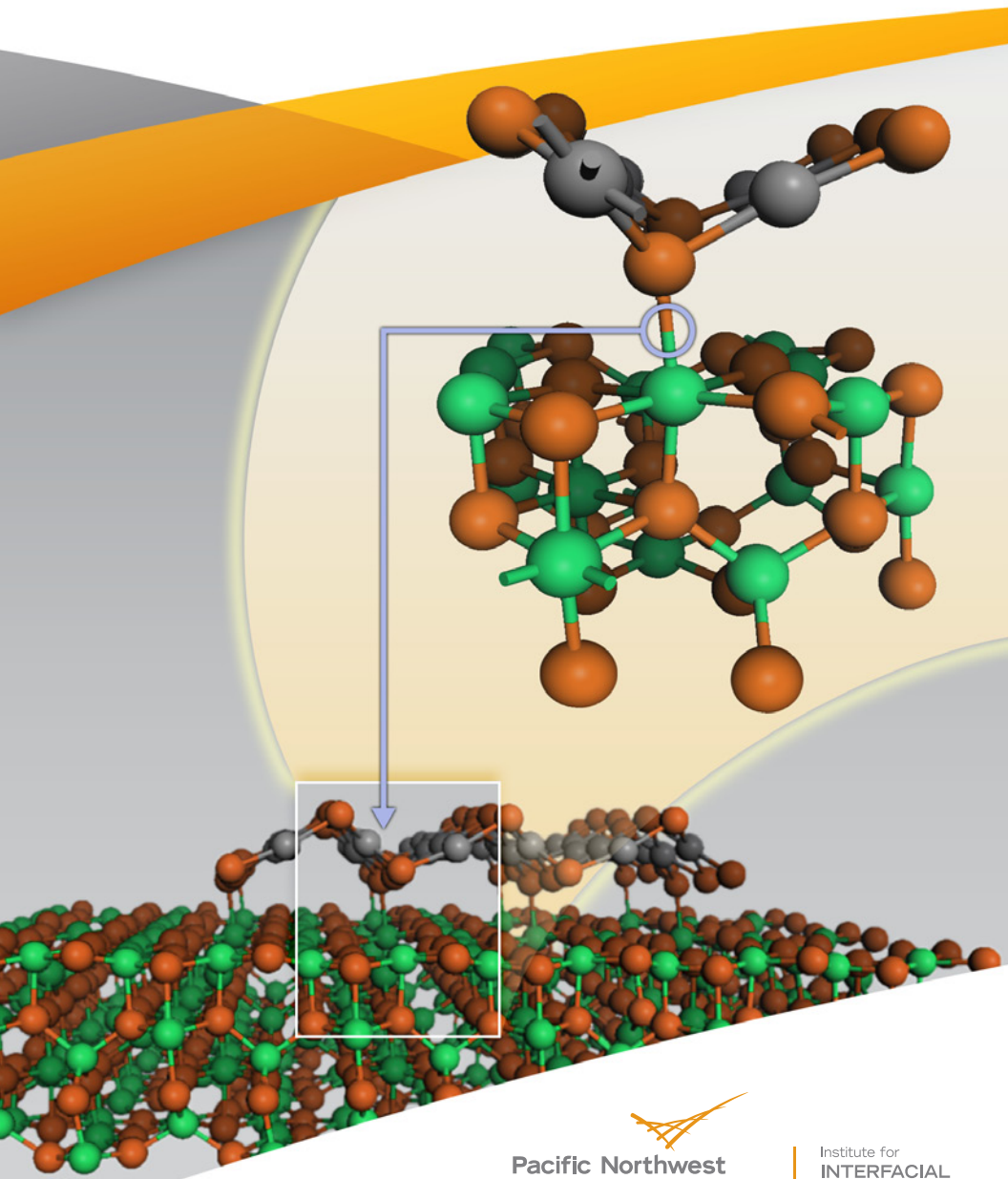


BES Catalysis Science

# 2010 PROGRAM BRIEFING



Pacific Northwest  
NATIONAL LABORATORY

Proudly Operated by **Battelle** Since 1965

Institute for  
**INTERFACIAL  
CATALYSIS**



## TABLE OF CONTENTS

Introduction . . . . .	1
Project Descriptions . . . . .	3
Early transition metal oxides as catalysts . . . . .	4
Fundamental studies of photocatalysis on TiO <sub>2</sub> . . . . .	7
Modular energy-based approach to molecular catalyst design . . . . .	11
Nanostructured catalysts for hydrogen generation from renewable feedstocks . . . . .	15
Chemistry on base-metal oxide nanostructures on oxide substrates: A model system approach. . . . .	16
New bio-inspired molecular catalysts for hydrogen oxidation and hydrogen production. . . . .	18
Control of hydrogen uptake and release in condensed phases . . . . .	21
Catalyst biomimics: A novel approach in catalyst design . . . . .	23
Center for Molecular Electrocatalysis . . . . .	25
Biological principles of energy transduction: Basis for the designed synthesis of hydrogen catalysts. . . . .	28
Computational studies on catalytic synthesis of mixed higher alcohols from biomass-derived syngas . . . . .	29
Development of multiscale computational modeling for heterogeneous catalysis . . . . .	31
Recognition and Awards . . . . .	33
Publications . . . . .	34
Staff Bios . . . . .	35
Aaron Appel . . . . .	36
Tom Autrey . . . . .	37
R. Morris Bullock . . . . .	38
Zdenek Dohnálek . . . . .	39
Daniel DuBois . . . . .	40
Michel Dupuis . . . . .	41
James Franz . . . . .	42
Michael A. Henderson . . . . .	43
Bruce D. Kay . . . . .	44
Greg A. Kimmel . . . . .	45
John C. Linehan. . . . .	46

## TABLE OF CONTENTS

### Staff Bios (continued)

Igor Lyubinetsky . . . . .	47
Donghai Mei . . . . .	48
Michael Mock . . . . .	49
Charles H.F. Peden . . . . .	50
Simone Rauegi . . . . .	51
John Roberts . . . . .	52
Roger Rousseau . . . . .	53
Gregory K. Schenter . . . . .	54
Wendy Shaw . . . . .	55
János Szanyi . . . . .	56
Yong Wang . . . . .	57
Jenny Yang . . . . .	58

## ACRONYM LIST

ACS	American Chemical Society
AVS	American Vacuum Society
BES	(DOE's) Office of Basic Energy Sciences
DFT	density functional theory
DOE	Department of Energy
EFRC	Energy Frontier Research Center
HFI	Hydrogen Fuel Initiative
IIC	Institute for Interfacial Catalysis
IINS	inelastic incoherent neutron scattering
IR	infrared
KMC	kinetic Monte Carlo
LANSCE	Los Alamos Neutron Science Center
MS	mass spectroscopy
M <sup>EB</sup>	multistate empirical valance bond approach
MAS	magic-angle spinning
NMR	nuclear magnetic resonance
PCET	proton-coupled electron transfer
PES	photoelectron spectroscopy
PNNL	Pacific Northwest National Laboratory
PSD	photon-stimulated desorption
SciDAC	(DOE's) Scientific Discovery through Advanced Computing
SPDE	stochastic partial differential equation
STM	scanning tunneling microscopy
TEM	transmission electron microscopy



## Institute for Interfacial Catalysis

The Institute for Interfacial Catalysis (IIC) at Pacific Northwest National Laboratory (PNNL) is pursuing a vision to advance greatly our ability to control chemical transformations and chemical-electrical energy inter-conversions to reduce significantly the carbon footprint of the global energy system.

In this context, the goals of the catalysis and chemical transformation programs in the IIC are to provide the fundamental understanding needed to realize the following:

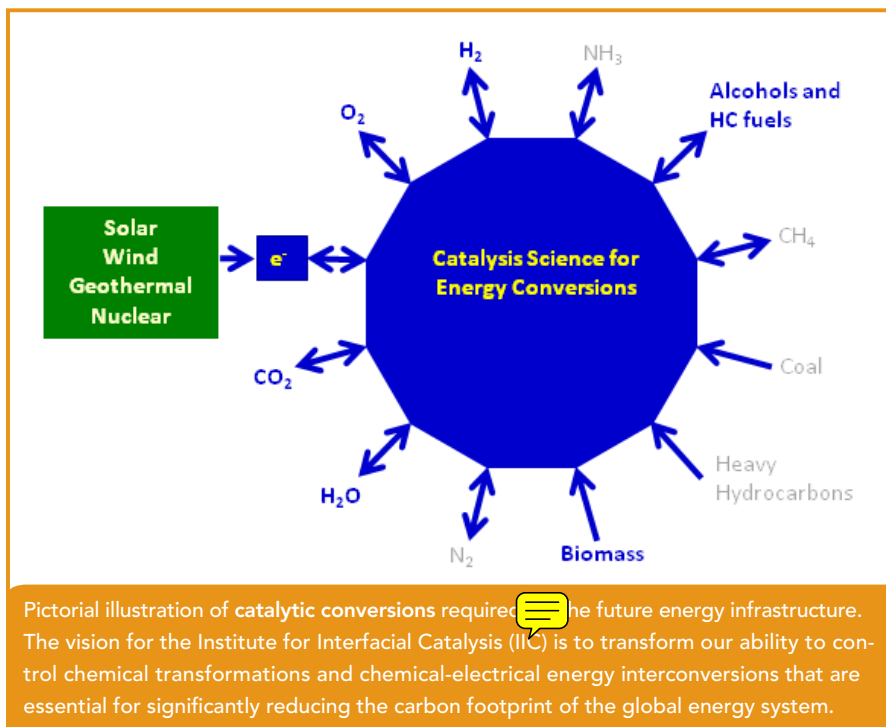
1. Inter-conversion of electrical energy and fuels with greatly enhanced efficiency to enable large-scale, inexpensive, and high energy-density storage of energy
2. Practical alternative feedstock-to-fuel conversions
3. Reduction of the carbon footprint of major energy-consuming chemical transformations.

In particular, the research focus of the IIC will include the catalysis science for three specific energy applications:

1. Biomass conversion to fuels
2. CO<sub>2</sub> conversion to fuels
3. Electrical-to-chemical energy conversions.

Such activities will involve basic research to understand the chemical aspects of catalysis, both heterogeneous and homogeneous.

Chemical transformations are at the heart of energy production and use, and catalysis plays a central role in facilitating and controlling these chemical transformations. Advances in the science of catalysis are required to move its practice toward greater efficiency and selectivity. Catalysis has been applied for decades, yet fundamental



research in catalysis is being newly invigorated by advances in our capabilities to control, measure, and compute chemical and physical properties accurately and with exquisite spatial and temporal resolution. Pushing the frontiers in the development and applications of such tools are of paramount importance to attacking this formidable challenge of greatly more efficient production and use of energy. This forms the essence of the catalysis science activities in the IIC.

This booklet provides a view of the current programs and capabilities that will serve as the basis for realizing the vision and goals of the IIC. Highlighted are core projects within the IIC that are currently supported by the Department of Energy (DOE) Office of Basic Energy Sciences

(BES) Catalysis Science program, as well as affiliated projects funded by other DOE BES program offices. All are fundamental science projects administratively located in the Catalysis Science Department in the Chemical and Materials Sciences Division in the Fundamental and Computational Sciences Directorate at PNNL. 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.

### Current BES Catalysis Science Projects include the core programs

- ▶ Early transition metal oxides as catalysts
- ▶ Fundamental studies of photocatalysis on  $\text{TiO}_2$
- ▶ Modular energy-based approach to molecular catalyst design
- ▶ Nanostructured catalysts for hydrogen generation from renewable feedstocks
- ▶ Chemistry on base-metal oxide nanostructures on oxide substrates: A model system approach.

### Hydrogen Fuel Initiative Programs

- ▶ New bio-inspired molecular catalysts for hydrogen oxidation and hydrogen production
- ▶ Control of hydrogen uptake and release in condensed phases.

### Early Career Program

- ▶ Catalyst biomimics: A novel approach in catalyst design.

### Affiliated Research Programs include

- ▶ Center for Molecular Electrocatalysis (Energy Frontier Research Center [EFRC])
- ▶ Biological principles of energy transduction: Basis for the designed synthesis of hydrogen catalysts (Physical Biosciences program)
- ▶ Computational studies on catalytic synthesis of mixed higher alcohols from biomass-derived syngas (Energy Efficiency and Renewable Energy)
- ▶ Development of multiscale computational modeling for heterogeneous catalysis (Laboratory-Directed Research and Development).

