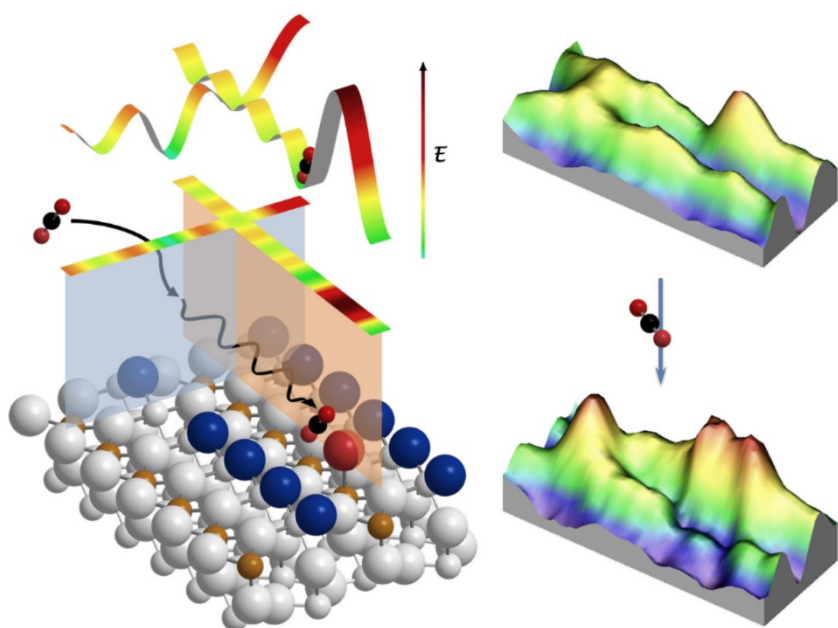


# 2017 Program Briefing



**Pacific Northwest**  
NATIONAL LABORATORY

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U.S. DEPARTMENT OF  
**ENERGY**

Office of Science

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## ABBREVIATIONS

AIMD	<i>Ab initio</i> molecular dynamic
ATP	Adenosine triphosphate
BES	Basic Energy Sciences
BOL	Binding organic liquids
CME	Center for Molecular Electrocatalysis
DFT	Density functional theory
DOE	U.S. Department of Energy
EA	Electron affinity
EPTM	Electron-proton-transfer mediators
FA	Fluoride affinity
FTIR	Fourier transform infrared spectroscopy
IIC	Institute for Integrated Catalysis
IR	Infrared
JACS	<i>Journal of the American Chemical Society</i>
MAS	Magic angle spinning
MD	Molecular dynamics
MEA	Monoethanolamine
NCE	Normalized clustering energies
NMR	Nuclear magnetic resonance
ORR	Oxygen reduction reaction
PI	Principal Investigator
PNAS	<i>Proceedings of the National Academy of Sciences</i>
PNNL	Pacific Northwest National Laboratory
RE	Relative energy
SCR	Selective catalytic reduction of NO <sub>x</sub>
SIMS	Secondary ion mass spectrometry
SSITKA	Steady-state isotopic transient kinetic analysis
STM	Scanning tunneling microscopy
TEM	Transmission electron microscopy
TPD	Temperature-programmed desorption

## INTRODUCTION

Economic wealth is directly correlated with the energy used to perform work, enable mobility, and provide the goods required to ensure our well-being. Today, more than 80 percent of chemicals and energy carriers are synthesized from fossil (hydro)carbon resources, which has led to an unprecedented increase in the levels of CO<sub>2</sub> in the atmosphere. Nearly all these chemicals and energy carriers are made using catalysis in at least one of the processing steps. Catalysis is,

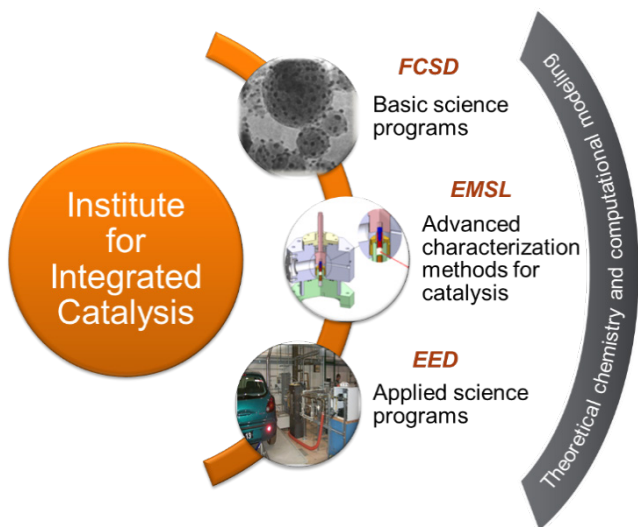
*The Institute for Integrated Catalysis explores and develops the chemistry and technology of catalyzed processes that enable a carbon-neutral future.*

therefore, not only key to sustainable development, characterized by transition from the current fossil carbon-based energy carriers to a zero-carbon footprint energy future, but it will also secure energy independence.

## Institute for Integrated Catalysis

Catalysis is key to sustainable development that secures energy independence, and it is critical to the transition from the current use of carbon resources for energy and chemicals toward solely using recycled and renewable carbon as well as renewable energy resources. Currently, 80 percent of all chemical products and energy carriers are made using catalysts in at least one of the processing steps, producing an economic impact estimated to be over \$10 trillion per year worldwide. The long-term transition to a sustainable economy requires not only reinventing the large processes of today, but also enabling the harvest and use of dispersed renewable carbon and energy resources. These challenges define the mission of the Pacific Northwest National Laboratory (PNNL) Institute for Integrated Catalysis (IIC):

- ▶ Provide the insight, the synthetic tools, and the engineering concepts to enable catalyzed chemical and chemical-electrical energy interconversions to minimize the carbon footprint of the global energy system.
- ▶ Develop experimental and theoretical tools to better understand the structure and properties of working catalysts to be used as guidelines for novel catalyst generations and novel reaction routes.
- ▶ Translate the fundamental insight into novel and improved catalytic technology.



The IIC integrates more than 120 scientists and engineers from different organizations at PNNL. These organizations include the Physical and Computational Sciences Directorate (PCSD), the Environmental Molecular Sciences Laboratory (EMSL), and the Energy and Environment Directorate (EED) and encompass a wide range of catalysis disciplines. The cross-disciplinary collaboration and mutual influence produces a unique creative environment, which is a prerequisite for transformative research. The key scientific challenges addressed within the IIC focus on adding hydrogen to oxo-functionalized carbon resources (such as biomass constituents or carbon dioxide), storing electric energy in hydrogen, oxygen, or nitrogen (key foci of the Center for Molecular Electrocatalysis (CME), an Energy Frontier Research Center, manipulating carbon-carbon and carbon-heteroatom bonds, and exhaust catalysis.

