phase intermediates produced by thermochemical conversion of biomass. Initially we are targeting metal-catalyzed hydrodeoxygenation, metal-catalyzed ring openings and acid-catalyzed reactions such as alkylation and dehydration. The initial models will be tuned to accord with experimental data provided to this program by Delaware and the TU Munich. Because the reaction networks are based on a microkinetic formulation, we will be able to extend them readily by adding elementary steps. Where needed, the Arrhenius parameters (enthalpies and entropies of activation) will be estimated from first-principles calculations of bond strengths and partition functions of the hypothesized intermediates. Because the correlations will be based on fundamentals of bonding with the catalysts, changes to the catalyst formulations will be accommodated through additional rounds of quantum chemical calculations or through simpler, linear scaling relations.

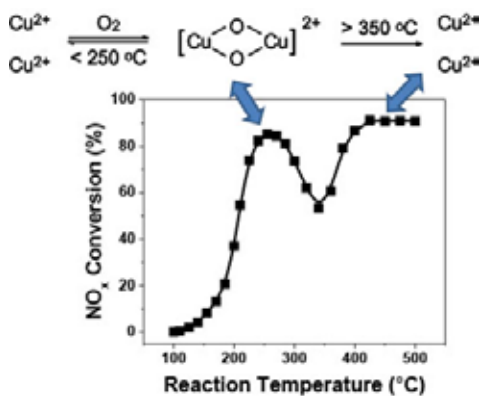
Vehicle Emission Control Research

Feng Gao, Ayman Karim, Donghai Mei, George Muntean, Chuck Peden, Larry Pedersen, Ken Rappe, Mark Stewart, Janos Szanyi, Diana Tran, and Robert Weber

Overview. The IIC at PNNL supports DOE's Vehicle Technologies mission of advanced combustion engine research and development through its work on emissions controls technologies that enable improved engine designs. Expertise and capabilities for this work have been developed in large part by programs funded by DOE's Office of Science. For example, our work in efficient particulate controls, hydrocarbons/carbon monoxide oxidation and NO_x reduction catalysts involves the use of sophisticated surface science techniques, advanced computational chemistry, modeling and simulation, and systems optimization. We also employ state-of-the-art characterization tools at the Environmental Molecular Sciences Laboratory, a DOE Office of Biological and Environmental Research user facility, as well as BES-funded facilities within the IIC. Our work focuses on reducing efficiency losses in emissions controls devices with improved catalyst materials and processes, by minimizing regeneration penalties, systems optimization, and enabling new combustion strategies.

We conduct this work with collaborators at several universities: Bill Schneider (Notre Dame University), Raul F. Lobo (University of Delaware); Fabio Ribeiro, Raj Gounder and Nick Delgass (Purdue University); and Jean-Sabin McEwen (Washington State University). We also collaborate with people at several companies: Alex Yezerets and Neal Currier (Cummins, Inc.), Christine Lambert and Bob McCabe (Ford Motor Company), Hai-Ying Chen (Johnson Matthey), and Chang Kim and Wei Li (General Motors).

Recent Highlights. Over the last 5 years or so, researchers in PNNL's IIC have been among the first to study a new generation of zeolite-based copper catalysts for the selective catalytic reduction of NO_x with ammonia (NH_3 SCR). In particular, these commercialized catalysts have the small pore chabazite structure and are both silica-aluminate ("SSZ-13") and silica-alumino-phosphate ("SAPO-34") zeolites. Because these catalysts have outstanding performance for selective catalytic reduction, high-temperature hydrothermal stability, insensitivity to unburned hydrocarbons, IIC scientists have been studying the fundamental properties of zeolites. After publishing the first open literature article comparing copper/chabazite catalysts' reactivity with other candidate zeolite-based catalysts, IIC scientists published on many of the fundamental properties of these catalyst materials including important information about the chemical and physical properties of the active copper species including results that identify likely location of copper in the zeolite structure. Very recently, our results (illustrated in the figure) indicate that the active zeolite-bound copper species is in the form of dimers at low temperatures, while higher temperature activity is due to monomeric copper species that are located at zeolite ion-exchange sites. These results explain the unusual NH_3 SCR performance data, where reactivity drops at intermediate temperatures where copper dimers dissociate to monomeric species.



Future Directions. In recognition of the need for high risk/highly efficient stoichiometric and lean combustion strategies to achieve superior performance, DOE and domestic automotive manufacturers through U.S. DRIVE are developing advanced engine technologies. However, before these advancements can be introduced into the U.S. market, they must be able to meet stringent emissions requirements. A significant roadblock to this implementation is the inability of current catalyst and aftertreatment technologies to provide the required activity at the much lower exhaust temperatures that will accompany highly efficient combustion processes and powertrain strategies. PNNL's IIC is investigating a number of novel approaches to this "low-temperature challenge" such as nano-phase catalysts, and catalyst supports that participate in the catalytic chemistry. These fundamental studies, which include mechanistic determinations of elementary reactions that limit reactivity at low temperatures, are aimed at providing revolutionary new materials and processes.

RECOGNITION AND HONORS

Ilke Arslan

- ▶ Kavli Fellow, National Academy of Sciences, 2013
- ▶ Editorial board, *Microscopy & Microanalysis*, 2014–present



Bojana Ginovska-Pangovska

- ▶ Adjunct Faculty, Computer Science at Washington State University Tri-Cities, 2011–2014



R. Morris Bullock

- ▶ Fellow, American Chemical Society, 2012
- ▶ Fellow, Royal Society of Chemistry, 2013
- ▶ Royal Society of Chemistry Homogeneous Catalysis Award, 2013



Michael Henderson

- ▶ Editorial board, *Surface Science Reports*, 2010–2011



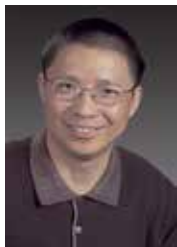
Mirosław Derewinski

- ▶ Member of Council, International Zeolite Association, 2010–present
- ▶ Editorial board, *Microporous and Mesoporous Materials*, 2010–present



Jian Zhi Hu

- ▶ R&D 100 Award, Graphene Nanostructures for Lithium Batteries, 2012



Daniel DuBois

- ▶ American Chemical Society Award in Inorganic Chemistry, 2013



Bruce D. Kay

- ▶ Editorial board, *Journal of Chemical Physics*, 2009–2011
- ▶ Past Chair, Energy Subdivision, American Chemical Society Physical Chemistry Division, 2011



Johannes Lercher

- ▶ Honorary Professor, China University of Petroleum, 2011
- ▶ Robert Burwell Lectureship in Catalysis of the North American Catalysis Society, 2011
- ▶ Zhang Dayu Lectureship of Dalian Institute of Chemical Physics, 2012
- ▶ Francois Gault Lectureship Award, 2013



Jun Liu

- ▶ Fellow, Materials Research Society, 2012



Charles H. F. Peden

- ▶ Affiliate Professor, University of Washington Department of Chemistry, 2009–present
- ▶ Adjunct Professor, Washington State University Department of Chemical Engineering, 2011–present
- ▶ Fellow, American Chemical Society, 2012



Simone Raugei

- ▶ Adjunct Professor, Biophysics at the German Research School for Simulation Sciences, Aachen, Germany, 2011
- ▶ Visiting Professor at the University of Montpellier II, France, November–December 2013



Wendy Shaw

- ▶ Kavli Fellowship, 2011



Yong Wang

- ▶ Fellow, Royal Society of Chemistry, 2013
- ▶ Fellow, American Institute of Chemical Engineers, 2013