## Early Transition Metal Oxides as Catalysts

PI – Charles H.F. Peden

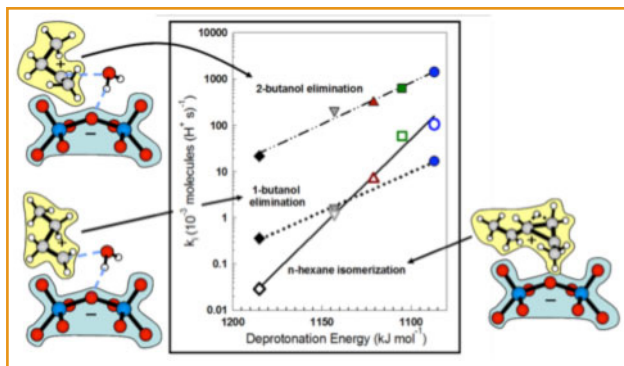
Co-PIs – Zdenek Dohálnek, Bruce D. Kay,  
and Roger Rousseau

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

**We are advancing**  
our ability to  
understand, design,  
and control the  
catalytic and  
surface chemistry  
of transition  
metal oxides.

### Catalyst Synthesis, Characterization, and Kinetics Studies.

We have provided evidence for the kinetics and mechanism of ether cleavage and alkanol elimination on Brønsted acids based on dispersed polyoxometalates in terms of elementary steps and of the stability of the transition states involved. Measured rates, kinetic isotope effects, and theoretical calculations (see figure) showed that the energy of cationic transition states and intermediates depends on properties of



1-Butanol and 2-butanol elimination (full symbols) and n-hexane isomerization (open symbols) rate constants as a function of deprotonation energy on 0.04H<sub>3</sub>PW/Si (●), 0.04H<sub>4</sub>SiW/Si (■), 0.04H<sub>5</sub>AlW/Si (▲) and 0.04H<sub>6</sub>CoW/Si (▼), and H-BEA (◆) for alkanol elimination and as physical mixtures with Pt/Al<sub>2</sub>O<sub>3</sub> for n-hexane isomerization. Late ion-pair transition state structures for each of the reactions are also shown.

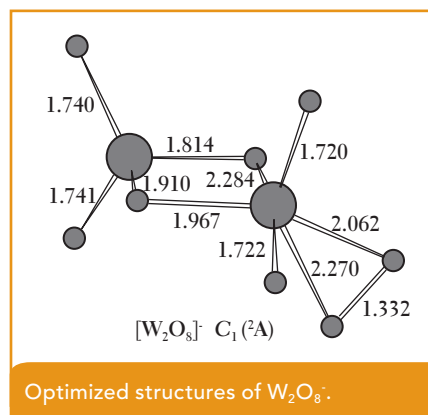


reactants (proton affinity), polyoxometalate clusters (deprotonation energy), and ion-pairs in transition states or intermediates (stabilization energy). These represent the critical features for the design of acid catalysts for specific and general reactions proceeding via cationic transition states.

We have investigated surface acid sites in dispersed tungsten oxide catalysts supported on SBA-15 mesoporous silica using a combination of pyridine titration, both fast-, and slow-magic angle spinning (MAS)  $^{15}\text{N}$  nuclear magnetic resonance (NMR) spectroscopies, and quantum chemical calculations. Our results indicate that pyridine is capable of acquiring the proton from the Brønsted acid site, suggesting that the acidity of the W–OH group is quite strong. The new methods also make it possible to quantitatively determine the relative ratio of the Brønsted-to-Lewis acid sites in the catalyst using the slow-MAS method. The results suggest that the stable surface acid structure most likely has the form of  $\equiv\text{WO}-\text{OH}$ ; i.e., each surface-bound tungsten site is associated with one Brønsted and one Lewis acid site.

**Electronic and Geometric Structure of Oxide Clusters.** Photoelectron spectroscopy (PES) and high-level computational chemistry of size-selected clusters is used to probe the electronic structure and chemical bonding of early transition metal oxide clusters with well-defined sizes and compositions. Tungsten oxides

are a major focus of this catalysis group project, and tungsten oxide clusters have also been a natural focus of this program component. Among the many related studies on  $\text{W}_x\text{O}_y^-$ -type clusters in this funding period, we investigated two oxygen-rich tungsten oxide clusters,  $\text{W}_2\text{O}_8^-$  and  $\text{W}_3\text{O}_{11}^-$ , using PES and DFT calculations. We found that the two anions are best considered as  $\text{O}_2^-$  bonded to  $\text{W}_2\text{O}_6$  and  $\text{W}_3\text{O}_9$  (see figure), each containing a side-on-bound superoxide ligand. In contrast, the neutral clusters  $\text{W}_2\text{O}_8$  and  $\text{W}_3\text{O}_{11}$  are predicted to contain a physisorbed  $\text{O}_2$  to the  $\text{W}_2\text{O}_6$  or  $\text{W}_3\text{O}_9$  stoichiometric cluster. This study shows that the extra electron in the  $\text{W}_2\text{O}_6^-$  or  $\text{W}_3\text{O}_9^-$  anionic cluster is capable of activating dioxygen by non-dissociative electron transfer ( $\text{W } 5d \rightarrow \text{O}_2 \pi^*$ ), and the two anionic clusters can be viewed as models for reduced defect sites on tungsten oxide surfaces for the chemisorption of  $\text{O}_2$ .



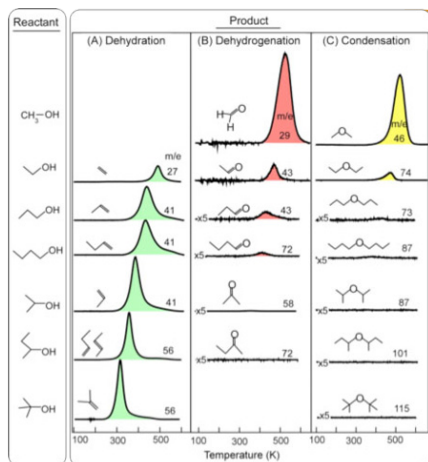
## Ultrahigh Vacuum Studies of Model Transition Metal Oxide Catalysts.

Planar model catalysts allow not only more precise control of metal oxide dispersion but also minimize structural variations, thereby enhancing the power of ensemble-averaging measurements by providing well-defined, uniform structures. We have initiated experimental and computational studies of the partial oxidation of alcohols on planar models, both single crystals and supported oxide clusters. The research is aimed at deciphering the mechanism of complex reaction process on these model catalysts.

An example of this is the complex catalytic mechanism of dehydration of alcohols by  $\text{TiO}_2$ -supported  $(\text{WO}_3)_3$  clusters. Our recent results indicate that the length and number of alkyl chains has a pronounced effect and determines the product branching ratios among the potential dehydration, dehydrogenation,

and alcohol condensation reactions. Dehydration was observed for all  $\text{C}_2 - \text{C}_4$  alcohols, while dehydrogenation was found to be active only for primary alcohols. Ether formation via condensation was observed only for methanol and ethanol. A summary figure displaying all reaction products is shown.

Our theoretical calculations reveal possible low-energy barrier mechanisms for all three reactions with dehydration being energetically favored over the other channels, in agreement with our experiment. The barrier for dehydration is found to be lowered proportionally with the electron-donating ability of the alkyl groups due to stabilization of the transition state. This is similar to the trend observed in our prior studies of alcohol dehydration on bridge-bonded oxygen vacancies of  $\text{TiO}_2(110)$ . Interestingly, the dehydration barrier on  $(\text{WO}_3)_3$  clusters is found to be  $\sim 11$  kcal/mol lower than that on  $\text{TiO}_2(110)$ , thereby reducing the reaction temperature by over 150K.



Temperature-programmed desorption spectra of all three reaction products (alkene, aldehyde, and dialkyl ether), corresponding to dehydration, dehydrogenation, and alcohol condensation, respectively, obtained from  $(\text{WO}_3)_3$  clusters ( $1.1 \text{ nm}^2$ ) dropped into a multi-layer ( $24 \text{ molecules nm}^{-2}$ ) of  $\text{C}_1$  to  $\text{C}_4$  aliphatic alcohols at 100K.

## Fundamental Studies of Photocatalysis on TiO<sub>2</sub>

PI – Michael A. Henderson

Co-PIs – Igor Lyubinetsky, Greg A. Kimmel,  
and Zdenek Dohnálek

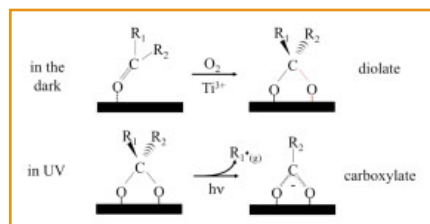
The objective of this project is to provide unique insights into the molecular-level details of photocatalytic transformations on TiO<sub>2</sub> through detailed experimental studies using organic photooxidation reactions on model TiO<sub>2</sub> materials. Our focus is on key areas of heterogeneous photocatalysis that provide insights into how light can be used to promote chemical transformations on surfaces. A variety of model reactions are used to explore charge-transfer reactions involving both oxidation and reduction processes. In this context, we have recently explored: (1) detailed mechanistic studies of the photocatalytic reaction pathways of organic carbonyl oxidation on TiO<sub>2</sub>, (2) the reactive states of oxygen on TiO<sub>2</sub>, and (3) insights into energy accommodation as a result of charge-transfer events in CO photooxidation.

### Choices in Charge-Transfer-Initiated Bond Breaking.

During photocatalysis on TiO<sub>2</sub>, charge transfer to or from adsorbates results in unstable states that lead to bond breaking. Generally speaking, the charge-transfer state associated with hole activity is toward neutralization (e.g., in the case of hole-mediated reactions with carboxylates) and that with electron activity it is toward ionization (e.g., electron scavenging of O<sub>2</sub> to form O<sub>2</sub><sup>-</sup> species). In either case, the “excited” adsorbate can be viewed from a thermodynamic perspective in which the system chooses the lowest energy pathway in response to the charge-transfer event. In some cases, dynamics in the “excited” state may cause thermodynamically unfavorable pathways to open up. Organic carbonyl molecules adsorbed on the TiO<sub>2</sub>(110) surface offer a unique opportunity to explore the interplay between dynamics and thermodynamics during charge transfer. The figure shows a schematic reaction mechanism that we have found to apply to a wide variety of organic carbonyls (acetone, butanone, acetaldehyde, etc.) adsorbed on TiO<sub>2</sub>(110). The first step involves a thermal

Provide unique insights into the molecular-level details of photocatalytic transformations on TiO<sub>2</sub> through detailed experimental studies.

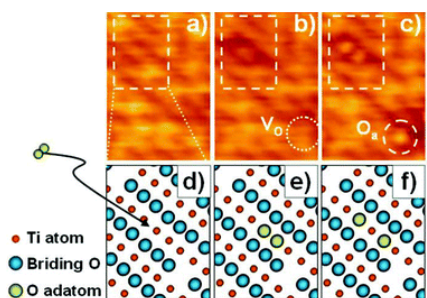
process that converts carbonyl ( $(R_1)(R_2)CO$ ) into diolate species ( $(R_1)(R_2)CO_2$ ) via reaction with a surface oxygen species. The second step involves photodecomposition of this diolate, via radical ejection, to adsorbed carboxylate. Looking at a variety of  $R_1$  and  $R_2$  groupings, comparing experimental observations and theoretical bond energy assessments, we find that the thermodynamic pathway is chosen (i.e., the weaker C-R bond breaks) in all cases except those involving highly halogenated substituents (e.g., trifluoroacetone). In the latter cases, there is a partitioning of the charge-transfer energy between the weaker and stronger bonds, allowing both channels to be observed. These results suggest that a deeper understanding of the dynamics of the “excited” state is needed to predict (and control) the mechanistic directions of photochemical reactions on surfaces.



With dissimilar substituents, photoactivation of adsorbed diolates on  $TiO_2(110)$  generally involves breaking the weaker of the two C–R bonds.

**Identifying Reactive Oxygen Species on  $TiO_2$  Surfaces.** As often is the case, species that are easily identifiable on surfaces tend to be those that are most

stable (hence, least reactive), while those that are the most active are both difficult to detect and more likely to be the key reactants/intermediates. In the case of photocatalysis on  $TiO_2$ , identifying and characterizing reactive oxygen species is a challenge because these species are difficult to differentiate from lattice oxygen with most spectroscopic tools (e.g., photoemission or vibrational spectroscopy). We have employed scanning tunneling microscopy (STM) to investigate the details of  $O_2$  chemistry on rutile  $TiO_2(110)$  that leads to the formation of oxygen adatom ( $O_a$ ) pairs at terminal titanium sites. An intermediate, metastable  $O_a-O_a$  configuration with two nearest-neighbor oxygen atoms is observed immediately after  $O_2$  dissociation at 300K; however, the nearest-neighbor  $O_a$  pair configuration is destabilized by Coulomb repulsion between the  $O_a$ 's leading to separation farther along the titanium row into the stable second-nearest-neighbor configuration. This is illustrated in the three STM frames (and their accompanying surface models) (see figure). In ‘a,’ an  $O_2$  molecule approaches the clean  $TiO_2(110)$  surface leading to adsorption and dissociation (‘b’). The metastable state in which the two  $O_a$ 's reside at neighboring sites is promptly stabilized by movement of one  $O_a$  away (‘c’). In contrast, the dissociation of an  $O_2$  at a vacancy ( $V_O$ ) results in only one  $O_a$  state (see bottom right of ‘b’ and ‘c’). The potential energy surface calculated for  $O_2$  dissociation on titanium rows and following  $O_a$ 's separation strongly



(a-c) Consecutive time-lapse STM images (126 s between frames) of the ( $3.5 \times 5.1$ ) nm<sup>2</sup> area taken during O<sub>2</sub> dosing at 300 K; (d-f) schematic models of the rectangular region marked in (a-c). (The event of O<sub>2</sub> dissociation at VO site can also be followed in the bottom right corner).

supports the experimental observations. Furthermore, our results show that the delocalized electrons associated with the oxygen vacancies are being utilized in the O<sub>2</sub> dissociation process on the titanium row, whereas two oxygen vacancies (four electrons) per O<sub>2</sub> molecule are required for this process to become viable. These results provide a window into a metastable configuration of two O<sub>a</sub>'s on TiO<sub>2</sub>(110) that might possess chemistry uniquely different from that of an isolated O<sub>a</sub>. For example, this metastable configuration may be important in O<sub>2</sub> formation reactions important in water photooxidation reactions.