# CORE BASIC ENERGY SCIENCES CATALYSIS PROGRAM:

## Low-Temperature Catalytic Routes for Energy Carriers via Spatial and Chemical Organization

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The program has been restructured and focuses on the elementary reactions of the reduction of oxygenates to hydrocarbon energy carriers (Figure 1). The two thrusts focus on the elementary steps of hydrogenation reactions of CO<sub>2</sub> and more complex (unsaturated) oxygenates (*i.e.*, alcohols, ethers) catalyzed by metals (hydrogen addition, hydrogenolysis) and acid-catalyzed reactions such as the elimination of water, hydrolysis of ether bonds, and alkylation of aromatic compounds. Our strategy is to explore and understand the molecular and atomistic pathways of selected reactions on catalysts spanning from single-crystal surfaces via dispersed, supported catalysts to molecular complexes. The fundamental understanding of the elemental steps of reaction sequences enables the emerging

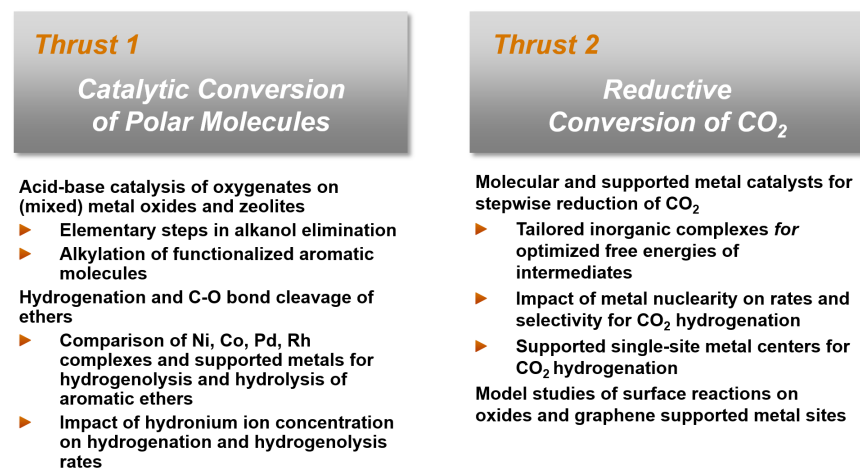


Figure 1. Program structure showing the three thrust areas and their focus.

knowledge-based design of novel catalysts that operate at lower temperatures and with higher rates than practiced today.

We are making rapid progress on our research objectives using an integrated approach enabled by the synergy within our multidisciplinary team focusing on three crosscutting research themes that are common to many of the research activities:

- ▶ Multifunctional catalytic sites or catalytic sites acting in concert
- ▶ Spatially constrained, chemospecific environments of active centers
- ▶ Use of the condensed phase to stabilize reactants, intermediates, and products for particular catalytic pathways.

## Thrust 1: Catalytic Conversion of Polar Molecules

Catalysis with polar biomass-derived molecules addresses individual reactions of the multistep conversion of polar molecules on surfaces and in the pores of metal oxides as well as on metal particles and coordination complexes. The aim is to develop a better understanding of the role of the metal (linking homogeneous and heterogeneous catalysts) as well as the acid-base and redox functions as they interact with polar bio-derived molecules. The goal is further to achieve relative stabilization of reactants, intermediates, and products as well as the impact of the local environment. We will characterize the nature of the catalytic sites as well as the steric environments around those sites. Our goal is to link insight into reactions by molecular catalysts and on surfaces, as well as in pores. We will make quantitative comparisons of the reactions in the condensed phase to analogous reactions at gas-solid interfaces. Hydrodeoxygenation and hydroalkylation will be the reactions we use to exemplify potential routes from lignocellulosic biomass to alkane energy carriers requiring several catalytic functions acting sequentially. These reactions start in an aqueous environment, but the products form a nonpolar phase as the conversion progresses. Thus, the effect of the polarity of the reaction environment on the catalytic site has to be explored. We will compare single-site solid catalysts with molecular catalysts.



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

*Donald M. Camaioni, Nigel Browning, Mirek Derewinski, John Fulton, Jian Zhi Hu, Andreas Jentys, Johannes Lercher, Donghai Mei, Yong Wang*

The catalyzed-conversion of lignin to alkane energy carriers requires a cascade of reactions for deconstructing and reducing the polymeric, highly oxofunctionalized material. While lignin is the most intractable component of lignocellulose, its conversion to useful products is particularly important, because the carbon in lignin is the most reduced fraction of lignocellulose. Our recent work has been structured to investigate the catalysis of steps important for the deconstruction of lignin, for hydrogenation and hydrodefunctionalization of oxygenated intermediates, and for C-C bond coupling reactions to adjust the size of the product molecules. This has been complemented by focusing on understanding the state and stability of catalysts in the reaction media. Mechanistic and kinetic studies have emphasized cooperative effects between acid and metal functionalities and the influence of the reaction environment (confinement and solvent) on reaction rates and transformation pathways. This has been complemented with advanced characterization of the catalyst and an understanding of the implications of catalyst structure on stability in diverse reaction media. The work emphasizes gaining fundamental insight into the principal chemistry of representative functionalities and their transformation at the active sites. This knowledge provides directions to synthesize a new generation of catalysts.

### **Dehydration of Alcohols within Zeolite Pores in Condensed Phase**

*Donald M. Camaioni, Nigel Browning, Mirek Derewinski, John Fulton, Jian Zhi Hu, Andreas Jentys, Johannes Lercher, Donghai Mei, Yong Wang*

The dehydration of cyclohexanol, a model compound for hydrogenated oxygenated intermediates in the transformation of bio-oil to fuel, has been explored to understand the mechanism of acid-catalyzed C-O bond cleavage. In the aqueous phase, inside or outside the zeolite pores, cyclohexanol dehydration proceeds via an E1 mechanism with the C-H bond cleavage as the rate-determining step. The reaction, however, proceeds with significantly higher rates with hydronium ions confined in zeolite pores. This is due in part to the two to three times higher intrinsic rate constant for dehydration in zeolite (BEA) than in water. Where the enthalpies of activation are similar in the zeolite and in water, the associated activation entropy is higher for hydronium ions in the zeolite pores than in water. The stark effect of confinement on rates, however, is mainly due to lower entropy losses when the association complex (alcohol-hydronium ion) is formed in

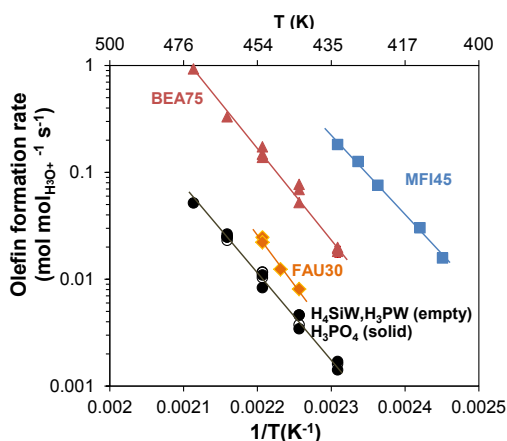


Figure 2. Measured turnover frequencies of cyclohexene formation in aqueous phase dehydration of cyclohexanol on different acid catalysts. For zeolites, the Si/Al ratio is denoted as the number following the framework type code. H<sub>4</sub>SiW and H<sub>3</sub>PW stand for tungstosilicic and phosphotungstic acids.

similar to those around active site pockets in enzymes.