Bob Weber

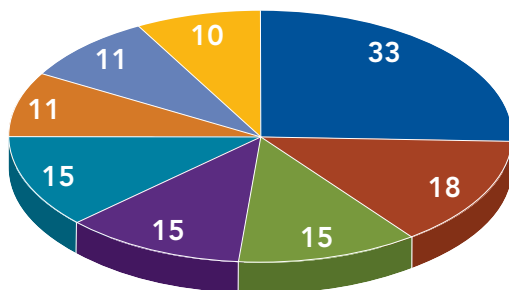
- ▶ Organizing Plenary Symposium and Thematic Sessions, ACS National Meeting, Spring 2015



PUBLICATIONS AND PRESENTATIONS (2011 TO 2014)

- ▶ 128 publications (out of 252) in the journals with the highest occurrence

■ J Phys Chem C	33
■ JACS	18
■ ACS Catalysis	15
■ Inorg Chem	15
■ J Phys Chem Lett	15
■ PCCP	11
■ Organometallics	11
■ J Catalysis	10



- ▶ 236 Invited Lectures

- 110 international conferences/meetings
- 341 universities, industry, national labs, and national meetings

*Researchers are internationally recognized leaders
in molecular and heterogeneous catalysis,
surface science and computational catalysis.*

Journal Covers (2011 to 2014)

STAFF BIOS

- ▶ Aaron Appel
- ▶ Ike Arslan
- ▶ Tom Autrey
- ▶ R. Morris Bullock
- ▶ Donald M. Camaioni
- ▶ Herman Cho
- ▶ Mirosław Derewinski
- ▶ Zdeněk Dohnálek
- ▶ Daniel L. DuBois
- ▶ Michel Dupuis
- ▶ Douglas C. Elliott
- ▶ John L. Fulton
- ▶ Feng Gao
- ▶ Bojana Ginovska-Pangovska
- ▶ Vanda Glezakou
- ▶ Richard Hallen
- ▶ David J. Heldebrant
- ▶ Monte L. Helm
- ▶ Michael A. Henderson
- ▶ John Holladay
- ▶ Jian Zhi Hu
- ▶ Abhi Karkamkar
- ▶ Bruce D. Kay
- ▶ Gregory A. Kimmel
- ▶ Johannes A. Lercher
- ▶ Mike Lilga
- ▶ Jun Liu
- ▶ Igor Lyubinetsky
- ▶ Donghai Mei
- ▶ Michael Mock
- ▶ Molly O'Hagan
- ▶ Charles H.F. Peden
- ▶ Simone Raugei
- ▶ John A. S. Roberts
- ▶ Roger Rousseau
- ▶ Gregory K. Schenter
- ▶ Wendy Shaw
- ▶ Janos Szanyi
- ▶ Yong Wang
- ▶ Zheming Wang
- ▶ Robert Weber
- ▶ Eric Wiedner
- ▶ Alan Zacher



Aaron Appel

Catalysis Science
Physical Sciences Division

Principal Investigator:

Subtask 2.2: An Energy-Based Approach to Bifunctional Molecular Catalysis for Carbon Dioxide Reduction and Fuel Utilization

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My research interests include the catalytic and electrocatalytic interconversion of energy and chemical fuels with an emphasis on thermodynamic considerations for both the individual reaction steps and the overall process. My approach is focused on the coupling of synthetic work with electrochemical and thermochemical studies to understand the limiting factors in catalytic systems (identification of high-energy steps). I have incorporated bifunctionality into catalysts to avoid high-energy species and to increase catalyst performance through improved rates and energy efficiency.

I am leading the subtask entitled “An Energy-Based Approach to Bifunctional Molecular Catalysis for Carbon Dioxide Reduction and Fuel Utilization,” which

is focused on developing an understanding of how to design new catalysts for the production and utilization of carbon-based fuels. This subtask has two themes:

- ▶ The use of an energy-based approach to design catalysts
- ▶ The use of bifunctional interactions.

Both of these themes can enable the development of molecular catalysts containing non-precious metals.

In addition to leading the subtask on the reduction of carbon dioxide, I am involved in the Center for Molecular Electrocatalysis, an Energy Frontier Research Center. Specifically, I work on thermochemical and electrochemical studies of molecular catalysts, especially those for the production and utilization of hydrogen.



Ilke Arslan

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Physical Sciences Division

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My research interests focus on the fundamental structure-activity relationships of heterogeneous catalysts using a combination of atomic resolution, three-dimensional, and *in situ/ex situ* imaging methods in the scanning transmission electron microscope. My research team has recently focused on characterizing two types of zeolite materials. The first is a layered zeolite, MCM-22, that is chemically and thermally treated to delaminate the layers without loss of active sites. A delaminated structure has the benefits of increasing the surface area and providing access to bulky molecules that would otherwise not be able to traverse the smaller zeolite pores. Using two steps—*ex situ* chemical and then thermal treatment—and imaging each of those steps, we directly

visualized the delamination process in three dimensions.

We are also studying the stability of ZSM-5 for biomass applications. By characterizing zeolites that have been boiled to several different temperatures and then cooled (maximum temperature 250°C), we determined the zeolite's structural stability at elevated temperatures relevant to reactions. We are imaging these zeolites in water in a transmission electron microscopy liquid holder to better understand their nanoscale properties in the environment native to the reaction. Through the correlation of these advanced characterization methods with catalyst activity measurements, we are gaining fundamental insights into what makes these catalysts work.



Tom Autrey

Catalysis Science
Physical Sciences Division

Principal Investigator:

Subtask 3.2: Activation of Small Molecules with Bifunctional Ambiphilic Catalyst Complexes

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My research is focused on the chemical and physical properties of catalytic ambiphilic sites with a goal of providing fundamental insight for the development of new catalyst materials designed for small molecule activation. As principal investigator on the subtask focused on activating small molecules with bifunctional ambiphilic catalyst complexes, I am leading research focused on the non-metal activation of molecular hydrogen in bifunctional molecular complexes. Sterics, electronics, and dynamical properties control the equilibrium between dative bonding and hydrogen activation in molecular complexes composed of Lewis acid-Lewis base pairs. We combine experimental and computational approaches to study how tunable environmental factors, such as electrostatic interactions, nano confinement, and pressure, enhance the kinetics and modify the thermodynamics

of hydrogen release and uptake in condensed phases. Specifically, we are developing and using research tools to investigate how the reaction environment can be used to control selectivity and enhance reactivity in chemical transformations. The heterolytic activation of molecular hydrogen, providing a catalyst-based complex containing both hydridic and protonic hydrogen, is of special interest. The team uses experimental spectroscopy methods (nuclear magnetic resonance, calorimetry, Raman, and neutrons) combined with computational methods (*ab initio* molecular dynamics) to gain fundamental insight into relationships between the structure and dynamical properties in these molecular complexes. Our basic research studies will provide the foundation for developing a rational approach to designing new catalyst materials.



R. Morris Bullock

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Director: Center for Molecular
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My research focus is on fundamental studies of the reactivity patterns of organometallic and inorganic complexes and development of these reactions into homogeneous catalysts. Much of our research involves organometallic synthesis of metal hydrides and related catalytically active complexes. A long-term interest has been *cheap metals for noble tasks*, including the study of nickel, cobalt, manganese, molybdenum, tungsten, and iron complexes. Because most fuel cells are based on platinum, an expensive, precious metal, the goal of my research is to develop electrocatalysts based on inexpensive, earth-abundant metals.

I serve as Director of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center led by Pacific Northwest National Laboratory. The

Center includes collaborators at the University of Washington, the University of Wyoming, the University of Wisconsin, and the University of Illinois. In the Center, we use experimental and theoretical approaches together to understand, predict, and control the intra- and intermolecular flow of protons in electrocatalytic multi-proton, multi-electron processes of critical importance to energy transformation reactions. We focus on the production of hydrogen, oxidation of hydrogen, reduction of oxygen, and reduction of nitrogen, by studying how proton relays regulate the movement of protons and electrons within and between molecules to enhance rates of electrocatalysis. Our research involves synthesis, mechanistic studies, electrochemistry, and determination of thermochemical properties.