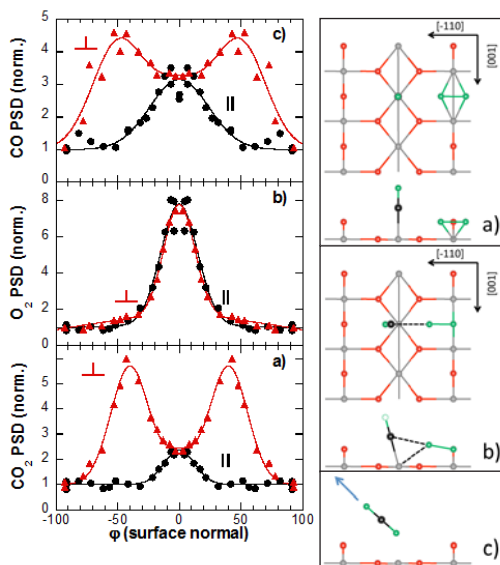
### Angular Dependence in the Photodesorption of CO and CO<sub>2</sub> During CO Photooxidation on TiO<sub>2</sub>.

One of the unexplored aspects of heterogeneous photocatalysis is that of energy partitioning as a result of charge-transfer chemistry. Charge carriers generated by photon absorption possess (essentially) the energy difference between the band edges of the photocatalyst absorbing the light. In the case of TiO<sub>2</sub>, this amounts to  $\sim 3$  eV per electron-hole pair. While some of this energy can be viewed as being invested in bond-forming and

bond-breaking events that result from transfer events to adsorbates, much of this potential energy becomes unaccounted for in the aftermath of the transfer event. Being able to “follow the energy” is critical in obtaining a fundamental understanding of heterogeneous charge-transfer catalysis and in developing photocatalytic systems that optimally utilize energy in photoconversion processes. We have employed the rutile TiO<sub>2</sub>(110) surface to explore the subject of energy partitioning during photocatalysis of a model photochemical reaction: CO oxidation. The figure provides detailed angular profiles from photon-stimulated desorption (PSD) measurements resulting from ultraviolet irradiation of coadsorbed mixtures of CO and O<sub>2</sub> on TiO<sub>2</sub>(110). Inspection of the profiles parallel ( $\langle 001 \rangle$  direction) and perpendicular to the surface rows shows that the angular dependence of O<sub>2</sub> PSD is quite different from that of CO<sub>2</sub> PSD, but that of CO resembles the product CO<sub>2</sub>. (No CO PSD is observed in the absence of coadsorbed O<sub>2</sub>.) But, perhaps most notable is that the CO<sub>2</sub> and CO PSD signals are highly oriented

away from the surface normal, titled at  $\sim\pm 50^\circ$  in directions perpendicular to the surface rows. In a situation in which the photoproduct ( $\text{CO}_2$ ) were allowed to reach energy accommodation with the surface, we would expect only PSD peaked normal to the surface. Observations of strong angular dependence in both the product and the reactant suggest that the PSD of both are accompanied with non-thermal energy distributions. Also, given that the reactant possesses the same profile as the product suggests that the reactant PSD results from exiting a transition state

in the photooxidation reaction. Based on these observations, we proposed the photoreaction depicted on the right in the figure, in which PSD of both the successful and unsuccessful photoreaction follows a trajectory of the attempted C–O bond formation. Extension of this concept to other photoreactions, as well as the reverse reactions (e.g.,  $\text{CO}_2$  photodecomposition), will provide fundamental insights into how energy is distributed among products and reactants during photocatalysis on  $\text{TiO}_2$ .



(Left: a-c) Angular dependence of  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{CO}$  PSD signals, respectively, during photoreaction of coadsorbed  $\text{CO}$  and  $\text{O}_2$  on rutile  $\text{TiO}_2(110)$ . The '0' point in each plot is the surface normal, and angular deviation in the PSD signals from this point are shown in directions parallel and perpendicular to the rows on the  $\text{TiO}_2(110)$  surface. (Right: a-c) Proposed mechanism for the angular dependence in  $\text{CO}_2$  PSD.

## Modular Energy-Based Approach to Molecular Catalyst Design

PI – Daniel DuBois

Co-PIs – James Franz, John C. Linehan, and Wendy Shaw

**Overview.** This project is being redirected from a project that has dealt with MS–H chemistry and associated homolytic bond dissociation energies and kinetics of radical reactions to a project that will develop electrocatalysts for the reduction of “C–O” bonds; e.g., carbon dioxide (CO<sub>2</sub>) reduction to carbon monoxide (CO), formate, formaldehyde, methanol, and methane and for the reverse oxidation reactions. The reduction reactions represent energy storage reactions in which electrical energy generated from renewable energy sources (wind, solar, geothermal) can be used to produce fuels. Catalysts developed for the reverse processes (oxidation of methane, methanol, formaldehyde, formate, and CO) could form the basis of direct fuel cells using carbon-based fuels. An ultimate technical objective is to make these catalysts so efficient that the conversion of electrical energy to carbon-based fuels and its reverse process would be as energy efficient as the charging and discharging of batteries (greater than 90% energy recovery). Significant advances in catalysis science will be needed to achieve these challenging technological goals.

**Goal and Approach.** The refocusing of this project on catalytic transformations of CO<sub>2</sub> to fuels and oxidation of fuels to CO<sub>2</sub> is part of a larger strategy to develop a comprehensive program in catalysis that deals with the interconversion between electrical energy and chemical energy. The goal of this project is to develop a modular energy-based approach for designing and developing molecular catalysts for the interconversion of electrical energy and chemical energy in carbon-based fuels. This modular approach involves detailed studies of first, second, and outer coordination spheres of potential catalysts. Studies of the first coordination sphere are designed to improve our understanding of such fundamental processes as M–H bond formation and cleavage, CO<sub>2</sub> binding, C–O bond cleavage, and C–H bond formation and cleavage. Design

**This project will** develop electrocatalysts for the reduction of “C–O” bonds.

of the second coordination sphere involves the incorporation of properly positioned acids/bases to enhance substrate binding, promote bond formation and cleavage, and facilitate intra- and intermolecular proton-transfer reactions. Stimulus-controlled catalysts are being used to exert control over catalyst properties such as solubility, rates, and specificity.

**Accomplishments and Future Directions.** Studies on thermodynamics and kinetics of MS–H systems where M = iron and molybdenum have been completed. This work provided a comprehensive understanding of MS–H bond energies for selected MoSH and FeSH complexes. The researchers obtained information on how changes in oxidation states, the metal, and the ligands of the first coordination sphere affected homolytic and heterolytic bond energies, and how this information could be used to understand the kinetics of S–H bond cleavage reactions and the overall reactivity of these MS–H complexes that are of importance in various types of catalytic reactions.

*Alcohol Production and Oxidation Catalysts.* Structural and thermodynamic studies of molybdenum and tungsten complexes (e.g., CpW(CO)<sub>2</sub>(IMes)H) have also been carried out. Complexes such as these have been shown to be effective hydrogenation catalysts for ketones. This reaction proceeds through an unusual mechanism involving sequential proton- and hydride-transfer steps. Understanding how the first coordination spheres of these complexes influence thermodynamic properties, such as acidities and hydricities of these complexes, should allow a more quantitative approach to the development of these catalysts, and allow us to rationally design catalysts for alcohol production and oxidation. These same concepts are also useful for developing catalysts for deoxygenation of alcohols derived from biomass. In short, the first coordination sphere of molybdenum and tungsten complexes can be used to control the thermodynamic properties of intermediates involved in catalytic cycles of importance in alcohol production, oxidation, and deoxygenation; this information will be used to guide the development of future catalysts of this class.

**Structural and thermodynamic studies** of molybdenum and tungsten complexes have been carried out.



*CO<sub>2</sub> Reduction and Formate Oxidation Catalysts.* The two-electron reduction of CO<sub>2</sub> can lead to either CO or formic acid. As a result, we have been interested in developing catalysts that operate via either intermediate. In collaboration with Philip Jessop at Queen's University, studies of CO<sub>2</sub> hydrogenation to formate have been carried out using derivatives of H<sub>2</sub>Ru(PMe<sub>3</sub>)<sub>4</sub> as catalysts. This complex and its derivatives are the most active molecular CO<sub>2</sub> hydrogenation catalysts reported with turnover frequencies of approximately 10<sup>5</sup> h<sup>-1</sup>. Studies of the [Pd(triphosphine)(solvent)]<sup>2+</sup> complex, [Pd(HOCH<sub>2</sub>P(CH<sub>2</sub>CH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>)(DMF)]<sup>2+</sup>, as an electrocatalyst for CO<sub>2</sub> reduction have demonstrated the production CO with a current efficiency of approximately 45% and a turnover frequency under 1.0 atm of CO<sub>2</sub> of approximately 50-60 s<sup>-1</sup>. These are some of the most active and energy-efficient electrocatalysts reported for CO<sub>2</sub> reduction to date. A collaboration with Professor Cliff Kubiak at the University of California, San Diego, has been initiated for developing new electrocatalysts for formate oxidation that are based on [NiP<sup>R</sup><sub>2</sub>N<sup>R'</sup><sub>2</sub>]<sub>2</sub><sup>2+</sup> complexes. These catalysts were originally developed at PNNL for H<sub>2</sub> oxidation and production. A quantitative understanding of the roles of the first and second coordination spheres will play an important role in further development of these catalysts.

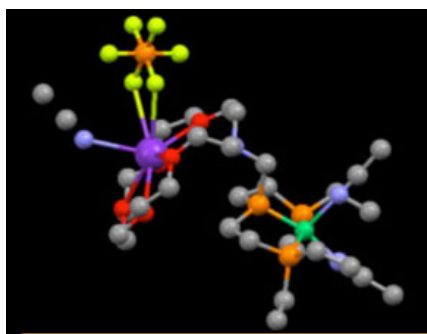
*Stimulus-Controlled Catalysts.* The concept of using the outer coordination sphere to control catalyst activity has been demonstrated with the product of the reaction of 4400 amu NH<sub>2</sub>-terminated-oligo(N-isopropylacrylamide) (pNIPAAm polymer) with [RhCl(CO)<sub>2</sub>]<sub>2</sub>. Ligand switching as a function of solvent prompted developing a more stable ligand bis-phosphorous complex. The P<sub>2</sub>N<sub>2</sub> ligands utilized in other areas of our program were incorporated into Rh-bis(COD) to give Rh[COD][P<sub>2</sub>N<sub>2</sub>], with a temperature and pH-sensitive polypeptide (polylysine) attached to the P<sub>2</sub>N<sub>2</sub> ligand. The hydrogenation reaction of 3-buten-1-ol to butanol was very slow at room temperature and

**A quantitative understanding** of the roles of the first and second coordination spheres will play an important role in further development of these catalysts.

increased to ~250 turnover/hour at 70°C. Further study is necessary to evaluate whether this was a response to structural change or a thermodynamic effect. Similar ligands with mono- and dipeptides attached have been incorporated into nickel-based hydrogenation catalysts. These are observed to be very active hydrogen production catalysts, comparable to catalysts without attached amino acids. The development of these smaller dipeptide catalysts is an essential foundation for the incorporation of stimulus-sensitive peptides, which will be the focus of research for the coming year.

**Relationships to Other Projects.** The refocusing of this project on catalytic transformations of CO<sub>2</sub> to fuels and oxidation of fuels to CO<sub>2</sub> is part of a larger strategy to develop a comprehensive program in catalysis that deals with the interconversion between electrical and chemical energy. The Center for Molecular Electrocatalysis deals with the development of nickel-based catalysts for H<sub>2</sub> oxidation and production, nitrogen reduction catalysts, and O<sub>2</sub> reduction catalysts. The Hydrogen Fuel Initiative (HFI) project focuses on the development of cobalt, iron,

and manganese catalysts for H<sub>2</sub> oxidation and production. All these projects share the common themes of controlling free-energy landscapes and using a modular approach that attempts to understand the role and contributions of each coordination sphere to substrate binding and activation. The over-arching goal is to obtain a comprehensive set of tools and concepts that will allow the rational development of catalysts for a wide range of important energy transformation reactions.