### Effect of Liquid Water and Framework Sites on Zeolite Lattice Stability and Catalytic Activity

Donald M. Camaioni, Nigel Browning, Mirek Derewinski, John Fulton, Jian Zhi Hu, Andreas Jentys, Johannes Lercher, Donghai Mei, Yong Wang

The key to the application of zeolites in the transformation of polar molecules in aqueous phase is their stability. Thus, strategies to understand and counteract the corrosive effects of hot water are being developed. The states of Al and Si atoms are characterized by cross-polarization enhanced <sup>29</sup>Si magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR), <sup>27</sup>Al MAS NMR, and infrared (IR) spectroscopy. The stability of the BEA zeolites has been found to be primarily determined by the

the zeolite. This is attributed to the low entropy of molecules diffusing within the pores, which increases the extent of association between substrate and acid site.

Confirming the correlation between confinement and enhanced rates, the systematic study of MFI, BEA, and FAU zeolites for cyclohexanol dehydration showed increasing rates with decreasing pore size (Figure 2). Hence, the association between hydronium ions and alcohol is enhanced by molecularly sized pores, which pose steric environments

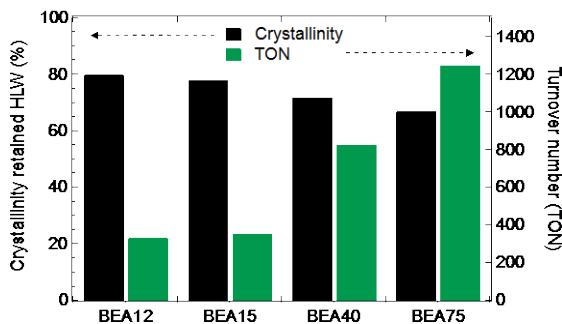


Figure 3. Comparison between the zeolite stability in pure hot liquid water (retained crystallinity) and for aqueous phase catalysis (*i.e.*, turnover number).

concentration of hydronium ions in the pores. Thus, reducing the water concentration slows down the hydrolysis of the zeolite. The concentration of framework defects, on the other hand, is important only at low concentrations of framework Al, which correlate with hydronium ion concentrations in the presence of water. Notably, the concentration of hydronium ions does not affect the rate of zeolite hydrolysis. Thus, the hydrolysis of the framework is a self-limiting process because the availability of mobile water molecules (needed for continuous hydrolysis) is limited by the presence of cyclohexanol as well as hydrolyzed silica species in the pores. The effect of cyclohexanol is illustrated in Figure 3, which shows opposing trends for the structural stability in liquid water and activity for cyclohexanol dehydration. The high affinity of BEA40 and BEA75 for cyclohexanol stabilizes the zeolite and compensates for the destabilizing effect of structural defects.

### Hydroalkylation to Adjust the Size of Alkanes

Donald M. Camaioni,  
Nigel Browning, Mirek Derewinski, John Fulton, Jian Zhi Hu, Andreas Jentys, Johannes Lercher, Donghai Mei, Yong Wang

Acid-catalyzed C-C coupling yields alkylated phenolics with carbon-numbers in the fuel range through the reactions of phenolics with alcohols. In zeolites, the catalytic activity, mechanism, and reaction pathways (C- or O-alkylation) depend on the concentration and strength of acid sites, space constraints for the reaction (whether or not the pore size allows the transition state) and alkylating

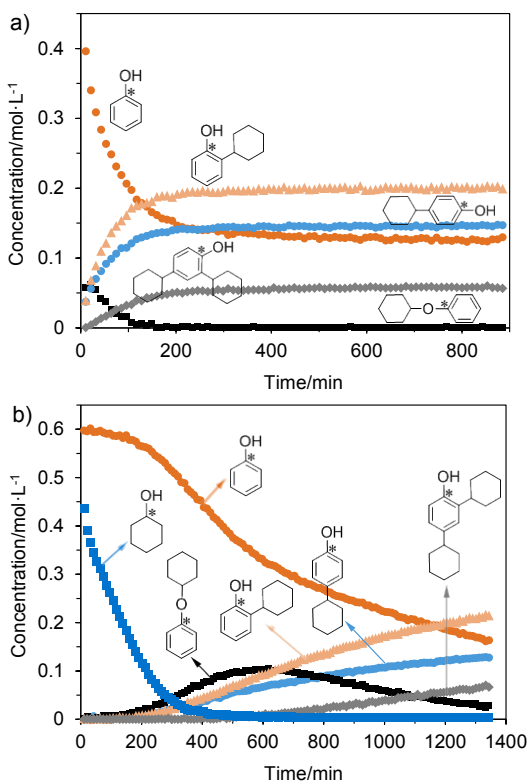


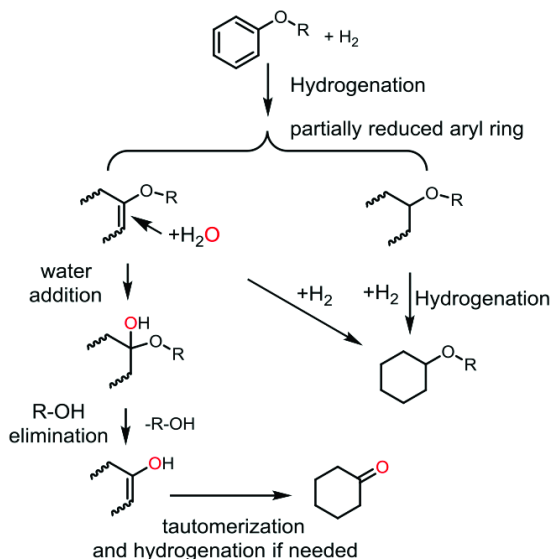
Figure 4. Concentration profiles, monitored by *in situ* NMR, during the alkylation of phenol with cyclohexene only (a) and with equimolar concentrations of cyclohexene and cyclohexanol (b) at 127 °C.

agent. Detailed kinetic analyses and *in situ*  $^{13}\text{C}$  MAS NMR spectroscopy in non-polar media show that phenol alkylation with cyclohexanol does not appreciably occur before a majority of the cyclohexanol has been dehydrated to cyclohexene. Figure 4 shows that alkylation reactions are slowed when cyclohexanol and cyclohexene are present. In contrast, alkylation products are readily formed when the solution initially contains just phenol and cyclohexene. The strict reaction sequence is not posed by competitive adsorption (phenol and cyclohexanol show similar adsorption strengths) but by the absence of a reactive electrophile. This is due to the preferential formation of protonated dimers of cyclohexanol at Brønsted acid sites, which hinders the adsorption of cyclohexene. At low coverage of the acid sites by protonated dimers, cyclohexene adsorption and protonation yields cyclohexyl carbenium ions, which perform an electrophilic attack on phenol to produce alkylated products. This further implies that protonated cyclohexanol dimers dehydrate without the formation of carbenium ions.