Donald M. Camaioni

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Physical Sciences Division

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My research interests center on reaction mechanisms, the activation of molecules, and theoretical correlation of reactivity with structure, solvation, and surface interactions. My areas of expertise include physical organic chemistry, thermochemistry, kinetics, spectroscopy, and computational chemistry. In relation to the catalysis research thrusts, I am investigating 1) the catalysis of routes from lignin to hydrocarbon energy carriers, 2) molecular catalysis for reduction of carbon dioxide, and 3) the use of Lewis acid-base pairs to activate hydrogen and catalyze reduction of unsaturated molecules.

In thrust 1, I am working on the team to examine the catalysis of reduction and deoxygenation reactions of lignin-derived molecules in water by combinations of metal and acid functions. We focus on monitoring the state of the reacting molecules by spectroscopic methods, in combination with first principles theory to interpret and simulate the states and

reaction mechanisms. This combined experimental and computational approach potentially allows understanding of the reaction pathways for the purpose of designing new catalysts and improving existing catalysts with respect to activity and selectivity.

In thrust 2, we are developing an understanding of how to design new catalysts for the production and utilization of carbon-based fuels. I support this effort using first principles-based theory to simulate structures and energetics of key intermediates in the catalytic cycles of target catalysts.

In thrust 3, we are elucidating the mechanism of activation of molecular hydrogen by non-metal Lewis pairs for use in catalysis. We are using experimental methods with computational electronic structure methods to develop thermodynamic and kinetic models of these novel systems for catalytic hydrogenation and small molecule activation.



Herman Cho

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I am engaged in a wide range of projects that use sophisticated magnetic resonance spectroscopic techniques for both chemical analysis and studies of molecular structure and dynamics. Multinuclear nuclear magnetic resonance spectroscopy of both solution and solid state samples proves especially informative in elucidating intra- and intermolecular dynamics, reactivity, and thermodynamics in investigations of catalytic systems.

Other recent projects have led to the successful demonstration of state-of-the-art spectroscopic measurements on radioactive and other highly hazardous materials. In the course of this work, my colleagues and I have developed new facilities, instrumentation, software, and spectroscopic methods to extract the whole spectrum of quantitative, structural, and dynamical insights contained in magnetic resonance data.



Miroslaw Derewinski

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My research is focused on fundamental studies of the formation and stability of ordered microporous materials and related solids and the use of that knowledge to design complex catalysts. To monitor and analyze elementary steps of nucleation and crystal growth of catalytic zeolite materials, I conduct both kinetic experiments with *in situ* magic angle spinning nuclear magnetic resonance spectroscopy and *in situ* transmission electron microscopy.

Substituting metal cations into zeolite lattices helps not only to create local structures, but also introduces controlled locations in a framework where

thermal and solvothermal degradation as well as reformation of bonds allows the generation of new and periodic structures. Using kinetic methods, I synthesize such structures in nanometric dimensions, *i.e.*, in sizes below the periodic detectability of the framework structure, yet these materials have the complete local properties that would be seen in such microporous materials. Structural features of crystalline microporous solids of various length scales—responsible for reduced thermal and hydrothermal stability—are explored in the quest to synthesize materials with unprecedented stability.



Zdenek Dohnálek

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My research is focused on experimental studies of fundamental model systems that are necessary to understand complex processes that take place in heterogeneous catalysis. This work concentrates on adsorption, diffusion, desorption dynamics and kinetics, binding, and reactivity of adsorbates on model, well-characterized surfaces and clusters. An experimental approach involving both atomically resolved imaging and ensemble-averaged methods is employed to provide a detailed, molecular-level understanding of catalyst structure and reactivity. Novel deposition methods, developed in our laboratory, are further

used to prepare clusters and nanoporous films of model oxide catalysts with tailored chemical properties. All studies are complemented by theoretical investigations carried out by collaborators and are intended to provide general structure-reactivity relationships. My team's current studies focus on understanding the partial oxidation of alcohols and diols on supported tungsten trioxide and molybdenum trioxide clusters, nanoporous tungsten trioxide films, and $\text{TiO}_2(110)$ surface. Most recently, my colleagues and I have also investigated adsorption and dissociation of carbon dioxide on $\text{TiO}_2(110)$.



Daniel L. DuBois

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Center for Molecular Electrocatalysis

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My research interests include the catalytic interconversion of fuels and electricity, synthetic organometallic and inorganic chemistry, thermodynamic studies relevant to catalysis, and the control of intramolecular and intermolecular proton transfer reactions during electrocatalytic reactions through the use of proton relays. My research teams developed new classes of electrocatalysts for carbon dioxide reduction, hydrogen oxidation, and hydrogen production;

new electrochemical methods for carbon dioxide separation and recovery; were the first to accurately measure the thermodynamic ability of transition metal hydrides to transfer hydride ligands—an important fundamental property with broad implications in catalysis; and were pioneers in the development of proton relays in molecular electrocatalysis—also with broad implications in catalysis.



Michel Dupuis

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Physical Sciences Division

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My research expertise and interests lie in theory and modeling in catalysis, in particular photocatalysis and molecular electrocatalysis. In the area of photocatalysis, my colleagues and I provided novel insights into the structure and transport of e^-/h^+ electrons in defected photocatalytically active materials and a framework for understanding their role in mediating the reactivity of surface absorbates and other photochemical processes. Our current efforts reside within the Center for Molecular

Electrocatalysis, an Energy Frontier Research Center, where computations and experiments are tightly integrated in the development of multi-electron, multi-proton catalysts, in particular molecular catalysts that include proton relays for the efficient delivery of protons. Computations based on electronic structure theories, molecular dynamics, and electron transfer theories provide vital insights and predictions about mechanisms, rates, and overpotentials.



Douglas C. Elliott

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Over the course of my 40-year career at Pacific Northwest National Laboratory (PNNL), my research and project management have mainly been directed toward development of fuels and chemicals from biomass and waste. My experience includes handling and processing coals, biomass, and wastes primarily in high-pressure batch and continuous-flow processing reactor systems. My research has also involved extensive study of catalyst systems. In addition to process development, chemical and physical analysis has also been a significant part of my work. While at PNNL, I have

been involved in the following areas of process research:

- ▶ Catalytic hydrothermal gasification of wet biomass and waste feedstocks
- ▶ Biomass liquefaction and catalytic hydroprocessing of derived liquid products
- ▶ International activities in bioenergy processes including pyrolysis, hydrothermal liquefaction, bio-oil hydrotreating, and related environmental effluent issues
- ▶ Chemicals from renewable sources through catalytic processing of bio-derived feedstocks.



John L. Fulton

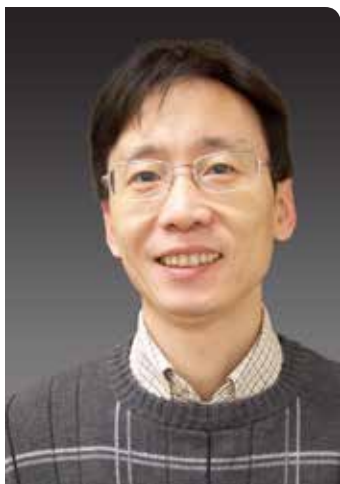
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My research focuses on describing the details of molecular structure, dynamics, and chemical state of various species in fluids, such as water, under extremely non-ideal conditions. The goal is to gain a molecular-level understanding of species such as catalysts under high temperatures and pressures. There are far-reaching fundamental issues regarding structure under non-ideal conditions that are not presently understood. Along with my colleagues, I employ spectroscopic techniques such as X-ray absorption fine structure spectroscopy and high-energy X-ray scattering. We

couple these techniques with theoretical methods such as density functional theory-molecular dynamics, and electronic structure calculations to test and refine structural models of catalytic and other systems. In total, these methods allow for a comprehensive assessment of the structure and chemical state of a catalyst or other solutes under any condition. This research provides a molecular understanding that is the scientific basis for thermodynamic and kinetic models, defining reaction pathways, and ultimately logical catalyst design.