By studying catalysts such as this one focused on electrochemical reduction of carbon dioxide, researchers are adding to the understanding necessary to design and develop molecular catalysts that interconvert electrical energy and chemical energy in carbon-based fuels.

## *Nanostructured Catalysts for Hydrogen Generation from Renewable Feedstocks*

PI – Yong Wang

This research program focuses on the development of highly active and selective catalysts for the production of hydrogen from alcohols. Alcohols, which can be produced from biomass, could be an important renewable source of energy and may help to reduce our dependence on dwindling foreign and domestic oil supplies. Methanol and ethanol are particularly promising energy sources because they can be reformed to produce hydrogen, which can then be used in highly efficient energy conversion devices such as fuel cells. Thus, this program specifically addresses DOE's Grand Challenge of obtaining catalytic control of molecular processes for hydrogen production from renewable sources. Our team, with experts in experimental and theoretical chemistry and chemical physics, is elucidating the basic science needed to develop nanoscale-engineered catalysts for the production of hydrogen from renewable methanol and ethanol feedstock. The specific catalytic systems that provide the initial focus of the research program are Pd and Co supported on ZnO. Our team is providing fundamental insight into the mechanisms of steam reforming of methanol and ethanol on Pd/ZnO and Co/ZnO catalysts, respectively. Through a combination of experimental and theoretical studies, we are elucidating the relationships between the structure and reactivity of this class of catalysts on the nanoscale. The research program includes detailed kinetic measurements with high-surface-area catalysts, synthesis of nanostructured catalytic materials with controlled metal deposition, mechanistic studies using single crystals, thorough catalyst characterization, and DFT computations of catalyst structure and reactivity. The results of these studies are providing the scientific basis needed for the development of highly active and selective catalysts for the production of H<sub>2</sub> and contribute to fundamental knowledge of chemical transformations on bimetallic catalysts.

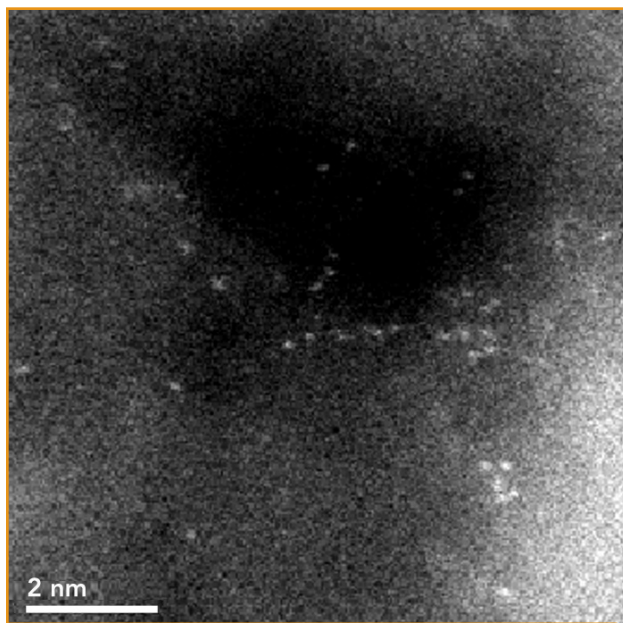
**This research focuses** on the development of highly active and selective catalysts for the production of hydrogen from alcohols.

## *Chemistry on Base-Metal Oxide Nanostructures on Oxide Substrates: A Model System Approach*

PI – János Szanyi

This program is aimed at the development of a fundamental understanding of the chemistry on base metal oxide nanostructures supported on metal and metal oxide substrates. Special emphasis is on exploring the basic steps in the conversion of base metal oxides to nitrates and carbonates, the interconversion of nitrates and carbonates, and the effect of water on the  $\text{NO}_x$  and  $\text{CO}_x$  chemistry. By the deposition of BaO in different coverages (using reactive layer-assisted deposition), we investigate the effect of the substrate (ultrathin  $\text{Al}_2\text{O}_3$  films, Pt(111)) on the surface chemistry. Detailed chemical kinetics data on idealized but well-characterized catalyst systems are useful for understanding the important elementary reactions.

**Develop a fundamental** understanding of the chemistry on base metal oxide nanostructures supported on metal and metal oxide substrates.

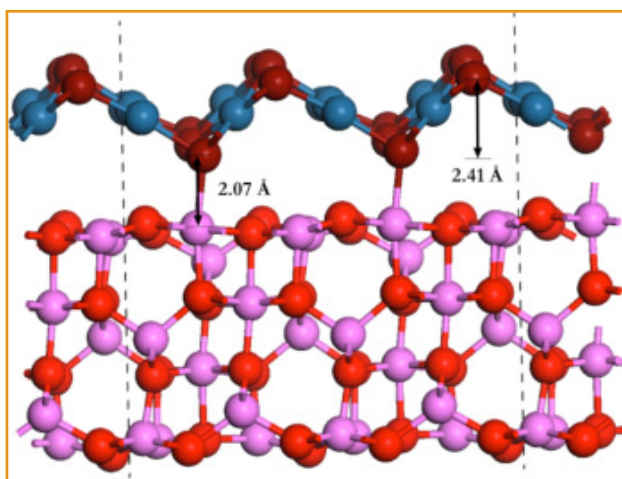


High-resolution transmission electron microscopy image of a 1 wt% Pt/ $\gamma\text{-Al}_2\text{O}_3$  sample showing atomically dispersed platinum.

Studies utilizing reflection-absorption infrared spectroscopy, temperature-programmed desorption, and x-ray photoelectron spectroscopy are aimed at identifying surface species that form in the interaction of  $\text{NO}_x$ ,  $\text{CO}_x$  with both the substrate and the base-metal oxide surfaces. It also provides invaluable information on the formation mechanisms and stabilities of different nitrite, nitrate, and carbonate species formed. We also investigate the decomposition/reduction mechanisms of  $\text{Ba}(\text{NO}_x)_2$  on the Pt(111)-supported model system. Based on the results of our studies on model systems, we have extended our work to supported high-surface-area catalysts. The primary goal of these studies is to understand the role of the strong interaction between the active catalyst components (BaO, Pt) and the oxide support ( $\gamma\text{-Al}_2\text{O}_3$ ) in the anchoring of active catalytic phases. The information these studies provide is essential in designing tailor-made catalysts with controlled active phase dispersion. These studies combine experimental work (high magnetic field (900-MHz) solid-state NMR, ultrahigh-resolution TEM) and theory (high-level DFT calculation) to identify the anchoring sites, visualize the dispersion, and obtain energetic for the interaction of active phases with the oxide support.

#### The information

these studies provide is essential in designing tailor-made catalysts with controlled active phase dispersion.



Side view of a two-dimensional PtO raft anchored to penta-coordinate  $\text{Al}^{3+}$  sites on a  $\gamma\text{-Al}_2\text{O}_3(100)$  facet.

## New Bio-Inspired Molecular Catalysts for Hydrogen Oxidation and Hydrogen Production

PIs – R. Morris Bullock and Daniel DuBois

**Overview.** Conversion between electrical and chemical energy is needed because of the temporal variations of renewable, carbon-free sources of energy, such as solar and wind. Storing energy in the H–H bond of hydrogen is attractive because oxidation of hydrogen in a fuel cell provides electricity efficiently and cleanly. *Electrocatalysts based on inexpensive, earth-abundant metals are needed because most fuel cells are based on platinum, an expensive, precious metal.* The cost of cobalt, manganese, or iron is at least a thousand times less than platinum, so dramatic cost savings would result from development of catalysts using these inexpensive, earth-abundant metals.

**Goals and Approach.** Our objective is to synthesize *biologically inspired functional models* that provide high catalytic activity with low overpotentials, by recognizing that some of the most salient features enabling the remarkable capabilities of nature’s catalysts can be replicated synthetically. In the [FeFe] enzyme, it is thought that a nitrogen atom near the iron assists in the heterolytic cleavage of H<sub>2</sub>, and that this pendant amine shuttles protons from the catalytically active metal site to the proton-conduction channel. Our efforts focus on the design of biologically inspired complexes that use abundant metals and have a pendant amine that may function as a proton relay. Our focus is on *functional* models; we do not attempt to prepare *structural* models. Our research has shown that pendant amines can have a profound influence on the reactivity of metal catalysts in multi-proton, multi-electron reactions such as the production of H<sub>2</sub> and oxidation of H<sub>2</sub>; we exploit that approach in the design and development of new complexes of cobalt, manganese, and iron. New metal complexes are synthesized and characterized, and stoichiometric reactivity is evaluated. We then attempt to use the knowledge of their reactivity patterns to design new catalysts.

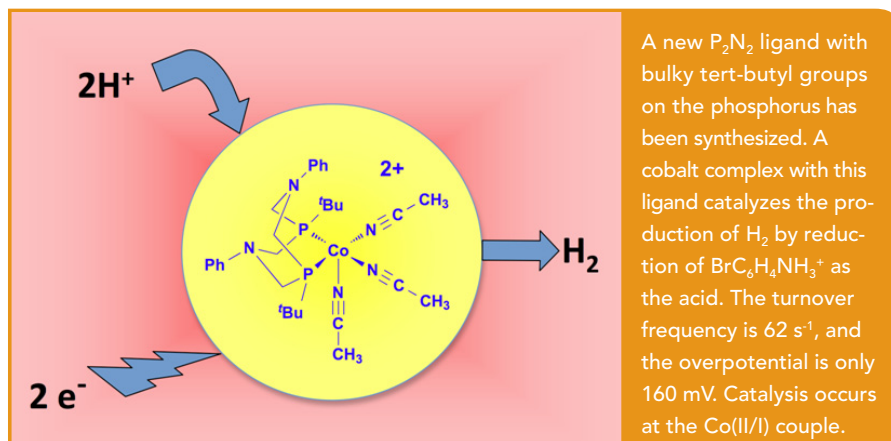
**Recognizing that** some of the most salient features enabling nature’s catalysts can be replicated synthetically.


## Accomplishments and Future

**Directions.** Our research on nickel complexes containing ligands bearing pendant amines has resulted in new catalysts for oxidation of hydrogen with an overpotential of less than 100 mV. A related family of nickel complexes indicates highly active electrocatalysts for production of hydrogen through reduction of protons. Mechanistic studies have provided insight into the intermediates involved in these reactions, including the large stabilization energy (by as much as 15 kcal/mol) provided by the pendant amines and the first observation of a Ni(IV) dihydride complex. Our focus in the project has transitioned away from nickel, but uses the concepts learned from the nickel chemistry to guide the development of new catalysts of other cheap metals (cobalt, manganese, and iron). New studies seek to understand how changes in the first and second coordination spheres will alter catalytic activity and the overall catalytic mechanism. Cobalt complexes for production of hydrogen were discovered. As found

in our nickel chemistry, a pendant amine on the ligand is a critical feature required for good catalysis. A manganese complex with a pendant amine in the ligand was found to give heterolytic cleavage of hydrogen, with the hydride being transferred to the metal and the proton being located on nitrogen of the amine.

In future work on the design and development of cobalt, manganese, and iron catalysts, we seek to obtain an understanding of the molecular reactivity that will allow us to design and discover new, robust, highly active catalysts for oxidation and production of H<sub>2</sub>. The use of two different diphosphine ligands on manganese complexes will be used to control the hydride acceptor ability of the metal and the pK<sub>a</sub> values of the corresponding hydrides, which will guide the design of new catalysts. New studies on iron complexes were begun recently; iron is a very attractive metal because it is cheap, non-toxic, and is the metal used by the biological catalysts that have the highest rates for H<sub>2</sub> production/oxidation.



A solid orange vertical bar is positioned on the left side of the page, extending from the top to the bottom.

**Relationship to Other Projects.** The work on nickel complexes that had been a part of this HFI project will be continued in the Center for Molecular Electrocatalysis (described later in this booklet). This transition will allow new work in the HFI project to focus on a detailed examination of complexes of cobalt, manganese, and iron. Thus, the work in manganese, cobalt, and iron complexes carried out in the fuel initiative's project is complementary to, but does not overlap, the research carried out in the Center for Molecular Electrocatalysis. The work in this HFI project relates to the broader goals for catalysis science at PNNL that focus on catalysts for conversion between electrical and chemical energy. The scientists working on the initiative project benefit from interactions with those working on the BES core project as well. Many of the fundamental concepts studied in the BES core project are applicable to studies carried out in the HFI project.