### Cleavage of Ether Bonds

*Donald M. Camaioni, Nigel Browning, Mirek Derewinski, John Fulton, Jian Zhi Hu, Andreas Jentys, Johannes Lercher, Donghai Mei, Yong Wang*

Cleavage of C-O bonds in aromatic ethers, a crucial step for the conversion of lignocellulosic biomass to fuels, is challenging due to the stability of these linkages. Hydrogenolytic cleavage requires high temperatures and pressures. Thus, alternative reaction pathways have been explored to optimize the transformations of aromatic ethers. Pd catalysts are active and highly selective toward hydrolysis of diaryl and aryl alkyl ethers in aqueous phase under mild conditions. This is a reductive transformation, which is initiated by partial hydrogenation of the arene ring yielding an enol ether intermediate that is highly reactive with water. This novel pathway (illustrated in Figure 5) contrasts with the acid-catalyzed mechanism for



**Figure 5.** Mechanistic pathways for reductive hydrolysis of aromatic ethers on Pd catalysts (R denoted phenyl, cyclohexyl and n-butyl).

ether cleavage. The mechanism can be generalized (solvolysis) as the analogous transformation and has been observed in methanol. In this case, the enol ether undergoes methanolysis to a ketal, which eliminates phenol/alkanol to generate methoxycyclohexene. The attack of water, however, is faster than the attack of methanol, which leads to more hydrolyzed products, compared to methanolysis products, in aqueous/alcohol media.

## Synergetic Effect of Support Acidity on the Metal-Catalyzed Hydrogenation of Phenol

*Donald M. Camaioni, Nigel Browning, Mirek Derewinski, John Fulton, Jian Zhi Hu, Andreas Jentys, Johannes Lercher, Donghai Mei, Yong Wang*

The enhancement of the activity of supported metal catalysts by the acidity of the support has been well documented in the gas phase albeit without a widely accepted interpretation. In contrast, this phenomenon is hardly documented for reactions in condensed phase, which poses particular challenges for fundamental studies. The mechanistic aspects of the synergetic effect of Brønsted acid sites on the metal functionality were studied with Pt clusters encapsulated in a MFI zeolite with varying acid site concentrations. Pt clusters in MFI zeolites with increasing hydronium ion concentrations exhibit increasing hydrogenation activity despite decreased affinities to adsorb phenol and H<sub>2</sub>. These observations and changes in the measured reaction orders support a shift of the rate-determining step from the first H addition at the *ortho*-position (in the absence of hydronium ions) to the second one at the *ortho*- and *para*-position (if hydronium ions are present). The decreased activation barrier for the first H addition (by 30 kJ·mol<sup>-1</sup>) is attributed to a mechanism, where a hydronium ion protonates the adsorbed phenol ring followed by an electron transfer from an adsorbed H. The latter replaces the hydronium ion upon being oxidized (Figure 6). The enhancing effect of hydronium ions on the activity of supported metals is of special importance for biomass conversion as it is a potential strategy to boost rates at mild conditions.

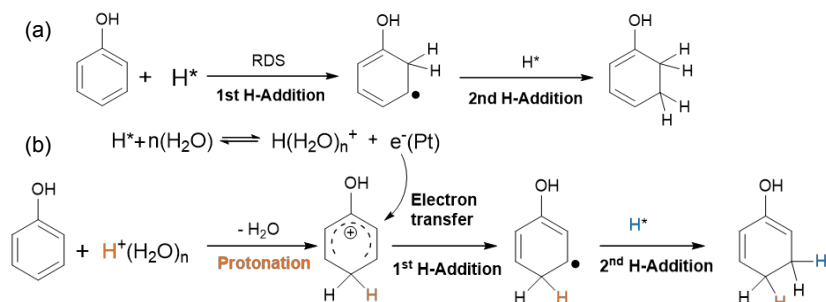


Figure 6. Phenol hydrogenation pathway on Pt sites in the absence (a) or in the presence (b) of hydronium ions.

## Fundamentals of Acid-Base and Redox Reactions on Metal Oxide Catalysts

David Dixon (University of Alabama), Zdenek Dohnálek, Feng Gao, Jian Zhi Hu, Enrique Iglesia (University of California, Berkeley), Bruce Kay, Jun Liu, Roger Rousseau, Huamin Wang, Yong Wang (Washington State University)

A primary goal of these activities is to advance our fundamental understanding of metal oxide-based catalysts and to design new and improved acid and redox-active catalysts. In particular, we seek atomic-level geometric and electronic structure descriptions of active sites and precise determinations of reaction mechanisms at the level of elementary steps. Where fundamental studies of oxide catalysts are limited by current methods and by materials that can be precisely characterized, we are developing new experimental and computational approaches, and synthesizing model catalysts. Our research team contains broad expertise in catalysis and surface science, materials synthesis, and computational chemistry. This breadth allows an integrated experimental/theoretical approach involving state-of-the-art characterization and mechanistic kinetics studies of high surface area model metal oxide catalysts, precise and detailed ultrahigh vacuum studies of single crystals, and the use of cluster and extended surface computational approaches that take advantage of the tractable and known structures of the catalysts used.

### Site-Specific Measurement of Acid-Base Properties on TiO<sub>2</sub>(110)

Zdenek Dohnálek, Vassiliki-Alexandra Glezakou, Igor Lyubinetzky, Roger Rousseau, Gregory Schenter

We have constructed a new combined supersonic molecular beam, scanning tunneling microscopy (STM) instrument and carried out novel measurements that in combination with *ab initio* molecular dynamics (AIMD) yield a detailed kinetic and dynamic description of dissociation and recombination of surface species.

We have utilized this approach for the first time and determined the relative stability of molecularly and dissociatively bound H<sub>2</sub>O on rutile TiO<sub>2</sub>(110) (Figure 7), which leads to the formation of pairs of terminal and bridging hydroxyl species, H<sub>2</sub>O ↔ HO<sub>t</sub> + HO<sub>b</sub>. The energetics of this process has been debated for decades, but it has never been successfully measured. The results of our measurements show the onset of

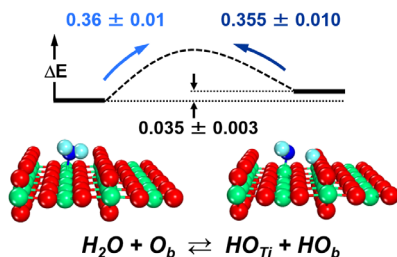


Figure 7. Potential energy surface for H<sub>2</sub>O deprotonation on TiO<sub>2</sub>(110) determined in this study.

H<sub>2</sub>O dissociation at 0.3 eV of H<sub>2</sub>O incident energy, independent of whether the molecules impinge along or across the Ti rows at an incident angle of 60° relative to surface normal. Following the onset, the dissociation probability increases linearly with increasing incident energy. Ensembles of AIMD simulations at several incident energies reproduce the product distribution seen in the STM. Additionally, the theoretical studies show that the dissociation occurs only for the impacts near surface Ti ions with an activation energy of ~ 0.3 eV and that the O-H bond cleavage is accomplished within the time of a single vibration. The AIMD simulations were further used to construct a classical potential energy surface for H<sub>2</sub>O/TiO<sub>2</sub>(110) interactions and execute classical molecular dynamics simulations that closely reproduce the onset and linear energy dependence of the dissociation probabilities. We quantify the deprotonation/protonation barriers of 0.36 eV and find that molecularly bound H<sub>2</sub>O is preferred over the surface-bound hydroxyls by only 0.035 eV. We demonstrate that long-range electrostatic fields emanating from the oxide lead to steering and reorientation of molecules approaching the surface, activating the O-H bonds and inducing deprotonation. The developed methodology for studying metastable reaction intermediates prepared with a high-energy molecular beam in the STM can be readily extended to other systems to clarify a wide range of important bond activation processes.