Feng Gao

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My research interests involve surface and interfacial chemistry in heterogeneous catalysis, specifically well-defined catalytically active centers (metals, metal ions, oxides, *etc.*) on well-defined high surface area supports. This research enables the development of structure-reactivity/selectivity relationships.

My current research has two focuses:

- ▶ Fundamental and applied studies of catalytic materials and processes for the control of diesel engine exhaust

emissions, including NO_x storage reduction and hydrocarbon and urea selective catalytic reduction with state-of-the-art copper/iron-zeolite catalysts

- ▶ Basic energy science research aimed at developing atomic-level structure/function relationships in supported transition metal oxide catalysts used in the chemical and petroleum industries.



Bojana Ginovska-Pangovska

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Center for Molecular Electrocatalysis

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My research interests focus on theory-based investigation and modeling of metal- and non-metal-based catalysts for energy applications using a variety of methodologies, including quantum mechanical calculations, classical and quantum mechanics/molecular mechanics simulations, and enhanced sampling techniques. Specifically, my work focuses on understanding the role of the outer coordination sphere on proton delivery in natural enzymes and biomimetic metal-based molecular catalysts.

Currently, I am exploring the effects of mutations on the proton delivery in hydrogenase enzymes, as well as accurate characterization on reaction

pathways and thermodynamics for hydrogen oxidation and production. The work extends to modeling synthetic molecular catalysts with peptide outer coordination sphere, probing the role of the proton relays and their effect on catalysis. My research on the non-metal molecular catalysts (frustrated Lewis pairs) focuses on fundamentally understanding the mechanism of hydrogen activation and subsequent catalytic hydrogenation of unsaturated bonds. This work is expanding to explore activation of other small molecules (methane and carbon dioxide), as well as the effects of the solvent environment on catalysis.



Vanda Glezakou

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My research portfolio includes condensed systems relevant to materials and carbon capture, sequestration, and conversion. The focus of my recent work is the structure, vibrational spectroscopy, and structure/activity correlations in a diverse ensemble of systems that commonly include carbon dioxide. These studies have enabled an intimate knowledge of carbon dioxide chemistry that is transferrable to other research problems, including the following:

- ▶ Catalytic activity of metal clusters for methane steam reforming
- ▶ Catalyst design for transmetalation reactions
- ▶ Mechanistic studies for secondary methane recovery

- ▶ Studies of carbon dioxide sorption mechanism in shale components
- ▶ Solvent transformation for post-combustion carbon dioxide separation
- ▶ Mechanistic studies for metal organic framework nucleation and growth
- ▶ Solvatochromic effects in surface-supported chromophores

As a computational chemist with experience in correlated methods and transition metal chemistry, I work closely with experimental groups and provide insights regarding mechanistic details, as well as guide synthesis of novel catalytic systems.



Richard Hallen

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Development
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My research on biomass conversion started in the early 1980's with fundamental studies of wood liquefaction funded by the U.S. Department of Energy's Office of Basic Energy Sciences. This work established the pathway for conversion of cellulosic materials to cyclic and aromatic bio-oils through condensation reactions of small degradation products. Over the years at Pacific Northwest National Laboratory, I have worked extensively with industry to develop catalyst technologies to support chemical and fuel production from alternative resources

with an emphasis on renewable resources. The research has involved catalytic upgrading of both thermo- and bio-chemical intermediates. Much of the work was conducted in collaboration with industrial partners, which resulted in patents for the most promising applications. With industrial support, many of the process concepts were reduced to practice and demonstrated at the bench scale. Key to this success has been establishing collaborations and partnerships with industry in the early stages of process development.



David J. Heldebrant

Materials Chemistry
Applied Materials Science Division

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My research focuses on applying the principles of green chemistry to improve atom and energy efficiency and reduce the toxicity of chemical processes. Specifically, I develop materials that can perform multiple tasks to reduce waste and improve energy efficiency in the fields of chemical separations and chemical conversions. My work applies these principles in areas of industrial gas separations, liquid/liquid separations, and catalysis. The work focuses on developing organic gas-separating liquids that can chemically remove carbon dioxide, carbonyl sulfide, sulfur dioxide, and hydrogen sulfide from combustion or natural gas streams. Developing such liquids is possible because my colleagues and I conduct applied and fundamental studies of gas

absorption kinetics, thermodynamics, and mechanistic studies. In addition, my research includes chemical fixation/catalytic conversion of alkylcarbonates (carbon dioxide surrogates) into chemicals such as fuels (methanol), polycarbonate polymers, and pesticide/drug precursors (such as formamide and carbamylide). My experimental approach for these systems includes design and fabrication of catalysts and kinetic/thermodynamic testing of catalytic systems to study mechanisms, catalyst structure, and selectivity/reactivity. Currently, my research combines catalytic conversions of alkylcarbonates with carbon dioxide-activating/concentrating solvents to develop catalytic systems to produce value-added products from carbon dioxide.



Monte L. Helm

Catalysis Science
Physical Sciences Division

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My research interests revolve around synthetic and structural main group chemistry with emphasis on the synthesis of new phosphorus-containing compounds for selective metal coordination, activation, and catalysis. Much of the research done by my team involves synthesis of new ligands to support first row transition metals for use in the electrocatalytic conversion of energy to and from chemical fuels. Because most fuel cells are based on platinum, an expensive, precious metal, our goal is to develop electrocatalysts based on inexpensive, earth-abundant metals.

I am the deputy director of the Center for Molecular Electrocatalysis, led by Pacific Northwest National Laboratory and with collaborators at the University of Washington, the University of Wyoming, the University of Wisconsin,

and the University of Illinois. In the Center, we combine experimental and computational approaches to understand, predict, and control the intra- and inter-molecular flow of protons in electrocatalytic multi-proton, multi-electron processes of critical importance to energy transformation reactions. We focus on the production of hydrogen, oxidation of hydrogen, reduction of oxygen, and reduction of nitrogen by studying how proton relays regulate the movement of protons and electrons within and between molecules to enhance the rates of electrocatalysis. This research involves synthesis; mechanistic studies; electrochemistry; determination of thermochemical properties; and nuclear magnetic resonance, infrared, and other spectroscopic studies.



Michael A. Henderson

Catalysis Science
Physical Sciences Division

Principal Investigator:

Subtask 3.1: Fundamental Studies of Water Splitting on Model Titanium Dioxide, Ruthenium Dioxide and Mixed Titanium Dioxide-Ruthenium Dioxide Catalysts

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My research interests center on the examination of molecular-level properties of clean and adsorbate-covered oxide surfaces. Model single crystal surfaces enable correlation between surface structure and surface chemistry. The studies are conducted under an ultra-high vacuum condition, which permits detailed control of adsorbate coverages and enables surface processes to be examined with a variety of molecular-level spectroscopies. Special interests include the following:

- ▶ Characterizing adsorbates using vibrational spectroscopy
- ▶ Examining adsorption-desorption processes and surface reaction pathways

- ▶ Probing the structure/reactivity of adsorbed molecules
- ▶ Examining the interactions of photons, low-energy electrons, and ions with adsorbed species.

The overall goal of my research activities is to provide fundamental understanding into the physical and chemical properties of complex oxide surface phenomena, such as catalysis and photocatalysis, through the examination of model molecular-level systems. Current programmatic work focuses on the fundamental properties of photon-initiated chemical events promoted through electron-hole pair formation in titanium dioxide surfaces.