## Control of Hydrogen Uptake and Release in Condensed Phases

PI – Tom Autrey

Co-PI – Gregory K. Schenter

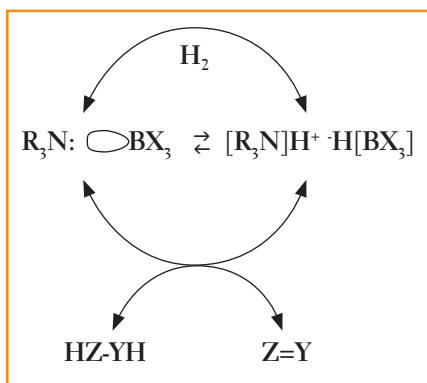
Our research group is studying the chemical and physical properties of bi-functional—ambiphilic molecular complexes with the goal of providing the fundamental insight required to rationally develop novel approaches to activate molecules for catalytic transformations. Current research focuses on the relationship between structure and dynamics in Lewis acid/base pairs to activate molecular hydrogen.



Sterics, electronics, and dynamical properties control the equilibrium between dative bonding and hydrogen activation in molecular complexes composed of Lewis acid/base pairs (see equation). 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. Of special interest is the heterolytic activation of molecular hydrogen providing a catalyst-based complex containing both hydridic and protonic hydrogen. Our group uses experimental spectroscopy methods (NMR, Raman, x-ray, 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. These basic research studies will provide the foundation for the development of a rational approach to the design of new catalysts materials.

**Providing the insight** to rationally develop novel approaches to activate molecules for catalytic transformations.

Activation of molecular hydrogen *without using metals* provides an approach to green chemistry that has relevance to economically important catalytic transformations, ranging from the conversion of carbon dioxide (CO<sub>2</sub>) to fuels, upgrading biomass, hydrogen (H<sub>2</sub>) utilization in fuel cells, methane (CH<sub>4</sub>) activation, to the conversion of nitrogen (N<sub>2</sub>) to ammonia.



*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 interested in quantum effects in H-bonding and H<sub>2</sub> activation reactions, the role of large amplitude motions and anharmonics in strained molecular complexes, and how weak interactions, e.g., van der Waals and electrostatic interactions, affect the structure and dynamics in the ionic salts of Lewis acid/base pair complexes. Our combined experimental and computational study is designed to provide insight into the tunable chemical

and physical parameters in Lewis acid/base pairs that will lead to a fundamental understanding of the heterolytic activation of molecular hydrogen.

Progress to date has provided insight into the relationship between the structure and dynamics of the parent Lewis acid/base complex, ammonia borane (NH<sub>3</sub>→BH<sub>3</sub>), and associated ionic pair, ammonium borohydride ([NH<sub>4</sub>][BH<sub>4</sub>]).

We have examined the effects of pressure on the vibrational modes of ammonia borane and related NBH<sub>x</sub> complexes in collaboration with the Carnegie Institute in Washington and Stanford University.

We combined NMR, x-ray powder diffraction, and anelastic spectroscopy approaches to study the effects of nano environments on the structure and dynamics of ammonia borane in collaboration with colleagues at Los Alamos Neutron Science Center, Advanced Photon Source, and La Sapienza.

We used a combination of neutron diffraction and inelastic neutron spectroscopy approaches to study the evolution of dihydrogen bonding interactions in ammonia borane.

We published the first comprehensive study of ammonium borohydride using experimental and computational approaches to understand the unique dynamical properties of this complex.

We showed how theory can be used to identify critical catalytic species in solution.

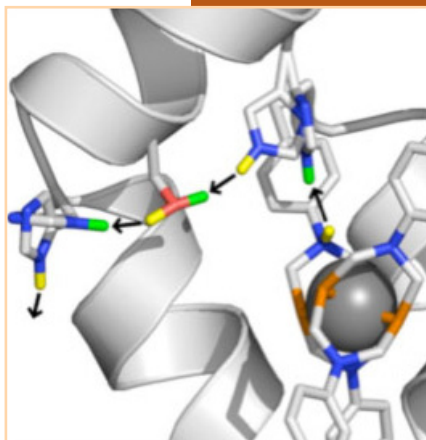
## Catalyst Biomimics: A Novel Approach to Catalyst Design

PI – Wendy Shaw

**Overview.** The objective of this research is to incorporate a rationally designed proton channel into homogeneous catalysts using advanced enzyme design methodology combined with superior molecular catalyst design. Proton channels, consisting 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 widely studied for their potential impact on energy and fuel storage. Hydrogenase enzymes (~90,000 Da) can reversibly oxidize or produce hydrogen with hydrogen production rates of 10,000 turnovers per second. This activity shuts down when the proton channel is deactivated. Small-molecule catalysts are notably unable to match these rates. However, recent work by Daniel DuBois and his team showed rate enhancements of three to four orders of magnitude for hydrogen production and oxidation catalysts by placing a fixed proton relay in a synthetic hydrogenase mimic. Based on these observations, the hypothesis of this research is that providing a proton channel to and from the active site is an essential characteristic necessary to further enhance the activity of synthetic analogs. *Thus, we are designing synthetic catalysts with an enzyme-like proton channel, exploiting the superior structure/function attributes that peptide chains demonstrate in enzymes, but maintaining a relatively small catalyst (1,000-9,000 Da).*

**Goal and Approach.** The approach has three components: (1) computer-aided design, (2) synthesis, and (3) characterization of the structure and activity. Using the Rosetta computational approach in collaboration with Dr. David Baker (University of Washington), energy-minimized computational structural models will be generated

**Incorporate** a rationally designed proton channel into homogeneous catalysts using enzyme design methodology.



Close-up view of a proton relay. By studying proton relays, which make up proton channels, researchers will gain the information necessary to rationally design a proton channel into homogeneous catalysts.

to develop potential peptide ligands with precisely positioned proton relays. The computationally determined “best” peptide ligands will be synthesized and incorporated into nickel-based hydrogenase catalyst mimics with already well-defined structure and activity. The catalyst will be probed for enhanced reactivity using electrochemistry and NMR and will be fully characterized with NMR, infrared (IR), x-ray absorption fine structure spectroscopy, and x-ray crystallography. Mechanistic studies to identify pathways and intermediates will be studied using NMR and IR. Initial efforts will focus on the enhancement in rate afforded by a channel consisting of two relays. Attributes such as the pKa of the relays, the distance between relays, the rigidity, structure, and surrounding environment of the relay, and ultimately the number of relays will be tested. As the number of relays increases, multiple relay paths will develop and the enhancement due to single vs. multiple paths will also be tested. In addition to and in support of the experimental effort, the multistate empirical valence bond (MS-EVB) approach that captures the complex and collective proton motion (including the Grotthuss mechanism) in solvated environments will be used to predict which stabilized structures might perform better than others. MS-EVB will also provide predictions of pKa values of relays in the proton channel, as well as preferred proton transport pathways. This molecular-level approach will allow us to develop a detailed understanding

of proton relays, revealing insights into how they can enhance homogeneous catalysts, as well as how they function in enzyme systems. In the long term, if successful, the enhanced rates afforded by the proton relay system could allow these catalysts, made of inexpensive metals, to compete with and replace expensive platinum catalysts in fuel cells.

### **Relationships to Other Programs.**

My research on several programs focuses on unique and synergistic aspects of the outer coordination sphere, or the regions of the ligands not directly attached to, or interacting with, the metal center. This project focuses on the development of proton relays. My role in the program “A Modular Energy-Based Approach to Molecular Catalyst Design,” led by Daniel DuBois, focuses on the incorporation of stimulus-controlled peptides to switch catalyst activity, specificity or selectivity, conceptually mimicking the level of control that enzymes have. My contribution to “Biological Principles of Energy Transduction,” led by Tom Squier, investigates the effect of dynamics, polarity, and regulatory protonation on the active site pocket. Finally, all of these programs are complementary to the Center for Molecular Electrocatalysis, led by R. Morris Bullock, in which they are investigating more fundamental questions in the first and second coordination sphere.

## Center for Molecular Electrocatalysis

Director – R. Morris Bullock

Deputy Director – Daniel DuBois

Theory/Computational Leader – Michel Dupuis

PNNL Staff Co-Principal Investigators (co-PIs) –

Aaron Appel, John Roberts, Simone Raugei,

Jenny Yang, Michael Mock, James Franz,

Wendy Shaw, Roger Rousseau, and John C. Linehan

Postdocs – Uriah Kilgore, Amy Groves,

Shentan Chen, Molly O'Hagan, and Stuart Smith

University Collaborators – James Mayer (University of

Washington), Bruce Parkinson (University of Wyoming),

Sharon Hammes-Schiffer (Pennsylvania State University)

**Overview.** The Center for Molecular Electrocatalysis began as an EFRC in August 2009, with funding from BES. **Our vision is to develop a fundamental understanding of proton-transfer reactions that will lead to transformational changes in our ability to design molecular electrocatalysts.** Electrocatalysts that efficiently convert electrical energy into chemical bonds in fuels or the reverse, converting chemical energy to electrical energy, will play a vital role in future energy storage and energy delivery systems. Electrocatalytic processes involving multi-proton and -electron redox reactions are pervasive in energy science. We seek to understand, predict, and control the intramolecular and intermolecular flow of protons in electrocatalytic multi-proton, multi-electron processes of critical importance to a wide range of energy transformation reactions, including the production of  $H_2$ , the oxidation of  $H_2$ , the reduction of  $O_2$ , and the reduction of  $N_2$ . To achieve this goal, we focus on fundamental studies that address how proton relays regulate the movement of protons and electrons within and between molecules to enhance rates of electrocatalysis.

**University Collaborators.** PNNL is leading the Center, and three university groups provide additional expertise required for a comprehensive approach to the problem. Jim Mayer (University of Washington) is leading the

**Develop** a fundamental understanding of proton-transfer reactions.

development of new electrocatalysts for oxygen reduction to water:  $O_2 + 4H^+ + 4e^- \rightarrow 2 H_2O$ . Bruce Parkinson of the Department of Chemistry and the School of Energy Resources at the University of Wyoming is studying the electrochemical behavior of the new electrocatalysts synthesized in the Center, complementing routine electrochemical studies carried out at PNNL. Sharon Hammes-Schiffer (Pennsylvania State University) pioneered the proton-coupled electron transfer (PCET) theory and other computational methods to account for nuclear quantum effects. The Penn State work is initially focused on the characterization of PCET steps in the catalytic cycles of the  $H_2$  oxidation/production reactions.

**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 important energy storage and utilization reactions. Closely coupled experimental and theoretical studies will include inorganic synthesis, ligand design, mechanistic studies, electrochemical measurements, determination of thermochemical values for metal hydride complexes, and evaluation of catalytic activity. A unique approach in this Center is a focus on proton relays, which are functional groups (typically amine bases) 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.** New nickel catalysts developed in the first year of this EFRC include  $H_2$  production catalysts with turnover frequencies of approximately  $1000 s^{-1}$ , and  $H_2$  oxidation catalysts with turnover frequencies of  $50 s^{-1}$ . These represent *the highest turnover frequencies to date for molecular electrocatalysts for  $H_2$  production and oxidation*. Water has a beneficial effect on catalytic rates and suggests new avenues for further catalyst development. NMR and electrochemical studies are providing a deeper understanding of the roles of proton relays during the catalytic process that will also contribute to the rational design of these complexes.

Theory efforts have focused on theoretical studies of a variety of Ni(II) complexes, specifically those that are studied experimentally. In this context, redox potentials, metal atom hydricities, and pKa values are key experimental quantities employed (measured or derived through thermodynamic cycles) to construct free-energy maps during the cycle. Therefore, our initial efforts have spanned two distinct subtasks: (1) the establishment of a reliable computational protocol for the calculation of the above thermodynamic properties; (2) detailed characterization of the reaction energy profiles, i.e., in particular for

$[\text{Ni}(\text{P}_2^{\text{Cy}}\text{N}_2^{\text{Me}})_2]^{2+}$ , which is a very efficient catalyst for  $\text{H}_2$  oxidation synthesized in the EFRC.

Our initial strategy in the nitrogen reduction area is to focus on the synthesis of complexes of molybdenum- and tungsten-containing ligands with proton relays; we focus on molybdenum- and tungsten-complexes because  $\text{N}_2$  ligands on those metals have been shown to be converted to  $\text{NH}_3$  upon reaction with acids. We have succeeded in the synthesis of complexes of molybdenum and tungsten with proton relays in the ligands; current synthetic efforts seek to convert these complexes to the desired complexes with  $\text{N}_2$  ligands.

**Relationship to Other Projects.** The research in the Center for Molecular Electrocatalysis complements the studies carried out in the HFI project and the BES core program. The scope of

work in the EFRC is much broader than that in the HFI project, because the research in the EFRC covers reduction of oxygen and reduction of nitrogen, in addition to the work on catalysts for oxidation and production of  $\text{H}_2$ . Electrochemical studies form a core focus of study in the EFRC, whereas in the HFI project electrochemistry is used as more of a routine tool for characterization and evaluation of metal catalysts. The work in the EFRC has a substantial theory component as well as experimental efforts. The fundamental studies on transformations of  $\text{CO}_2$  in the core BES program complement the work on small molecules in the EFRC. The goals are different, though the techniques and approaches are related, allowing for substantial synergy between the projects and the postdoctoral fellows and staff members.