### Surface Species Following Water Adsorption on Oxidized RuO<sub>2</sub>(110)

*Zdenek Dohnálek, Vassiliki-Alexandra Glezakou, Igor Lyubinetsky, Roger Rousseau*

Identifying and understanding how the extent of surface oxidation affect the adsorption and dissociation of H<sub>2</sub>O on metal oxides is crucial for the understanding the acid-base properties of different surface sites on oxides. Here, by means of high-resolution scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, we show that excess oxygen atoms on the stoichiometric RuO<sub>2</sub>(110) significantly change the clustering, conformation, and deprotonation equilibrium of adsorbed H<sub>2</sub>O. To elucidate effects of oxygen on H<sub>2</sub>O adsorption, we considered two reaction sequences at room temperature: (1) the stoichiometric surface is first exposed to H<sub>2</sub>O followed by reaction with oxygen

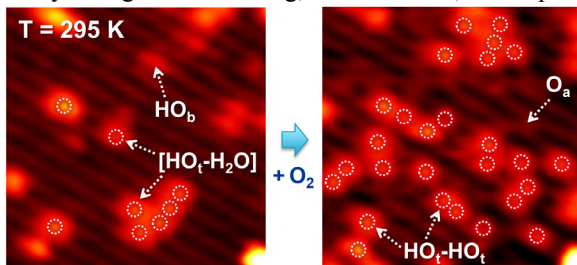


Figure 8. Consecutive STM images of the same area of the RuO<sub>2</sub>(110) dosed with H<sub>2</sub>O at 295 K (left) and subsequently with O<sub>2</sub> (right). The image sequence illustrates the following surface reaction: HO<sub>t</sub>-H<sub>2</sub>O + HO<sub>b</sub> + ½O<sub>2</sub> → 2HO<sub>t</sub>-HO<sub>t</sub> + O<sub>b</sub>.

(Figure 8) and (2) the surface is first in part oxidized then H<sub>2</sub>O is dosed. In both cases, the [OH-OH] complex on Ru rows is the dominant species, showing a significant difference from H<sub>2</sub>O-only adsorption on the stoichiometric surface in which the [OH-H<sub>2</sub>O] species is found to be prevalent. We have also studied surface reactivity at almost full O coverage; there we show that site selectivity of the surface for H adsorption and dissociation of H<sub>2</sub>O is hindered, notwithstanding the increase of the dynamical motion of both species.

## Ceria and Titania Nanoclusters on Supported Graphene as New Model Systems for Catalytic Studies

*Zdenek Dohnálek, Bruce Kay*

We have investigated the growth of CeO<sub>2</sub> and TiO<sub>2</sub> nanoclusters on single-layer graphene/Ru(0001) with a view toward fabricating stable systems for model catalysis studies. Both oxides were deposited by evaporating Ce and Ti metals as a function of oxygen pressure and substrate temperature. Quartz crystal microbalance measurements and AES were used to determine the oxygen pressure for growth of stoichiometric oxides. Depositions performed at 300 K resulted in the formation of nano-sized clusters nucleating on intrinsic defects in the graphene layer, with an average separation between clusters of ~11 nm. The saturation cluster density decreased with increasing substrate growth temperatures from 300 to 650 K. While, the CeO<sub>2</sub> clusters are of (111) type already at 500 K (Figure 9), only a fraction of TiO<sub>2</sub> clusters shows crystallographic order even at 650 K. Thermal stability of the clusters was evaluated with AES after annealing the clusters prepared at 300 K. No chemical reduction of clusters or etching of the graphene film was observed up to ~900 K, although AES indicated significant sintering of clusters. STM studies of annealed clusters prepared at 300 K demonstrated that Smoluchowski ripening is the dominant sintering mechanism up to 800 K. Above 900 K, the clusters undergo reduction accompanied by concomitant oxidation and etching of the graphene. Our studies demonstrate that highly thermally stable CeO<sub>2</sub> and TiO<sub>2</sub> nanoclusters with varying morphologies can be successfully prepared on graphene supports.

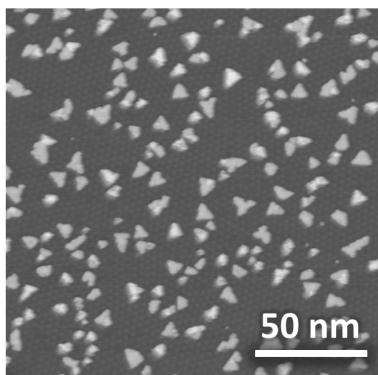


Figure 9. Ceria nanoclusters deposited on Gr on Ru(0001) via reactive deposition of Ce in  $1 \times 10^{-7}$  Torr of O<sub>2</sub> at 500 K.



## Acid-Base Reactions on Shape-Selected Anatase TiO<sub>2</sub> Nanocrystals

Zdenek Dohnálek, Feng Gao, Jian Zhi Hu, Enrique Iglesia, Bruce Kay, Donghai Mei, Roger Rousseau, Huamin Wang, Yong Wang

We continued to study single facet anatase TiO<sub>2</sub> (101) and (001) nanomaterials as model catalysts for alcohol dehydration to better bridge the single crystal and practical high surface area studies. We synthesized and applied two anatase titania model catalysts, with preferential exposure of (101) and (001) facets for isopropanol dehydration, a representative probe reaction for bio-derived alcohol dehydration. A series of microscopic and spectroscopic techniques, including X-ray diffraction, scanning electron microscopy, TEM, NH<sub>3</sub>-TPD, and pyridine-IR, were employed to correlate the structure properties of the model catalysts to their catalytic performance. The Lewis site was found to be the active site, based on active site poisoning titrations using 2,6-di-tert-butyl pyridine titrants. The higher activity for TiO<sub>2</sub>(101) catalyst was ascribed to its higher acid strength and density as compared to TiO<sub>2</sub>(001) (Figure 10). Reaction rate profiles as a function of partial pressure showed a Langmuir-Hinshelwood mechanism for both model catalysts, where the surface dehydration was the rate-limiting step. The kinetic isotope effect measurement indicated that the β C-H bond cleavage governed the reaction rate and the dehydration appeared to follow a concerted E2 elimination pathway. This notion was fully supported by theoretical calculations using density functional theory. This work clearly revealed the nature of active sites, mechanisms, and faceting effects for model anatase catalysts in alcohol dehydration. The results shed lights on designing highly efficient metal oxide catalysts for dehydration process during the conversion of biomass-derived molecules.