John Holladay

Energy and Environment Sector
Energy & Environment Directorate

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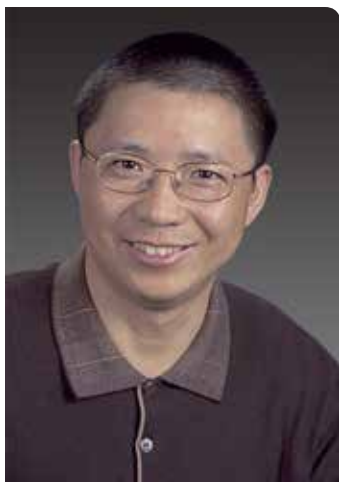
As a scientist, I have spent more than a decade helping make biofuels and bio-based chemicals. These processes have led to more than a dozen U.S. patents, numerous commercial licenses, including one practiced at the full commercial scale.

As manager of the Biomass Sector at Pacific Northwest National Laboratory (PNNL), I oversee the development of PNNL's \$20-million-a-year biomass research program. The program focuses on two areas:

- ▶ Developing cost-effective catalysts for biomass conversion
- ▶ Learning from the great efficiency that fungi and other organisms use to naturally process biomass.

I facilitate PNNL's collaboration with others in academia, industry, and government to advance the nation's biofuels research. Also, I help shape the direction of PNNL's biomass research and am currently examining which specific liquid transportation fuels—gasoline, diesel, or jet fuel—have a greater need to be replaced with biofuels.

I have served as Chief Scientific Officer for the National Advanced Biofuels Consortium and Chief Operations Officer for the National Alliance for Biofuels and Bioproducts.



Jian Zhi Hu

Biochemistry & Structure Biology
Biological Sciences Division

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My research experience includes nearly 30 years experience in solid state and liquid state nuclear magnetic resonance (NMR), magnetic resonance spectroscopy, and magnetic resonance imaging. I have developed or originated a range of slow and ultra-slow magic angle spinning or magic angle turning NMR techniques with sample spinning rates ranging from 1 to ~1000 Hz for enhanced spectral resolution in solids, semi-solids, and biological materials. Recently, I introduced the combined high-temperature and high-pressure magic angle spinning NMR for high-resolution NMR studies of the catalytic reaction mechanisms *in situ*.

My current research interests and expertise include the following:

- ▶ Development and application of *in situ* constant flow and the combined and high-pressure magic angle spinning NMR capabilities
 - ▶ *In situ* NMR capability development and applications for energy storage systems, such as live/functioning lithium-ion, lithium-sulfur, and non-aqueous redox flow batteries
 - ▶ Ultra-high field (850 MHz) NMR and computational modeling of NMR parameters
 - ▶ Development of unique high-resolution slow magic angle spinning NMR metabolomics tools for bio-signature discovery in biological tissues with sample volume from less than about 0.2 μl to more than 1 cm^3 using a single probe.
- ▶ *In situ* and *ex situ* NMR characterization of heterogeneous solid catalyst materials, surface functional groups and active sites, molecular dynamics at the interface, reaction mechanisms and pathways



Abhi Karkamkar

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Physical Sciences Division

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My research is focused on the synthesis of multifunctional catalysts that are created by an approach based on surface organometallic chemistry. This approach is being developed using silsesquioxane-based molecular compounds as single site catalysts for conversion of carbon dioxide to fuels and

activation of hydrogen on ambiphilic surfaces. My research interests also involve calorimetric studies of hydrogen storage materials and synthesis and characterization of zeolites, mesoporous materials, oxide nanoparticles, chalcogenides, and alloy materials.



Bruce D. Kay

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My catalysis-related research focuses on exploring the dynamics, kinetics, and reactivity of adsorbates on model oxide surfaces with an emphasis on understanding heterogeneous catalytic processes on early transition metal oxides. These fundamental studies employ a combination of molecular beam surface scattering and surface-analytical techniques to study model oxide catalysts, such as single crystals,

nanoscale thin films, and vapor-deposited supported clusters. This experimental work is performed in collaboration with Zdenek Dohnálek and is strongly coupled with Roger Rousseau's theoretical work. During the past year, we studied the growth and catalytic activity of nanoporous tungsten oxide films and the adsorption and reactivity of carbon dioxide and ethylene glycol on $\text{TiO}_2(110)$.



Gregory A. Kimmel

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Physical Sciences Division

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My catalysis-related research focuses on exploring the dynamics, kinetics, and reactivity of adsorbates on model oxide surfaces. This experimental work is performed in collaboration with Nikolay Petrik and other scientists involved in Michael Henderson's Subtask 3.1. We use ultra-high vacuum surface science techniques to study thermal and non-thermal reactions on model oxides surfaces such as $\text{TiO}_2(110)$. Recently, we have investigated the photooxidation of

carbon monoxide, and the adsorption and reactivity of carbon dioxide on $\text{TiO}_2(110)$. We have also investigated hydrogen reactivity on highly hydroxylated $\text{TiO}_2(110)$. Currently, we are investigating the photooxidation of acetone on $\text{TiO}_2(110)$. The goal of these investigations is to provide a fundamental understanding of the physical and chemical properties of oxide surfaces that are relevant for their use in catalysis and photocatalysis.



Johannes A. Lercher

Physical Sciences Division
Director
Institute for Integrated Catalysis

Principal Investigator:

Subtask 1.1: Multifunctional Solid Catalysts for Lignin to Hydrocarbons — Understanding and Controlling Scalable Catalytic Routes in the Aqueous Phase

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My research interests focus broadly on elucidating common principles in catalytic reactions facilitated by molecular, surface model, and complex multifunctional catalysts. Specifically, my team is addressing fundamental aspects of industrially relevant catalyzed reactions to understand the reaction steps on the surface of solid catalysts on an elementary level. This knowledge is used to design and synthesize nanoscopically well-defined chemically functionalized surfaces and materials. The synthesis and modification of the target materials is controlled on the level of the individual chemical reactions during the genesis of the (nanoscopic) particles and the assembly of the pre-functionalized entities. The materials explored primarily include highly structured micro- and mesoporous materials containing protons,

metal ions, metal, and metal-oxide clusters. Advanced characterization methods (*in situ* X-ray diffraction; X-ray absorption spectroscopy; and infrared, Raman, and inelastic neutron scattering spectroscopy) are used to characterize these materials in stages of preparation and during/after sorption and catalysis. Catalytic target reactions are the low-temperature, acid-catalyzed activation, functionalization, and transformation of alkanes; the oxidative activation of light alkanes, including methane; and the hydrogenation and hydrodefunctionalization of biogenic and fossil feedstocks (such as lignin and aromatic molecules containing oxygen, nitrogen, and sulfur). The elementary steps and selective control of sorption and diffusion in molecular sieves is another significant focus of my work outside the catalysis area.



Mike Lilga

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Development
Energy Processes and Materials

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My research focuses on the catalytic conversion of biomass-derived materials to renewable transportation fuels and chemicals. Processes that use catalysts to enable high carbon efficiencies, low temperature and/or pressure conditions, and control of product selectivities are of particular interest. A goal for fuel production is to develop methods for the production of open-chain hydrocarbon blend stocks for jet and diesel fuels. Routes to both drop-in and new chemical products are being developed. With my colleagues at the Bioproducts, Sciences, and Engineering Laboratory, we use a wide range of techniques and technologies to discover and test catalysts for reductions, oxidations, condensations, dehydrations, and other conversions. Methods range from catalyst screening using combinatorial methods, to 1-5 cc flow reactors, to 30-70 cc flows reactors,

and 50-300 mL batch reactors. Example processes we've studied include dehydration reactions of sugars, lactic acid, and 3-hydroxypropionic acid; oxidation and reduction of hydroxymethylfurfural; cracking of sorbitol to polyols; olefin oligomerization; and olefin metathesis. We've recently begun studying the electrochemical stabilization of bio-oils as part of an upgrading strategy that could minimize hydrogen usage and enable decentralized facilities. We are conducting theoretical studies to gain a first-principles understanding of catalyst behavior, product selectivity, and reaction mechanisms. This work, which has resulted in my being issued 15 patents in the area of catalysis and renewable fuels and chemical production, has been conducted for the U.S. Department of Energy and for numerous industrial collaborators.