**The vision of the Center for Molecular Electrocatalysis** is to develop a fundamental understanding of proton-transfer reactions that will lead to transformational changes in our ability to design molecular electrocatalysts.

## Biological Principles of Energy Transduction: A Basis for Design and Synthesis of Hydrogen Catalysts

PI – Thomas C. Squier

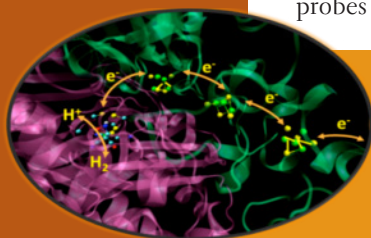
The motivation for this program is to understand how hydrogenase enzymes optimize proton-coupled electron transfer mechanisms for optimal catalytic rates. To this end we aim to: (a) understand and test how active site geometry modulates hydricity and catalytic rates for hydrogen production; (b) clarify how protein dynamics control proton-coupled electron transfer and rates of hydrogen production; and (c) determine how orientation and dynamics of Fe/S clusters affects electron transfer rates.

Our approach includes (1) expressing and purifying hydrogenase mutants using newly developed heterologous expression system in *Shewanella* to control active site properties and introduce tagging sites for labeling by spectroscopic probes; (2) carrying out hybrid quantum mechanics/molecular mechanics and molecular dynamics calculations to identify how electron densities of Fe/S clusters and dynamics affect electron transfer rates; and (3) synthesize molecular catalysts that incorporate protein structural elements that test how local environment and proton buffering affect rates of hydrogen formation.

This program bridges enzymology and strengths in molecular catalysis at PNNL through linked hypothesis testing. A new expression system permits testing of ideas developed using nickel-phosphines in enzyme systems (e.g., V71C will compress diatomic ligands on active site iron to alter bite angle). Newly developed molecular probes and single molecule spectroscopic measurements

permit direct comparison with computational predictions of linked protein motions and catalysis.

Understand how hydrogenase enzymes optimize proton-coupled electron transfer mechanisms for optimal catalytic rates.



Proton-coupled  
electron transfer  
in hydrogenase



## Computational Studies on Catalytic Synthesis of Mixed Higher Alcohols from Biomass-Derived Syngas

PI – Donghai Mei

Catalytic conversion of biomass-derived synthesis gas (CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O) to ethanol and other oxygenates has been a major DOE mission due to the strong demand for alternative, renewable energy sources. In conjunction with the experimental effort, this project focuses on rapid discovery and rational design of new efficient catalysts using computational methods, including quantum chemistry calculations and kinetic Monte Carlo (KMC) simulations.

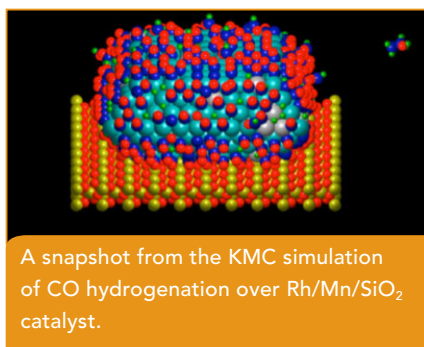
The production of mixed higher alcohols from syngas has received considerable attention in recent years for its use in automobiles, as well as the potential hydrogen source for fuel cells. Currently, mixed higher alcohols, such as ethanol, are produced primarily by fermentation of biomass-derived sugars. Gasification of biomass to syngas, followed by catalytic conversion, provides a promising alternate route to produce ethanol in large quantities. In spite of the substantial amount of research on this catalytic conversion route, no commercial process yet exists due to the challenging chemical and technological barriers. Low yield and poor selectivity for targeted mixed higher alcohol production remain the major hurdles associated with the use of known catalysts. To make this catalytic conversion route commercially attractive, it is very important to develop more effective catalysts with high activity and selectivity.

In the past year, we investigated the reaction mechanism and kinetics of ethanol synthesis from CO hydrogenation over SiO<sub>2</sub>-supported Rh/Mn alloy catalysts using DFT calculations and KMC simulations. The assumption of Rh/Mn alloy nanoparticle as being the active catalyst phase is supported by experimental characterizations including x-ray photoelectron spectroscopy, TEM, and x-ray diffraction. On the basis of DFT-calculated reaction energies of the Rh/MnO<sub>x</sub> nanoparticles under *in situ* reducing conditions, we found that the stability of the

**Focuses on rapid discovery** and rational design of new efficient catalysts using computational methods.

binary Rh/Mn alloy nanoparticle is preferred over a mixed Rh/MnO<sub>x</sub> system. The calculated activation barriers and reaction energies of methane formation and three CO insertion steps CO+CH<sub>x</sub> (x=0~3) on rhodium and Rh/Mn alloy nanoparticles indicate that methane formation is inevitable due to low activation barriers for rhodium-based catalysts. Doping rhodium with manganese does not dramatically change activation energies for methane formation, but lowers the activation barrier of CO insertion into CH<sub>x</sub> species. We developed a first-principles KMC model to simulate the reaction kinetics of CO hydrogenation to ethanol over SiO<sub>2</sub>-supported, three-dimensional Rh/Mn alloy nanoparticles. The KMC simulation results are in qualitatively good agreement with experimental data. This indicates that the new KMC simulation model developed in this project can capture the essential chemical and kinetic features of complicated ethanol synthesis from CO hydrogenation (~230 reaction steps involved) over the supported Rh/Mn catalysts. The optimum reaction temperature of 280 °C is found in the simulations where the highest

ethanol selectivity (12%) is reached. Finally, we studied the effects of other promoters (M = Ir, Ga, V, Ti, Sc, Ca, and Li) in Rh/M catalysts for ethanol production. We found the lower CO insertion barriers correspond to the Rh/M catalysts with the electronegativity difference ( $\chi \approx 0.7$ ) between Rh and the promoter (M). This theoretical prediction is in accord with previous experimental observations that the promoters with  $\chi \approx 0.7$  deliver higher selectivity and productivity for the Rh/M/SiO<sub>2</sub> catalysts. We believe the general trend found in this work can help improve current rhodium-based catalysts for mixed higher alcohol production. This work has been published in the *Journal of Catalysis*.<sup>1</sup>



<sup>1</sup> *Journal of Catalysis* 271, 325–342 (2010).

## Development of Multiscale Computational Modeling for Heterogeneous Catalysis

PI – Donghai Mei

This project is aimed at developing a new modeling capability for reactor-scale catalytic processes informed by lower-scale simulations of chemical transformations on supported catalyst nanoparticles and molecular-scale characterization of reactive processes at phase interfaces and in fluid phases.

A formidable challenge in catalysis research lies in the fundamental understanding of the mechanisms and dynamics of molecular transformations over catalyst materials under operating reaction conditions. Molecular-level understanding of catalytic reactions can enable one to design catalysts with improved efficiency (selectivity, yield, and cost) toward targeted products. However, the operating conditions in reactors give rise to inhomogeneous temperature and pressure gradients experienced by catalyst particles, a situation that dramatically complicates the macroscopic prediction of global reaction kinetics.

Our approach includes the combination of theories and modeling at varied scales of length and time, i.e., DFT for the dynamics information of elementary surface reaction step, KMC for chemical kinetics over supported industrial catalyst particles, and stochastic partial differential equation theory (SPDE) for mass and heat transport in reactive fluid flow phases (or phase boundaries) in the reactor. The most challenging task in this unique computational module is to link seamlessly and dynamically various theories and models at different time and length scales. We accomplish this linkage by describing non-uniform flow-phase (sub-domain) boundaries with a combination of the KMC and SPDE methods. The two different methods are formulated in separate sub-domains and are coupled in an overlapping region by communicating state variables.

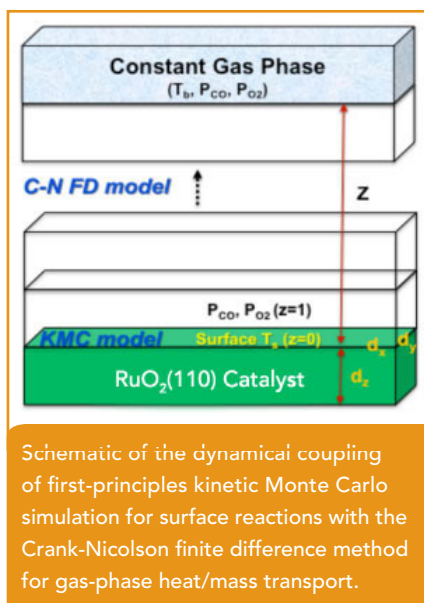
In the past year, we developed a model that dynamically couples KMC simulation with a three-dimensional, grid-based SPDE model in real time. Surface reactions are described using KMC simulation. The varying surface

**This project is** developing a new modeling capability for reactor-scale catalytic processes.

temperature, as well as the partial pressures of reactants and products in the gas phase over the catalyst surface, which directly influence surface reactions and thus macroscopically global kinetics, is accounted for by SPDE model. To validate this new multiscale simulation model, we studied the effects of mass and heat transport on the reaction kinetics of CO oxidation kinetics on RuO<sub>2</sub> catalyst. Simulation results show that both the thickness of catalyst and the diffusions of species have pronounced effects on the predicted reaction kinetics. For example, we found that the surface temperature would rise (up to 200K) for very thin-film RuO<sub>2</sub> catalyst, if the reaction heat is not removed fast enough. The actual pressures experienced by the active catalysts are also quite different from the nominal bulk flow-phase pressures. Currently, we are preparing a manuscript describing these modeling results.

Accurate implementation of mass flux boundary condition presents a big challenge for grid-based macroscale numerical models, especially if boundaries are geometrically complex. We developed an improved numerical method for diffusion equations subject to Neumann or Robin boundary conditions. Based on

the approximation of the sharp boundaries with diffused interface and the continuum surface force model, the new method allows us to efficiently implement the Neumann and Robin boundary conditions. The criteria for the width of the diffused interface, as well as its accuracy of the new method, were thoroughly investigated by comparing with analytical and finite difference solutions. A manuscript describing this method was submitted to the *Journal of Computational Physics*.



## RECOGNITION & AWARDS

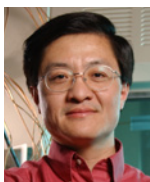
### Charles H.F. Peden, Interim Director of the IIC

- ▶ American Association for the Advancement of Science Fellow (2009)



### Yong Wang, Deputy Director of the IIC

- ▶ Voiland Distinguished Professor at Washington State University (2009)
- ▶ American Association for the Advancement of Science Fellow (2009)
- ▶ Washington State University Distinguished Alumni Award (2008)



### Michael A. Henderson

- ▶ Editorial board member, *Surface Science Reports* (2008)



### Zdenek Dohnálek

- ▶ Executive board member of Nanometer Scale Science and Technology Division of AVS (2009)
- ▶ President of Pacific Northwest Chapter of American Vacuum Society (2006–2008)



### Michel Dupuis

- ▶ American Association for the Advancement of Science Fellow (2008)
- ▶ *Journal of Physical Chemistry* Advisory Board member (2009)
- ▶ Adjunct Professor at Washington State University (2010)



### Bruce D. Kay

- ▶ *Journal of Chemical Physics* Editorial Board member (2009)
- ▶ Appointed to the U.S. Department of Energy's Basic Energy Sciences Advisory Committee (2008)



### Gregory K. Schenter

- ▶ American Physical Society Fellow (2009)
- ▶ Pacific Northwest National Laboratory Fellow (2009)



### Wendy Shaw

- ▶ Received DOE Early Career Research Program Grant (2010)



### János Szanyi

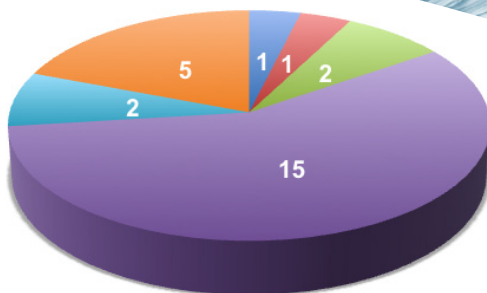
- ▶ Received Fulbright Fellowship (2009)



# PUBLICATIONS



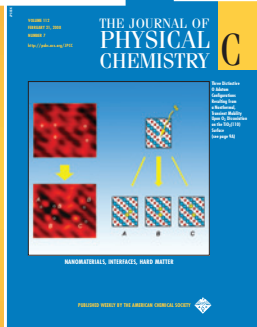
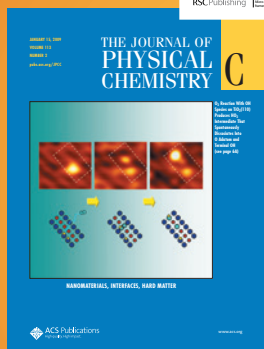
- *Chemical Society Reviews*
- *Surface Science Reports*
- *Angewandte Chemie International Edition*
- *Journal of the American Chemical Society*
- *Science*
- *Journal of Catalysis*



## Publications

From 2007 through present, the Institute for Interfacial Catalysis has been featured in 145 invited lectures and 136 publications (see pie chart for details on top publications).