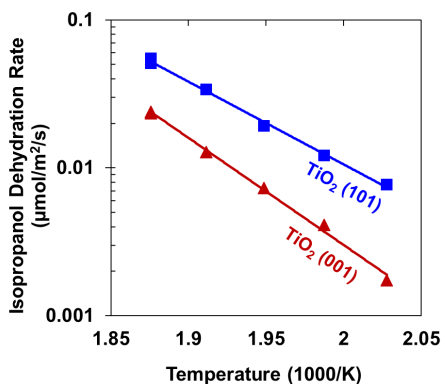


Figure 10. Arrhenius plots of isopropanol dehydration on (■) TiO<sub>2</sub> (101) and (▲) TiO<sub>2</sub> (001) catalysts. 1 bar, 2 kPa isopropanol, 220–260 °C, and GHSV = 2 L•min<sup>-1</sup>•g<sup>-1</sup><sub>cat</sub>.

## Formation of Gas Phase Radicals in Surface Reactions: Deoxygenation of Phenylmethanol on Rutile TiO<sub>2</sub>(110)

Zdenek Dohnálek, Vassiliki-Alexandra Glezakou, Bruce Kay, Roger Rousseau

The role of radicals in the reaction mechanisms leading to functionalized aromatics has been extensively argued. The involvement of radical species has been firmly established for a small number of simple reactions on high surface area oxide catalysts, such as oxidative coupling of CH<sub>4</sub> and selective oxidation of

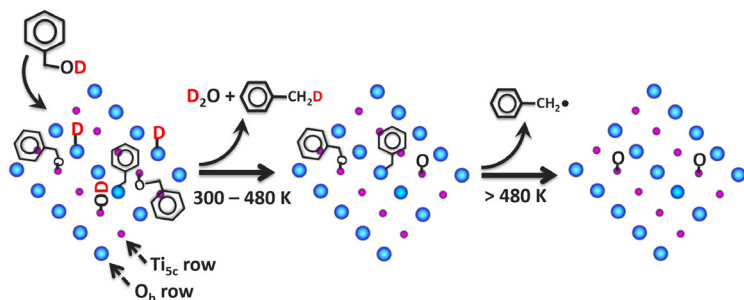


Figure 11. Proposed reaction pathways for the conversion of phenolmethanol on TiO<sub>2</sub>(110).

propylene. As a part of our ongoing studies of alcohol and diol deoxygenation, we have focused on the reaction pathways of simple lignin-derived aromatic alcohols, *i.e.*, phenol, phenylmethanol, and 2-phenylethanol, on rutile TiO<sub>2</sub>(110), using a combination of molecular beam dosing and TPD. For phenylmethanol, the coverage dependent TPD data show that about 40 percent of molecules adsorbed on the surface at a saturation coverage are converted to reaction products indicating that the reactions proceed on regular five-fold coordinated Ti sites. This is in contrast to aliphatic alcohols where the reactions are shown to proceed exclusively on bridging oxygen vacancy defect sites. The studies of OD-labelled phenylmethanol demonstrate that a fraction of OD hydrogen is transferred to the benzyl group to form toluene that desorbs between 300 K and 480 K (Figure 11). In the competing reaction, the OD hydrogen is converted to H<sub>2</sub>O at ~350 K. Once the OD hydrogen is depleted above 480 K, the remaining phenylmethoxy surface species dissociate yielding benzyl radicals in the gas phase (Figure 11). Combined, these results show that the conversion of phenylmethanol on TiO<sub>2</sub>(110) proceeds via a unique chemistry. In contrast, both phenol and 2-phenylethanol exhibit expected surface chemistry analogous to that of aliphatic alcohols. These findings reveal for the first time the formation of free radical species from the interaction of phenylmethanol with TiO<sub>2</sub>(110) and demonstrate a new direct mechanism for deoxygenation of lignin-derived benzylic alcohols to aromatics on TiO<sub>2</sub>.

## 1,2-Ethanediol and 1,3-Propanediol Conversions over (MO<sub>3</sub>)<sub>3</sub> (M=Mo, W) Nanoclusters

*David Dixon, Zdenek Dohnálek, Bruce Kay, Roger Rousseau*

The dehydration and dehydrogenation reactions of one and two 1,2-ethanediol and 1,3-propanediol molecules on (MO<sub>3</sub>)<sub>3</sub> (M=Mo, W) nanoclusters have been studied computationally using density functional and coupled cluster (CCSD(T)) theory (Figure 12). The reactions are initiated by formation of a Lewis acid-base

complex with an additional hydrogen bond. Dehydration is the dominant reaction proceeding via a metal bisdiolate. Acetaldehyde, the major product for 1,2-ethanediol, is produced by  $\alpha$ -hydrogen transfer from one  $\text{CH}_2$  group to the other. For 1,3-propanediol, the C-C bond breaking pathways to produce  $\text{C}_2\text{H}_4$  and  $\text{HCH}=\text{O}$  simultaneously and proton transfer to generate propylene oxide have comparable barrier energies. The barrier to produce propanal from the propylene oxide complex is less than that for epoxide release from the cluster. On

the  $\text{Mo}_3\text{O}_9$  cluster, a redox reaction channel for 1,2-ethanediol to break the C-C bond to form two formaldehyde molecules and then to produce  $\text{C}_2\text{H}_4$  is slightly more favorable than the formation of acetaldehyde. For  $\text{W}^{\text{VI}}$ , the energy barrier for the reduction pathway is larger due to the lower reducibility of  $\text{W}_3\text{O}_9$ . Similar reduction on  $\text{Mo}^{\text{VI}}$  for 1,3-propanediol to form propene is not a favorable pathway compared to the other pathways as additional C-H bond breaking is required in addition to breaking a C-C bond. The dehydration and dehydrogenation activation energies for the selected glycols are larger than the reactions of ethanol and 1-propanol on the same clusters. The CCSD(T) method is required as density functional theory (DFT) with the M06 and B3LYP functionals does not predict quantitative energies on the potential energy surface. The M06 functional performs better than does the B3LYP functional.

## Benchmark Calculations of the Energetic Properties of Transition Metal Compounds

*David Dixon*

The heats of formation and the normalized clustering energies (NCEs) for the group 4 and group 6 transition metal oxide trimers and tetramers have been calculated by the Feller-Peterson-Dixon method. New and improved heats of formation for  $(\text{CrO}_3)_n$  clusters were obtained using PW91 orbitals instead of Hartree-Fock orbitals. Diffuse functions are necessary to predict accurate heats of formation. The fluoride affinities (FAs) are calculated with the CCSD(T)

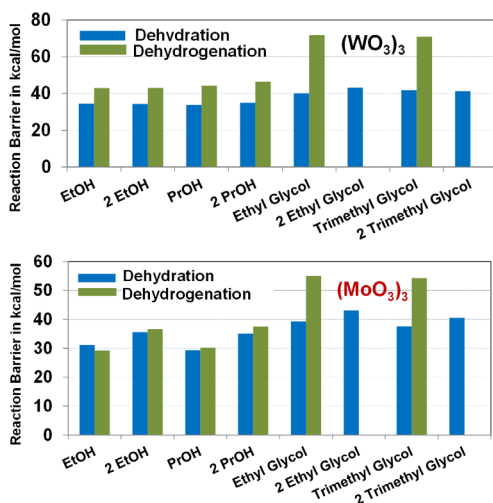


Figure 12. Lowest maximum CCSD(T) barriers in kcal/mol for the conversion of ethanol, 1-propanol, ethylene glycol, and trimethylene glycol on  $\text{M}_3\text{O}_9$  ( $\text{M} = \text{Mo}, \text{W}$ ) clusters at 298 K.