John C. Linehan

Catalysis Science
Physical Sciences Division

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My major research goal is to determine catalytic mechanisms using *in situ* and *operando* spectroscopies, including nuclear magnetic resonance (NMR), Fourier transform infrared, and X-ray absorption fine structure. These studies are conducted *operando* (under actual catalytic conditions at high pressure and/or high temperature) and interrogate the metal catalyst species prevalent during catalysis. Meanwhile, the substrates and products also are investigated so that catalytic rates can be correlated with the metal-containing catalytic species present in a time-dependent manner. In combination with high-level theoretical studies, my colleagues and I determined the catalyst resting state structures for rhodium clusters important in both hydrogenation and dehydrogenation chemistries, as well as a plausible catalytic mechanism for the

loss of hydrogen from ammonia boranes. *Operando* high-pressure NMR studies have revealed a more accurate picture of carbon dioxide to formic acid catalysts. The determination of the role of the alcoholic co-catalysts was most important in this work, which also showed us how to remove this unnecessary additive, producing more stable catalysts without affecting the catalytic rates. New studies on formic acid-to-carbon dioxide, electrons, and protons have led to an extremely fast and efficient nickel-phosphine-based electrocatalyst. Continuing work includes determining kinetics, thermodynamics, and mechanisms of small molecule interactions with organometallic catalysts, which are active in energy conversions including molecules of interest to the Center for Molecular Electrocatalysis, an Energy Frontier Research Center.



Jun Liu

Energy Processes & Materials Division
Energy & Environment Directorate

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My research is focused on synthesis of multifunctional materials through self-assembly and controlled nucleation and growth. My group has developed a new class of functionalized mesoporous materials with great potential for catalysis and separation, with this research featured in journals such as *Science* and *Angewandte Chemie International Edition*. With my colleagues, I have conducted extensive research in controlled nucleation and growth for complex nanocrystalline metal oxides and hierarchical mesoporous materials, with research in the *Journal of the American Chemical Society*, *Nature Materials*, and *Advanced Functional Materials*.

Recently, I have begun exploring new approaches to combine controlled nucleation and growth with three-dimensional self-assembly to prepare

multicomponent composite materials. Examples include ordered graphene-metal oxide nanocomposites with high electrochemical activity and stability for energy storage and electrocatalytic applications.

My group developed a range of highly crystalline, high-surface-area mesoporous metal oxides materials; these materials showed high thermal stability for catalytic applications. Recently, my group synthesized new zeolite materials with controlled micro- and meso-porosities. More importantly, nuclear magnetic resonance (NMR) lattice relaxation methods were used to quantify the dispersed and non-dispersed catalyst phases. Such information cannot be obtained from traditional NMR, transmission electron microscopy, or X-ray diffraction techniques.



Igor Lyubinetzky

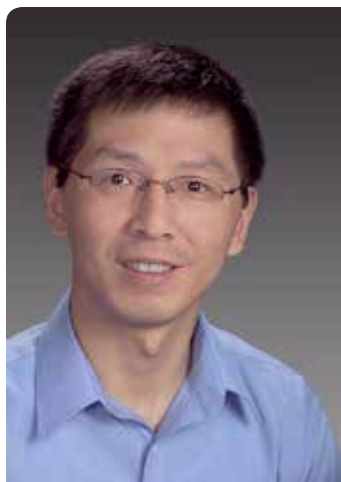
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My research interests and expertise include application of the ultra-high vacuum scanning tunneling microscopy to study—at the atomic level—physical and chemical processes governing the thermal- and photo-induced reactivity of adsorbed molecules on metal oxide surfaces. Among important fundamental aspects are site-specific adsorption, binding, and desorption, diffusion kinetics, and reaction pathways on model single crystal surfaces. In addition

to the scanning probe techniques, a variety of molecular-level spectroscopies in collaboration with theoretical studies are used. In the past year, my team has continued our work on identifying reaction pathways and mechanisms related to surface reactivity and photocatalytic processes on reduced $\text{TiO}_2(110)$. In particular, we have examined the critical role of surface point-defects on the photocatalytic properties of reduced $\text{TiO}_2(110)$ surfaces.



Donghai Mei

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Physical Sciences Division

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My major research expertise focuses on the quantitative understanding of molecular-level reaction mechanisms underlying the macroscopic phenomena in chemical transformation processes, envisioning rational design of novel catalysts, and improving renewable energy production and storage technologies. Of particular relevance are hierarchically multi-scale models and simulations across all relevant time and length scales. At the molecular level, first-principles electronic structure calculations such as density functional theory unravel the making and breaking of chemical bonds. At the mesoscopic scale, statistical mechanistic kinetic Monte Carlo simulations account for the interplay between all elementary

processes involved in the catalytic cycle, and at the macroscopic scale the effects of heat and mass transfer will be described by continuum theories, which ultimately scale up to reactor level. In the past year, I focused on the theoretical modeling of catalytic conversion of lignin-derived phenolic compounds to long-chain hydrocarbons via hydrodeoxygenation and carbon-carbon coupling processes using bifunctional zeolite-based transition metal catalysts. In particular, the aqueous-phase effects on the catalytic activity and selectivity have been investigated with the explicit description of aqueous phase using *ab initio* molecular dynamics simulations.



Michael Mock

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Center for Molecular Electrocatalysis

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My current research interests focus on the preparation and reactivity of transition metal complexes, specifically for the activation of small molecules such as hydrogen and nitrogen. Work in this area includes the development of a multi-step process for the regeneration of the hydrogen storage material ammonia borane using transition metal diphosphine complexes to catalyze the formation of boron-hydrogen bonds from hydrogen and a base. Current efforts within the Center for Molecular Electrocatalysis, an Energy Frontier Research Center, are focused on the preparation and reactivity of tungsten,

molybdenum, and chromium dinitrogen complexes with diphosphine ligands containing proton relays. Recent efforts expanded these systems to include iron and vanadium as well. These studies seek to answer fundamental questions regarding the role of proton relays in the second coordination sphere and their ability to modulate reduction-oxidation potential, promote proton-coupled electron transfer reactions, and facilitate proton movement from solution to metal-bound dinitrogen ligands in the multi-proton/electron electrocatalytic reduction pathway of dinitrogen to ammonia.



Molly O'Hagan

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My research interests focus on mechanistic studies of molecular catalysts for hydrogen production and oxidation. Using nuclear magnetic resonance spectroscopy, my team works to identify catalytic intermediates, understand structural dynamics, probe the mechanism of proton movement, and understand how these processes affect the rate of catalysis. Recent studies have focused on how bio-inspired nickel-based catalysts containing pendant amines, in the Center for Molecular Electrocatalysis (an Energy Frontier Research Center), move protons during catalysis. We have identified *intermolecular* proton transfer from

the medium to the catalyst as a slow step in catalytic turnover due to the steric inaccessibility of the active site. This result has provided a basis for new catalyst design to optimize *intermolecular* proton transfer. We have also extended our mechanistic studies to investigate the impact the medium has on *intermolecular* proton transfer events. In media such as protic ionic liquids, we are working to characterize the rate of proton movement and the specific interaction of the medium with the catalyst. In the future, we plan to extend these studies to aid in the development of catalysts for oxygen and nitrogen reduction.