Research from the Institute for Interfacial Catalysis for BES has been featured on several covers:





## STAFF BIOS

- ▶ Aaron Appel
- ▶ Tom Autrey
- ▶ R. Morris Bullock
- ▶ Zdenek Dohnálek
- ▶ Daniel DuBois
- ▶ Michel Dupuis
- ▶ James Franz
- ▶ Michael A. Henderson
- ▶ Bruce D. Kay
- ▶ Greg A. Kimmel
- ▶ John C. Linehan
- ▶ Igor Lyubinetzky
- ▶ Donghai Mei
- ▶ Michael Mock
- ▶ Charles H.F. Peden
- ▶ Simone Rauei
- ▶ John Roberts
- ▶ Roger Rousseau
- ▶ Gregory K. Schenter
- ▶ Wendy Shaw
- ▶ János Szanyi
- ▶ Yong Wang
- ▶ Jenny Yang

## Aaron Appel

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 375-2157

E-mail: [aaron.appel@pnl.gov](mailto:aaron.appel@pnl.gov)



My research interests and expertise are in the area of electrochemical transformations for the control and interconversion of chemicals, fuels, and energy. My recent work includes electrocatalysis for hydrogen production and utilization as well as carbon dioxide capture and conversion. The general approach in my research is the synthesis and study of species relevant to electrocatalysis, particularly for fuel production and utilization. Synthetic work is coupled with electrochemical and fundamental thermochemical studies to understand the limiting factors in catalytic systems (high-energy steps), and thereby synthesize improved catalysts.

I am currently leading the hydrogen production team of our Energy Frontier Research Center: The Center for Molecular Electrocatalysis. The goal of the hydrogen production team is the development of catalysts that exceed the performance of hydrogenase enzymes. By establishing structure-activity relationships for our electrocatalysts, key structural features can be utilized to improve rates and decrease overpotentials for our electrocatalysts. Through improvements in our catalytic conditions, we have been able to achieve catalytic rates exceeding 850 turnovers per second.





## Tom Autrey

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 375-3792

E-mail: [tom.autrey@pnl.gov](mailto:tom.autrey@pnl.gov)

My research group is interested in the chemical and physical properties of amphiphilic functional centers with a goal of providing fundamental insight for the development of new catalysts designed for small molecule activation. Current research focuses 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/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. Of special interest is the heterolytic activation of molecular hydrogen providing a catalyst-based complex containing both hydridic and protonic hydrogen. Our group uses experimental spectroscopy methods (nuclear magnetic resonance, Raman, x-ray, 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. These basic research studies will provide the foundation for the development of a rational approach to design of new catalysts.

## R. Morris Bullock

CATALYSIS SCIENCE

Center for Molecular Electrocatalysis  
and Institute for Interfacial Catalysis

Phone: (509) 372-6589

E-mail: morris.bullock@pnl.gov



My research interests focus on fundamental studies of the reactivity patterns and thermochemical properties of organometallic and inorganic complexes, and the development of these reactions into homogeneous catalysts. A long-term interest has been “Cheap Metals for Noble Tasks.” In research funded by the Hydrogen Fuel Initiative, my team studies cobalt, manganese, and iron complexes. Our goal is to develop electrocatalysts based on inexpensive, earth-abundant metals, because most fuel cells are based on platinum, an expensive, precious metal. In 2009, the Center for Molecular Electrocatalysis ([efrc.pnl.gov](http://efrc.pnl.gov)) began operations. This center is led by Pacific Northwest National Laboratory, and includes collaborators at the University of Washington, the University of Wyoming, and Penn State University. In the Center, we seek to understand, predict, and control the intra- and inter-molecular flow of protons in electrocatalytic multi-proton, multi-electron processes of critical importance to a wide range of energy transformation reactions. We focus on 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.



## Zdenek Dohnálek

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 371-6150

E-mail: [zdenek.dohnalek@pnl.gov](mailto:zdenek.dohnalek@pnl.gov)

My research concentrates on fundamental model system experimental studies necessary to understand complex processes that take place in heterogeneous catalysis and the environment. The work focuses on adsorption, diffusion, and desorption dynamics and kinetics, binding, and reactivity of adsorbates on models with well-characterized surfaces and clusters. In the past year we studied the rotational dynamics of alkoxy species on  $\text{TiO}_2(110)$  and partial oxidation of aliphatic alcohols on monodispersed  $(\text{WO}_3)_3$  clusters supported on  $\text{TiO}_2(110)$ . Our long-term effort in the area of oxide chemistry resulted in an invitation to write a review article entitled “Thermally-Driven Processes on Rutile  $\text{TiO}_2(110)-(1 \times 1)$ : A Direct View at the Atomic Scale,” currently being published in *Progress in Surface Science* (DOI:10.1016/j.progsurf.2010.03.001).

## Daniel DuBois

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 375-2331

E-mail: [daniel.dubois@pnl.gov](mailto:daniel.dubois@pnl.gov)



My research interests include the catalytic interconversion of fuels and electricity, synthetic organometallic and inorganic chemistry, and thermodynamic studies relevant to catalysis. Currently, I am

- ▶ Principal Investigator on the subtask, “A Modular Energy-Based Approach to Molecular Catalyst Design”
- ▶ Deputy director of the Energy Frontier Research Center for Molecular Electrocatalysis
- ▶ Co-Principal Investigator with R. Morris Bullock on the Hydrogen Fuel Initiative subtask, “Bio-Inspired Molecular Catalysts for Oxidation of Hydrogen and Production of Hydrogen: Cheap Metals for Noble Tasks.”

In the past year, my teams have continued the work of developing new electrocatalysts for carbon dioxide reduction and for hydrogen production and oxidation and initiated new studies in the areas of formate and alcohol oxidation catalysts. This work emphasizes the role of pendant bases and acids in the second coordination sphere and their role in substrate binding and activation as well as their role as proton relays.



## Michel Dupuis

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 375-2617

E-mail: [michel.dupuis@pnl.gov](mailto:michel.dupuis@pnl.gov)

My research expertise and interests focus on the application of quantum chemical electronic structure and molecular dynamics methods to characterize electro-chemical processes in photo-catalysis and in molecular electro-catalysis. In the past year, we completed our work in photo-catalysis with studies that provided novel insights into the structure of excess electrons in defected photo-catalytically active surfaces and a framework for understanding their role with regards to the reactivity of surface adsorbates and other photo-chemical processes. We initiated our work in the Energy Frontier Research Center for Molecular Electrocatalysis, mainly the coordination of the theory activities including the collaboration with Professor Hammes-Schiffer as well as the characterization of efficient molecular catalysts for hydrogen oxidation and production.

## James Franz

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 375-2967

E-mail: james.franz@pnl.gov



My research interests center around understanding heterogeneous and homogeneous pathways for the production and oxidation of hydrogen and the catalysis of bond breaking in organic molecules. The approach taken is to measure kinetic and thermodynamic properties of homogeneous catalytic systems to establish a quantitative and comprehensive thermochemical kinetic basis for controlling the cleavage of strong bonds (e.g., H–H, C–H, MS–H M–H) by homolytic (free-radical) and heterolytic (acidic and hydridic) pathways. Studies of homogeneous organometallic systems provide insight into the detailed molecular-level function of heterogeneous catalysts. Such systems include nanometer-scale iron sulfide and molybdenum sulfide catalysts for oxidation and production of hydrogen and for hydrogenation and hydrogenolysis of organic structure. Subjects of research include determination of M–H and S–H homolytic, hydridic, and acidic bond strengths and kinetic reactivity of novel Fe( $\mu$ -SH)Fe and Mo( $\mu$ -SH)Mo structures. Kinetics and bond strengths of formation of MS–C bonds by reaction of carbon-centered radicals with Mo( $\mu$ -S<sub>2</sub>)( $\mu$ -S)<sub>2</sub>Mo are explored using thermodynamic, kinetic, and theoretical methods. Activation of H<sub>2</sub> by reaction with metal-centered radicals is under study.

Work in this group seeks to achieve efficient, fully reversible systems for the production and oxidation of hydrogen using nickel and other metals. Our work seeks to develop hydrogen activation pathways that are more efficient than nature's hydrogenase enzymes.

This work combines measurement of thermochemistry and kinetics of reactive intermediates, synthesis of homogeneous organometallic and nanometer heterogeneous catalysts, design of new homogeneous hydrogenation catalysts, *operando* and *in-situ* spectroscopic and kinetic methods, and computational chemistry.



## Michael A. Henderson

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 371-6527

Email: [ma.henderson@pnl.gov](mailto:ma.henderson@pnl.gov)

My research interests center on examination of the molecular-level properties of clean and adsorbate-covered oxide surfaces. Model single-crystal surfaces enable correlation between surface structure and surface chemistry. Studies are conducted under an ultrahigh 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 characterization of adsorbates using vibrational spectroscopy, examination of adsorption-desorption processes and surface reaction pathways, probing the structure/reactivity of adsorbed molecules, and examinations of the interactions of photons, low-energy electrons, and ions with adsorbed species. The overall goal of these 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.

## Bruce D. Kay

CHEMICAL PHYSICS AND ANALYSIS

Institute for Interfacial Catalysis

Phone: (509) 371-6143

E-mail: [bruce.kay@pnl.gov](mailto:bruce.kay@pnl.gov)



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 process 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 the theoretical efforts of Roger Rousseau. During the past year, we studied the rotational dynamics of alkoxy species on  $\text{TiO}_2(110)$  and the partial oxidation of aliphatic alcohols on monodispersed  $(\text{WO}_3)_3$  clusters supported on  $\text{TiO}_2(110)$ .





## Greg A. Kimmel

CHEMICAL PHYSICS AND ANALYSIS

Institute for Interfacial Catalysis

Phone: (509) 371-6134

E-mail: [gregory.kimmel@pnl.gov](mailto:gregory.kimmel@pnl.gov)

Energetic processes at surfaces and interfaces are important in fields such as radiation chemistry, waste processing, advanced materials synthesis, and photocatalysis. Low-energy electrons ( $<100$  eV) frequently play a dominant role in these energetic processes because the higher-energy primary particles produce numerous low-energy secondary electrons that are chemically active. In addition, the presence of surfaces or interfaces modifies the structure of the water film and thus the thermal and non-thermal reactions and other processes compared to what occurs in the bulk. We use quadrupole mass spectroscopy, Fourier transform infrared spectroscopy, and temperature-programmed desorption to investigate thermal and non-thermal reactions at surfaces and interfaces in thin molecular films in ultrahigh vacuum. We also investigate the structure of thin aqueous films at interfaces, and how the structure influences the reactivity. This work addresses several important issues, including the need to understand the relative importance of the primary excitation source compared to the secondary electrons it produces, energy transfer at surfaces and interfaces, and new reaction pathways at surfaces.

## John C. Linehan

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 375-3983

E-mail: john.linehan@pnl.gov



My main research goals are to determine catalyst resting states and 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, high-pressure and/or high-temperature) and interrogate the metal catalyst species prevalent during catalysis. In combination with high-level theoretical studies, we have determined the catalyst resting state structures for  $\text{Rh}_4$  clusters important in both hydrogenation and dehydrogenation chemistries and determined a plausible catalytic mechanisms for the loss of hydrogen from ammonia boranes. *Operando* high-pressure NMR studies have revealed a more accurate picture of ruthenium  $\text{CO}_2$ -to-formic acid catalysts. Most important in this work was the determination of the role of the alcoholic co-catalysts. This work has shown us how to remove this unnecessary additive, producing more stable catalysts without affecting the catalytic rates. 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 Energy Frontier Research Center for Molecular Electrocatalysis.



## Igor Lyubinetsky

ENVIRONMENTAL MOLECULAR  
SCIENCES LABORATORY

Institute for Interfacial Catalysis

Phone: (509) 371-6267

E-mail: igor.lyubinetsky@pnl.gov

My research interests and expertise include an application of the ultrahigh vacuum scanning tunneling microscopy for studying, at the atomic level, the physical and chemical processes governing the thermal- and photo-induced reactivity of adsorbed molecules on metal oxide surfaces. In the past year, my team continued our work on identifying reaction pathways and mechanisms related to surface reactivity and photo-catalytic processes on reduced  $\text{TiO}_2(110)$  surfaces. We explored adsorption states, mobility, and charge transfer upon adsorption of oxygen, carboxylic acid (trimethyl acetic acid), and water/oxygen co-adsorption. We initiated studies of the oxygen physisorption at cryogenic temperatures, and also the highly hydroxylated  $\text{TiO}_2(110)$  surfaces formed after trimethyl acetate photodesorption.