method. The relative energies (REs) of different isomers, NCEs, electron affinities (EAs), and FAs of  $(\text{MO}_2)_n$  ( $M = \text{Ti}, \text{Zr}, \text{Hf}, n = 1-4$ ) and  $(\text{MO}_3)_n$  ( $M = \text{Cr}, \text{Mo}, \text{W}, n = 1-3$ ) clusters have been benchmarked with 55 exchange-correlation density functional theory (DFT) functionals including both pure

and hybrid types (Figure 13). The absolute errors of the DFT results are mostly less than  $\pm 10$  kcal/mol for the NCEs and the EAs, and less than  $\pm 15$  kcal/mol for the FAs. Hybrid functionals usually perform better than the pure functionals for the REs and NCEs. The performance of the two types of functionals in predicting EAs and FAs is comparable. The B1B95 and PBE1PBE functionals provide reliable energetic properties for most isomers. Long-range corrected pure functionals usually give poor FAs. The standard deviation of the absolute error is always close to the mean errors and the probability distributions of the DFT errors are often not Gaussian (normal). The breadth of the distribution of errors and the maximum probability are dependent on the energy property and the isomer. In addition, the heats of formation and bond dissociation energies for a benchmark set of first row transition metal diatomics have been predicted using the Feller-Peterson-Dixon approach. A number of the experimental values were re-evaluated and found to have issues. This work showed that the Feller-Peterson-Dixon approach based on CCSD(T) provides good predictions for the heats of formation of transition metal compounds in contrast to previous reports.

## Larger Scale Molecular Simulations Accessing *Operando* Morphology and Reactivity of Catalytic Systems

*Vassiliki-Alexandra Glezakou, Roger Rousseau*

Modern electron structure theory coupled with molecular dynamics allows one to examine the structure and dynamics of complex reactive systems at elevated temperatures. These simulations can both rationalize the way catalysts work, but also allow for unique discoveries that may arise spontaneously out of the simulations. Using advances simulations consisting of hundreds of atoms for millions of configurations, several new transient phenomena have been discovered. For

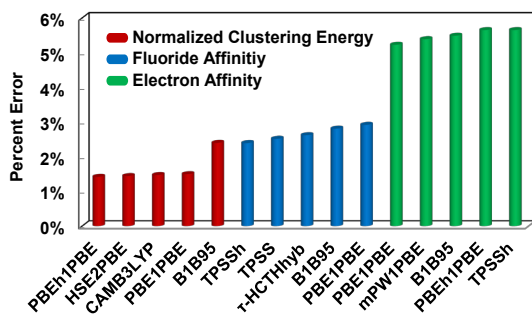
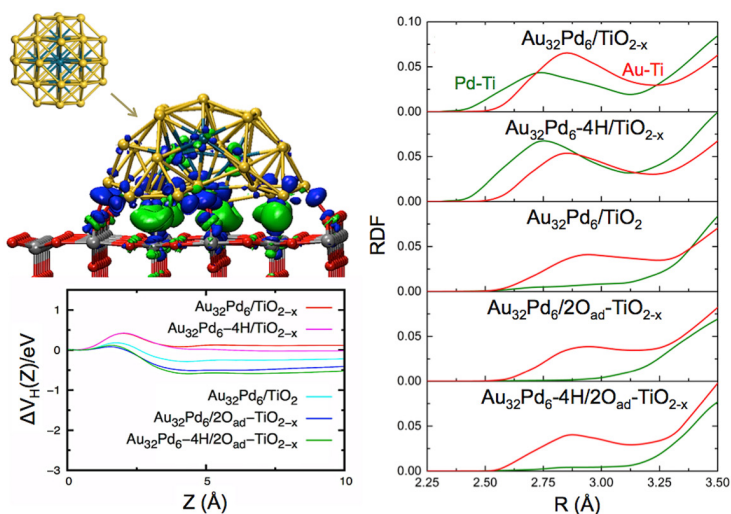


Figure 13. Errors in the best functionals for each property in comparison to the Feller-Peterson-Dixon values.



**Figure 14. Redox effects on the structure and morphology of supported AuPd nanoalloys.**

instance, simulations have that  $Au_{20}$  on a rutile  $TiO_2$  exhibits liquid-like morphology upon CO adsorption, due to charge transfer from the support during catalytic conversion of CO to  $CO_2$ . Likewise, the reactivity and dynamics of Au nanoparticles on both titania and ceria reveal the dynamic formation of single Au atoms forming  $Au-CO^+$  intermediates before  $CO_2$  is formed. The Au atom is re-integrated with the Au nanoparticle to fully complete the catalytic cycle. Similar studies have shown that modulations of the redox state of both the support and nanoparticles can have a dramatic impact on the accessibility of Pd atoms in mixed AuPd nanoalloys (Figure 14).

## Conversion of Ethanol to 1,3-butadiene over Na Doped $Zn_xZr_yO_z$ Mixed Metal Oxides

*Yong Wang*

In this effort, we have been focusing on the effects of surface acidity on the cascade ethanol-to-isobutene conversion using  $Zn_xZr_yO_z$  catalysts. The ethanol-to-isobutene reaction was found to be limited by the secondary reaction of the key intermediate, acetone, namely the acetone-to-isobutene reaction. Although catalysts with coexisting Brønsted acidity could catalyze the rate-limiting acetone-to-isobutene reaction, the presence of Brønsted acidity is also detrimental. First, secondary isobutene isomerization is favored, producing a mixture of butene isomers. Second, undesired polymerization and coke formation prevail, leading to rapid catalyst deactivation. Most importantly, both steady-state and kinetic reaction studies as well as Fourier transform infrared spectroscopy (FTIR) analysis

of adsorbed acetone-d<sub>6</sub> and D<sub>2</sub>O unambiguously showed that a highly active and selective nature of balanced Lewis acid-base pairs was masked by the coexisting Brønsted acidity in the aldolization and self-deoxygenation of acetone to isobutene. As a result, Zn<sub>x</sub>Zr<sub>y</sub>O<sub>z</sub> catalysts with only Lewis acid-base pairs were discovered, on which nearly a theoretical selectivity to isobutene (~88.9 percent) was successfully achieved, which has never been reported before. Moreover, the absence of Brønsted acidity in such Zn<sub>x</sub>Zr<sub>y</sub>O<sub>z</sub> catalysts also eliminates the side isobutene isomerization and undesired polymerization/coke reactions, resulting in the production of high purity isobutene with significantly improved catalyst stability (< 2 percent activity loss after 200 h time-on-stream). Our integrated experimental and theoretical work suggested that Lewis acid-base pairs on a ZrO<sub>2</sub> catalyst can catalyze the acetone aldolization reaction to form mesityl oxide. The formed mesityl oxide strongly adsorbs and blocks the Lewis acid-base active site, resulting in the dominant acetone decomposition (Figure 15, red highlighted pathway), as well as other possible side reactions, such as polymerization. However, adding ZnO significantly modifies the properties of surface Lewis acid-base pairs. As a result, the cascade acetone aldolization and self-deoxygenation reactions are significantly accelerated, leading to the highly active and stable Zn<sub>x</sub>Zr<sub>y</sub>O<sub>z</sub> catalyst for both acetone-to-isobutene and ethanol-to-isobutene reactions.