Charles H.F. Peden

Catalysis Science
Physical Sciences Division

Principal Investigator:

Subtask 1.2: Well-Defined Metal Oxide Catalysts — Understanding Fundamental Chemical Transformations and the Role of Water for Catalyzed Reactions

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My research interests primarily involve the surface and interfacial chemistry of inorganic solids in general, and the heterogeneous catalytic chemistry of metals and oxides in particular. The Subtask 1.2 team, which I lead, utilizes an integrated experimental/theoretical approach to significantly advance our current ability to understand, design, and control chemical transformations on transition metal oxide catalysts, specifically for redox and acid-base chemistries. The approach combines novel synthesis methods for preparing supported metal oxides with controlled structures and atomic connectivity on a wide range of well-defined “scaffolds.” Utilizing the synthesized catalysts, we are conducting catalyst material and mechanistic organic chemistry studies of these realistic and model catalysts, as well as detailed surface science studies on planar model systems to address this

complex challenge. Further, we strongly couple electronic structure and kinetic calculations with the experimental efforts. In this subtask, we are addressing fundamental issues related to the surface chemistry of metal oxide catalysts useful for individual reactions in biomass conversion and the effects of water on the reactivity and stability of metal oxide catalysts. We are using novel solution-based atomic layer deposition methods to controllably synthesize sub- and multi-layer structures of catalytically active oxides on inert oxide supports. Because these methods still generally result in a distribution of active oxide structures, we also utilize pre-formed molecular cluster ions with well-defined geometrical structures, the polyoxometalates with Keggin structures, and diverse compositions dispersed as intact clusters on inert supports.



Simone Rauegi

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Center for Molecular Electrocatalysis

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My scientific activity focuses on the application of quantum mechanical, molecular mechanics and hybrid quantum mechanical/molecular mechanics simulation methodologies to study the relationships between structure and function in biomolecules and metal complexes as well as chemical-physics processes in the liquid phase.

I am the principal investigator of the U.S. Department of Energy's Basic Energy Sciences Biophysical Sciences Program at Pacific Northwest National Laboratory. The program's focus is to uniquely characterize key biochemical and biophysical features of enzymatic processes related to production of a suite of small sustainable energy carriers to drive the design of synthetic catalytic platforms with enhanced performances.

Initial efforts are directed toward understanding hydrogenase and nitrogenase enzymes using a variety of computational and experimental approaches.

I am also a member of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center, where I am leading a theoretical effort for the design of electrocatalysts for energy storage and energy delivery. In particular, I am focusing on the theoretical characterization of novel nickel-based electrocatalysts for hydrogen production and oxidation as well as oxygen reduction by porphyrin-like catalysts. In this context, I am developing a fundamental understanding of proton transfer reactions that will help design molecules that catalyze the conversion between electrical energy and chemical bonds in fuels, and the reverse.



John A. S. Roberts

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Center for Molecular Electrocatalysis

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My work spans two focus areas: the study of electrocatalyst kinetics and thermochemistry, and the synthesis and characterization of new catalytically active electrode surface architectures. I lead the electrochemistry capability within the Center for Molecular Electrocatalysis, an Energy Frontier Research Center. The interdisciplinary nature of this work and my background in homogeneous catalysis have furnished opportunities to collaborate with colleagues in Pacific Northwest National Laboratory's Physical Sciences Division, the Environmental Molecular Sciences Laboratory (a scientific user facility), and at academic institutions.

One of our most fertile areas of study in the Center is in catalyst-medium

interactions, specifically how these interactions influence catalytic energy efficiency and kinetics. This work has led to a more detailed and general understanding of these interactions, and has contributed to the discovery of catalyst systems with unprecedented performance. Our current efforts include the development of synthetic routes to produce catalytically active electrode surfaces with molecular-level structural control. These efforts leverage our understanding of molecular electrocatalysis toward the development of new strategies in heterogeneous electrocatalysis to address both energy challenges and electrosynthetic transformations.



Roger Rousseau

Catalysis Science
Physical Sciences Division
Center for Molecular Electrocatalysis

Principal Investigator:

Subtask 2.1: Catalysts for Carbon Dioxide Reduction to Energy Carriers

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My research focuses on the application of quantum mechanical methods in simulations of the properties and reactivity of molecules, solids, and surfaces. My current research interests involve the application and development of *ab initio* molecular dynamics methods to study hetero- and homogeneous catalysis reaction mechanisms.

In the past year, my team has contributed to theoretical studies of itinerant electrons in metal oxide catalytic materials, which provided novel insights into how these excess charge carriers

influence the reactivity of surface adsorbates and supported metal clusters. We also contributed to studies of catalysts for C₂-oxygenate synthesis from syngas and steam reforming of biomass-derived tars. Also, the team has contributed to the Center for Molecular Electrocatalysis (an Energy Frontier Research Center) with multiple theoretical studies related to mechanistic studies of hydrogen oxidation and production catalysts, as well as initial studies on potential nitrogen reduction catalysts.



Gregory K. Schenter

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On Subtask 3.2, my research focuses on the development of statistical mechanical techniques to better understand molecular interactions and processes in complex condensed phase systems. Development of new simulation capabilities that enhance the interpretation of experimental measurement is an important component of my work. Teaming with Tom Autrey, we are examining the chemical and physical properties of catalytic amphiphilic sites with a goal of providing fundamental insight into the development of new catalytic materials designed for small-molecule activation. Our current research focuses on the non-metal activation of molecular hydrogen in bifunctional molecular complexes. We are developing molecular simulation techniques to elucidate the role of steric hindrance, the nature of electronic states, and the role of dynamical fluctuations in the equilibrium between dative bonding and hydrogen activation in molecular complexes composed of Lewis acid-Lewis base pairs. We combine experimental

and computational approaches to study how tunable environmental factors, such as electrostatic interactions, nano confinement, and pressure, enhance the kinetics and modify the thermodynamics of hydrogen release and uptake in condensed phases. Specifically, we are developing and using research tools to investigate how the reaction environment can be used to control selectivity and enhance reactivity in chemical transformations. The heterolytic activation of molecular hydrogen, providing a catalyst-based complex containing both hydridic and protonic hydrogen, is of special interest. Our group uses experimental spectroscopy methods combined with computational methods to gain fundamental insight into relationships between the structure and dynamical properties in these molecular complexes. These basic research studies will provide the foundation for the development of a rational approach in designing new catalyst materials.



Wendy Shaw

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Center for Molecular Electrocatalysis

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My research focuses on developing a more mechanistic understanding of the outer coordination sphere of molecular catalysts. Together with my colleagues, we are building on the well-understood nickel-phosphine-based electrocatalysts for hydrogen production and oxidation and incorporating peptides into the outer coordination sphere to provide some of the features of an enzyme without re-creating the entire enzyme. Three areas are being investigated:

- ▶ Role of proton channels (Early Career Research Award)
- ▶ Stimulus-sensitive peptides and polymers as enzyme mimics (Molecular Catalysis Program)
- ▶ Physical-chemical characteristics of the active site pocket (Biological Principles of Energy Transductions in the Physical Biosciences Program).

In the past year, my colleagues and I have synthesized and characterized

hydrogen oxidation catalysts with two-relay amino acid based proton channels resulting in water-soluble catalysts that are some of the fastest reported hydrogen oxidation catalysts to date, while functioning at overpotentials close to enzymes. The development of a series of hydrogen production catalysts with appended β -hairpin peptides incorporated into the outer coordination sphere always results in a rate enhancement. The rates vary over two orders of magnitude and from 2 to 50 times faster than the parent complex. There is also strong evidence that the β -hairpin structure is critical to the enhanced rates. In developing stimulus-sensitive catalysts, we have identified a core rhodium-based catalyst that shows a sensitivity to the outer coordination sphere by changing the electron density at the metal and in pendant amines near the metal.