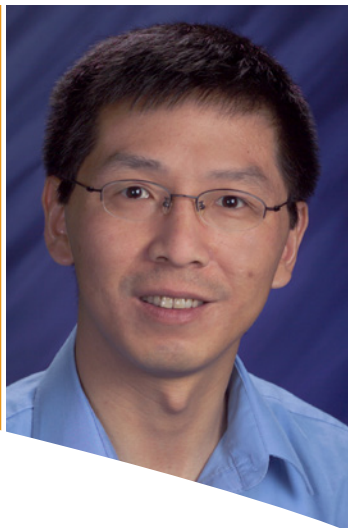
## Donghai Mei

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 375-6303

E-mail: donghai.mei@pnl.gov



My research expertise and interests focus on multiscale computational modeling of heterogeneous catalysis. In the past year, my team has developed a new multiscale model that combines first-principles density functional theory calculations, kinetic Monte Carlo simulation, and stochastic partial differential equation theory to describe catalytic phenomena under realistic operating reaction environments. We tested the model with a benchmark catalytic system, i.e., CO oxidation over  $\text{RuO}_2$  catalyst. Computational methods were successfully used to gain fundamental insight into the complex reaction mechanisms and obtain the reaction kinetics of alcohol synthesis from syngas over  $\text{Rh/Mn/SiO}_2$  catalysts under operating conditions. In conjunction with concurrent experimental efforts, we discovered a two-dimensional raft-like platinum oxide overlayer formed on the  $\gamma$ -alumina support. The unique anchoring role of penta-coordinated surface aluminum atoms was unambiguously identified.



## Michael Mock

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 375-2975

E-mail: michael.mock@pnl.gov

Our current research interests focus on the preparation and reactivity of transition-metal complexes, specifically for the activation of small molecules such as  $H_2$  and  $N_2$ . Recent 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 B–H bonds from  $H_2$  and a base. This work examines the thermodynamic hydride donor abilities of rhodium and cobalt diphosphine complexes and surveys their reactivity with selected  $BX_3$  compounds. Our current efforts within the Energy Frontier Research Center for Molecular Electrocatalysis are focused on the preparation and reactivity of tungsten and molybdenum dinitrogen complexes containing proton relays to examine mechanistic details of the multi-proton, multi-electron reactions for the electrocatalytic reduction of nitrogen to ammonia.

## Charles H.F. Peden

INTERIM DIRECTOR

Institute for Interfacial Catalysis

Phone: (509) 371-6501

E-mail: [chuck.peden@pnl.gov](mailto:chuck.peden@pnl.gov)



My group's 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. My team participates collaboratively in a program that is employing an integrated experimental/theoretical approach with an overall goal of significantly advancing our current ability to understand, design, and control chemical transformations on transition metal oxide catalysts, specifically for reduction-oxidation and acid-base chemistries. We also participate in an effort to obtain a fundamental understanding of catalytic nitrogen oxide reactions on oxide surfaces. We obtain detailed chemical kinetics data on idealized but well-characterized catalyst systems useful for understanding important elementary reactions. This program has made critical contributions to the understanding of a number of practical issues associated with the development of new catalytic vehicle emission control technologies.



## Simone Raugei

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 372-6902

E-mail: [simone.raugei@pnl.gov](mailto:simone.raugei@pnl.gov)

My scientific activity has focused on the application of quantum mechanical, molecular mechanics and hybrid quantum mechanical/molecular mechanics simulation methodologies to the study of the relationships between structure and function in biomolecules and metal complexes as well as chemical-physics processes in the liquid phase. I recently joined the Energy Frontier Research Center for Molecular Electrocatalysis where I started a research line in homogeneous catalysis for energy storage and energy delivery. I am currently focusing on the theoretical characterization of novel nickel-based electrocatalysts for H<sub>2</sub> production and oxidation by using first-principle molecular dynamics simulations coupled to advanced sampling techniques. Specifically, I am addressing issues that are crucial to developing improved catalysts such as understanding the global free-energy landscape along the full catalytic cycles and fine-tuning the structural flexibility of the metal ligands to optimize the proton flow via bond making and breaking.

## John Roberts

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 372-4407

E-mail: [john.roberts@pnl.gov](mailto:john.roberts@pnl.gov)



My research efforts are directed toward understanding molecular electrocatalysis involving both proton and electron transfers from a mechanistic and thermodynamic point of view, using solution electrochemical methods as a complement to the spectroscopic and theoretical approaches being employed within the Center for Molecular Electrocatalysis. I have initiated collaborative work with Prof. Bruce Parkinson, University of Wyoming, in developing lines of research focused on solution electrochemical methods. My colleagues and I at PNNL have established catalyst testing protocols and garnered insights into the role of reaction media on the energy efficiency and reaction rates of hydrogen production electrocatalysts. These efforts are a critical step in the rational development of electrocatalyst systems.





## Roger Rousseau

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 372-6092

E-mail: roger.rousseau@pnl.gov

My research work has focused 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 the study of hetero- and homogenous catalysis reaction mechanisms.

In the past year, my team 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. We also contributed to studies of Rh/Mn/SiO<sub>2</sub>-based catalysts for the conversion of biomass-derived syngas to oxygenated hydrocarbons, which provide a mechanistic understanding of the role of manganese promoters for increasing the selectivity/activity toward ethanol production. The team has also initiated work in the Energy Frontier Research Center for Molecular Electrocatalysis, mainly the characterization of efficient molecular catalysts for H<sub>2</sub> oxidation and production.

## Gregory K. Schenter

CHEMICAL PHYSICS AND ANALYSIS

Institute for Interfacial Catalysis

Phone: 509) 375-4334

E-mail: [greg.schenter@pnl.gov](mailto:greg.schenter@pnl.gov)



Our research focuses on the development of statistical mechanical techniques to better understand molecular interactions and molecular processes in complex condensed-phase systems. An important component of this work is the development of new simulation capabilities that enhance the interpretation of experimental measurement. Teaming with Tom Autrey, we are interested in the chemical and physical properties of ambiphilic functional centers with the goal of providing fundamental insight into the development of new catalyst materials designed for small-molecule activation. 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 hinderance, 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/base pairs. Efforts are underway to correlate electric field fluctuations and charge transfer to the stabilization of selected thermodynamic and electronic states. Specific simulation techniques have been developed to enhance the interpretation of spectroscopy methods (nuclear magnetic resonance, Raman, x-ray, and neutrons) 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 to design new catalyst materials. Because these are internationally important scientific research questions, we are co-organizing a workshop sponsored by Centre Européen de Calcul Atomique et Moléculaire to bring together experimental and computational scientists to develop novel tools and approaches to address these critical scientific challenges.



## Wendy Shaw

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 375-5922

E-mail: [wendy.shaw@pnl.gov](mailto:wendy.shaw@pnl.gov)

My research expertise and interests focus on developing a more mechanistic understanding of the outer coordination sphere of molecular catalysts. Building upon the well-understood nickel-phosphine-based electrocatalysts for hydrogen production and oxidation, peptides are being incorporated into the outer coordination sphere to provide some of the features of an enzyme, without re-creating the entire enzyme. The role of proton channels is being investigated within the context of the Early Career Research Program award, stimulus-sensitive peptides and polymers because enzyme mimics are the focus of the Molecular Catalysis Program, and the physical-chemical characteristics of the active site pocket are the focus of the related “Biological Principles of Energy Transductions” in the Physical Biosciences program. Within the Energy Frontier Research Center, similar catalysts are being investigated using 2D and 3D nuclear magnetic resonance techniques to understand proton movement and catalyst structure. In the past year, we developed a successful synthesis route to incorporate amino acids and peptides into the nickel-based catalysts, an essential first step for the success of each of these projects. We have also initiated our work in the Energy Frontier Research Center for Molecular Electrocatalysis and in the Early Career Research Award on “Catalyst Biomimics.”

## János Szanyi

CATALYSIS SCIENCE

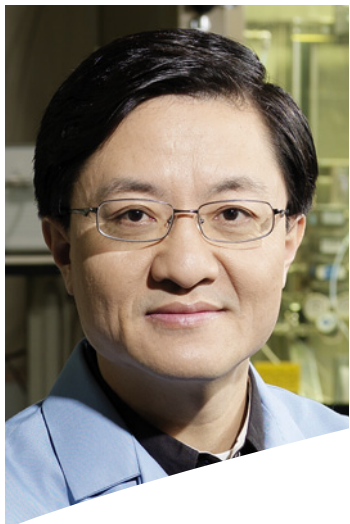
Institute for Interfacial Catalysis

Phone: (509) 375-6524

E-mail: janos.szanyi@pnl.gov



My current research focuses on understanding the structure-reactivity relationships in model and high-surface-area catalyst materials using an array of spectroscopy and microscopy tools. My team's efforts have been concentrated on investigating the chemistry of alkaline earth oxides nanostructures, the active storage materials in lean nitrogen oxide ( $\text{NO}_x$ ) catalysts. These investigations follow a parallel path, i.e., we are working on both high-surface-area ("real-world") catalysts, as well as model (single-crystal-based) 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 us identify active catalytic centers, and their structures in supported catalyst systems. Most of our work on the high-surface-area catalysts utilizes *in-situ* and/or *operando* spectroscopy tools (high-resolution, solid-state nuclear magnetic resonance, and, primarily, Fourier transform infrared (FTIR) spectroscopy). We are also regularly using synchrotron-based spectroscopy techniques (x-ray diffraction, x-ray absorption, near-edge structure, and extended x-ray absorption fine structure) in collaboration with our colleagues at the National Synchrotron Light Source. We are also very much interested in understanding the mechanisms of photocatalytic reactions on high-surface-area semiconducting oxides. Our efforts are directed at photocatalytic oxidations of organic molecules and photochemical reactions of atmospheric relevance. These studies are conducted on a combined FTIR/mass spectroscopy system that allows us to follow the species present on the surfaces of the catalyst materials, as well as the desorbing species, under ultraviolet irradiation.



## Yong Wang

HYDROCARBON PROCESSING

Institute for Interfacial Catalysis

Phone: (509) 371-6273

Email: [yong.wang@pnl.gov](mailto:yong.wang@pnl.gov)

My research is focused on the fundamental understanding of the roles of bimetallic catalysts on the steam reforming of alcohols to produce hydrogen. My contributions on this project include the synthesis of bimetallic 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 bimetallic catalysts in steam-reforming renewable feedstock for hydrogen and fuel production.

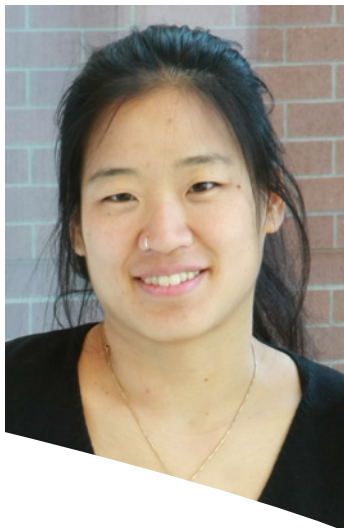
## Jenny Yang

CATALYSIS SCIENCE

Institute for Interfacial Catalysis

Phone: (509) 372-4639

E-mail: [jenny.yang@pnl.gov](mailto:jenny.yang@pnl.gov)



My research expertise and interests are focused on the generation of electrocatalysts for small-molecule transformations of importance to chemical fuel production and utilization. My approach emphasizes a comprehensive mechanistic understanding of the catalytic cycle and intermediates to determine the necessary electronic and structural requirements for high performance. This includes quantitative study of kinetic and thermodynamic properties to identify the most productive modifications in catalyst design. I am currently leading the hydrogen oxidation team of the Energy Frontier Research Center for Molecular Electrocatalysis. Recent efforts have applied this mechanism-based approach toward hydrogen oxidation catalysts, leading to the discovery of the highest performing catalysts to date. I am also using my prior expertise in the field of oxygen-reduction catalysis for the Center's collaboration with the University of Washington in that area.



## About Pacific Northwest National Laboratory

Pacific Northwest National Laboratory, located in southeastern Washington State, is a Department of Energy Office of Science national laboratory where interdisciplinary teams advance science and technology and deliver solutions to America's most intractable problems in energy, national security and the environment. PNNL employs 4,700 staff, has an annual budget of nearly \$1.1 billion, and has been managed by Ohio-based Battelle since the lab's inception in 1965.

► [www.pnl.gov](http://www.pnl.gov)

► [iic.pnl.gov](http://iic.pnl.gov)

### CONTACTS

**Charles H. F. Peden**

*Interim Director of IIC*

Phone: (509) 371-6501

E-mail: [chuck.peden@pnl.gov](mailto:chuck.peden@pnl.gov)

**Bruce Garrett**

Phone: (509) 372-6344

E-mail: [bruce.garrett@pnl.gov](mailto:bruce.garrett@pnl.gov)



**Pacific Northwest**  
NATIONAL LABORATORY

*Proudly Operated by **Battelle** Since 1965*

P.O. Box 999  
Richland, WA 99352  
1-888-375-PNNL (7665)  
[www.pnl.gov](http://www.pnl.gov)

Institute for  
**INTERFACIAL  
CATALYSIS**