Janos Szanyi

Catalysis Science
Physical Sciences Division

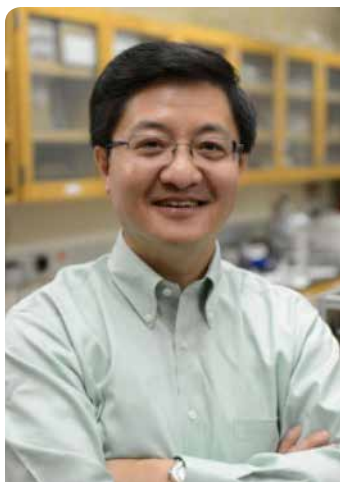
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My research focuses on understanding the structure-reactivity relationships in model and high-surface-area catalyst materials using an array of spectroscopy and microscopy tools. Working with my colleagues, we conduct investigations that follow a parallel path and include model and practical materials. Our experimental efforts are supplemented by density functional theory calculations aimed at validating reaction mechanisms by predicting energetically favorable reaction paths and intermediates, as well as helping identify active catalytic centers and their structures in supported catalyst systems. Our goal is to understand the activity and selectivity pattern variations of supported metal heterogeneous catalysts, in particular, as the active metal phase approaches atomic dispersion, in the demanding reaction of carbon dioxide reduction with hydrogen.

The catalytic activities of metal particles are determined by their sizes and by their

interactions with other catalyst components. Although sub-nanometer-sized metal particles are always present in supported heterogeneous catalysts, their contribution to the overall reactivity and selectivity is far from well understood. In our research, we are preparing active metals on different support materials in a wide range of dispersion. Our focus is understanding the reactivities of atomically dispersed metals on a variety of support materials. We are conducting high-resolution scanning transmission electron microscopy studies on model gamma-aluminum oxide particles to understand the surface and defect structures, porosity, and phase transformations of this widely used support material. We then prepare supported metal catalysts with a wide range of metal loadings, and study their structural and catalytic properties, and use the data to establish structure-reactivity/selectivity relationships.



Yong Wang

Hydrocarbon Processing
Energy Processes & Materials Division

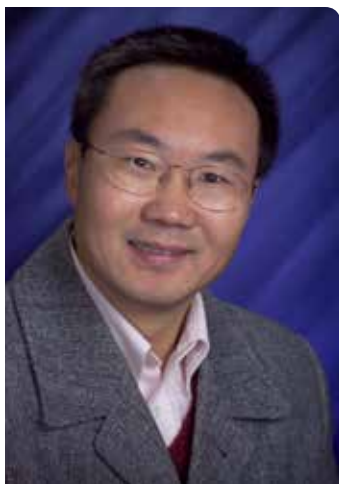
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My research is focused on the fundamental understanding of the roles of bimetallic and transition metal oxide catalysts on the conversion of bio-derived molecules. My contributions to this area include the synthesis of catalysts with controlled morphology and composition,

the study of structure and function relationships, and providing insight into the factors that ultimately control the selectivity and activity of catalysts in the conversion of renewable feedstocks for chemical and fuel production.



Zheming Wang

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My research interests are developing and applying optical and laser spectroscopic techniques in the areas of materials and catalyst synthesis and characterization, mineral transformation, environmental science, lanthanide and actinide chemistry, microbial redox chemistry that contributes to energy materials, and sustainable fuels.

I led the development of the world-class cryogenic laser-induced time-resolved spectroscopy capabilities at EMSL. The techniques significantly increased spectral resolution and detection limits of fluorescent nanomaterials and heavy metal (W, Mo, Re, Tc, U, and Cm) bearing materials and mineral phases. For the first time, we reported the discovery of luminescence from the *trans*-dioxotechnetium-(V)-pyridine/4-picoline complexes, providing the opportunity to directly compare fundamental luminescence properties of second- and third-row d² metal-oxo

congeners and offering the potential for the design of a spectroelectrochemical sensor for detection of pertechnetate in the environmental waters.

As the principal investigator, I led the development of an *in situ* optical spectroscopy platform for supercritical carbon dioxide for investigation of the molecular mineral transformation processes in supercritical carbon dioxide fluids.

With scientists in PNNL, I developed a suite of optical spectroscopy, electrochemistry, and stopped-flow measurements for the investigation of Fe_{3-x}Ti_xO₄ nanoparticles as tunable probes of microbial metal oxidation, metal reduction transformation proteins, and whole cell microorganisms molecularly imprinted polymer sensors and polyhedral oligomeric silsesquioxane[®]-supported transition metal(V, Cr, W, Mo, Y)-oxo mesoporous catalyst.



Robert Weber

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Physical Sciences Division

Principal Investigator:

Subtask 3.3: Heterogeneously Catalyzed
Reactions in Condensed Media

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I apply synthetic, spectroscopic, analytic, and informatic methods to construct microkinetic models of the networks of elementary steps to represent the rates of heterogeneously catalyzed reactions. The microkinetic approach encourages the development of structure/activity relationships, helps focus experimental work, and facilitates archiving and re-using kinetic motifs across varied sets of applications and reaction conditions.

Currently, the kinetic modeling effort focuses on reactions in condensed media, where bulk polarizability can alter the energetics of charged and polar intermediates, compared with their stabilities in reaction media that have low dielectric constants. The immediate application is in modeling the upgrading reactions of the oxygen-containing intermediates produced by thermochemical processing of biomass into fuel precursors. Those intermediates report to polar domains in the product stream and their upgrading—to enhance their

energy content and the compatibility with petrofuels—produces additional water. So, if the reaction medium plays a role in directing the reaction in this application, the effects are likely to be highly dependent on the extent of conversion.

In this subtask, my colleagues and I are using solvatochromic shifts in the spectra of luminescent surface-supported chromophores to probe the composition, structure, and dynamics of complex, partially miscible reaction media in the vicinity of catalytic sites. We have found catalysts that exhibit strong solvatochromic shifts and parallel strong changes in the activation of hydrogen. We infer from the data that the catalyzed transfer of hydrogen involves heterolytic bond breaking and formation.

The work is funded through Laboratory-Directed Research and Development and an annual allocation from the Bioenergy Technologies Office.



Eric Wiedner

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My research interests focus on the rational design of new and/or improved molecular catalysts for the interconversion of electrical energy and chemical fuels. My approach is to first understand the factors limiting catalysis, whether kinetic or thermodynamic in nature, then to design and synthesize new molecular catalysts that can potentially overcome these limitations. Thermochemical measurements of new systems are determined using a combination of experimental and computational methods to provide both an anchoring point for values and the ability to obtain

parameters for reactive species. This work relies heavily on the synthesis of both new ligand platforms and potential catalytic intermediates. I am working on electrochemical hydrogen production as part of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center, and the electrocatalytic reduction of carbon monoxide as part of Subtask 2.2, An Energy-Based Approach to Bifunctional Molecular Catalysis for Carbon Dioxide Reduction and Fuel Utilization, funded by the U.S. Department of Energy Basic Energy Sciences.



Alan Zacher

Chemical Process Development
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Of the wide variety of research I have been involved in at PNNL over the last 20 years, catalyst development has been an integral part of many of my efforts. My research has included chemical products from catalytic conversion of plant-derived and fermentation-derived compounds, biomass to liquid transportation fuels, and waste-to-energy. Of my 24 U.S. patents granted to date, 95 percent of them focus on the development of catalysts and processes for thermochemical conversion of various plant materials to a variety of useful products.

Much of the work has been in conjunction with industrial partners to develop the applied catalysts and processes with the ultimate goal of commercialization to a useful contribution to the economy. Foremost among my research is development of the Propylene Glycol from Renewable Sources currently practiced at the industrial scale by Archer Daniels Midland to produce food- or drug-grade product. This process produces propylene glycol from agriculturally derived feedstocks.

About Pacific Northwest National Laboratory

Interdisciplinary teams at Pacific Northwest National Laboratory address many of America's most pressing issues in energy, the environment and national security through advances in basic and applied science. PNNL employs 4,300 staff, has an annual budget of nearly \$950 million, and has been managed for the U.S. Department of Energy by Ohio-based Battelle since the laboratory's inception in 1965. For more information, visit the PNNL News Center, or follow PNNL on Facebook, LinkedIn and Twitter.

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