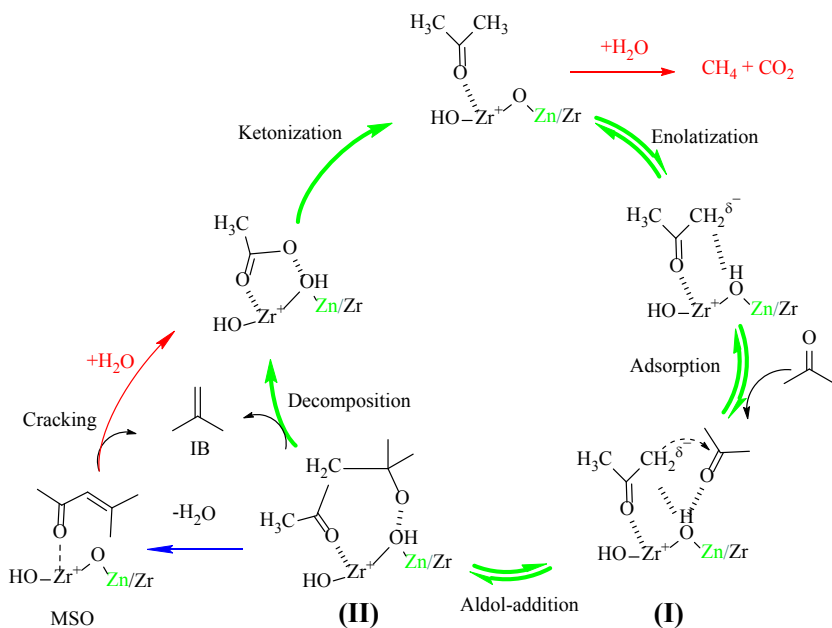


Figure 15. Proposed acetone-to-isobutene reaction mechanism over Zn<sub>x</sub>Zr<sub>y</sub>O<sub>z</sub> catalyst.

## Thrust 2: Reductive Conversion of CO<sub>2</sub>

This thrust focuses on mechanistic understanding of the catalytic reduction of CO<sub>2</sub> to energy carriers (*e.g.*, CH<sub>4</sub>, CH<sub>3</sub>OH, formaldehyde, and formic acid, as well as C<sub>2</sub> and fuels with higher molecular weight). The bifunctional sites for CO<sub>2</sub> reduction in enzymes guide the synthesis of sites in heterogeneous and homogeneous catalysts. Mechanistic aspects of the chemistries observed in different environments are compared to gain a molecular-level understanding of the fundamental reaction steps, identify the reaction intermediates and their stability, and determine the role that reaction conditions can have on the energetics and kinetics.

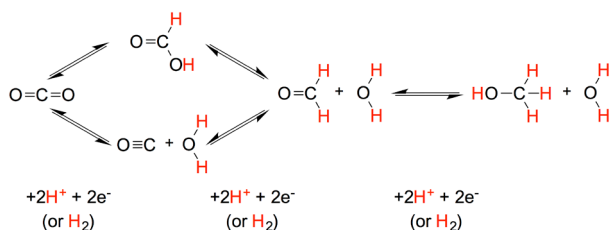
The unifying theme is the catalytic activity of single metal centers in the presence of second functionality on both heterogeneous and homogeneous catalysts aimed at comparing and contrasting thermal CO<sub>2</sub> reduction in homogeneous and heterogeneous environments.

### Designing Molecular Catalysts Using an Energy-Based Approach

*Aaron Appel, R. Morris Bullock, John Linehan, Eric Wiedner*

This activity is focused on understanding and controlling the reactivity of potential catalysts for the reduction of CO<sub>2</sub> to fuels, such as CH<sub>3</sub>OH (Figure 16). With this goal in mind, the conversion is divided into steps consisting of reduction by one equivalent of H<sub>2</sub>. For each step, we aim to control the thermodynamic driving force as well as kinetic parameters, such that we can design catalyst systems with unprecedented performance for critical transformations.

Many different precious metal complexes have been demonstrated to be active for hydrogenation reactions; however, the number of non-precious metal complexes for the hydrogenation of CO<sub>2</sub> is far more limited. One of our goals is to use our focus on thermodynamic and kinetic parameters to enable the use of non-precious metal complexes to perform a variety of energy storage reactions (Figure 17). The conversion of CO<sub>2</sub> to formate is an example transformation, which is

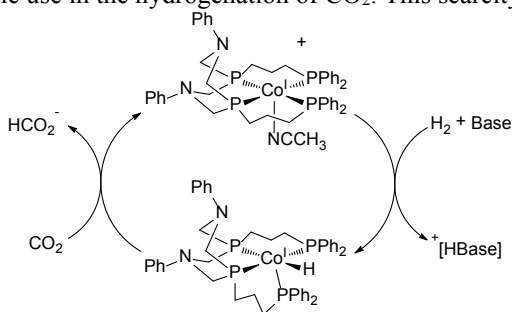


**Figure 16.** Production of fuels requires designing catalysts for the individual steps, illustrated here for converting CO<sub>2</sub> to CH<sub>3</sub>OH.

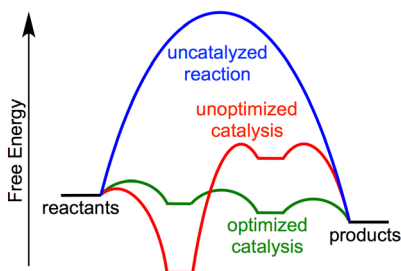
dependent on the transfer of  $\text{H}^-$  from the metal complex to  $\text{CO}_2$ . The favorability of hydride transfer can be predicted based on the hydricity of the metal-hydride complex relative to the hydricity of formate, and therefore can serve as a design parameter for the catalytic conversion of  $\text{CO}_2$  to formate.

We have previously demonstrated that cobalt hydride complexes are active catalysts for the hydrogenation of  $\text{CO}_2$  to formate but require the use of a very strong organic base, such as Verkade's superbases to regenerate the cobalt hydride complexes. Using DFT calculations previously reported from our laboratory, we predicted that a cobalt complex containing a tetradentate phosphine ligand would be a catalyst for  $\text{CO}_2$  hydrogenation when using a much weaker organic base (Figure 18). Experimental studies on the cobalt catalyst confirmed the computational prediction: this catalyst afforded a turnover frequency of  $150 \text{ h}^{-1}$  for  $\text{CO}_2$  hydrogenation at room temperature and low pressure (1.7 atm) using a guanidine base that is 7  $\text{pK}_a$  units weaker than Verkade's superbases. The unusual geometric constraints imparted by the tetradentate phosphine ligand were critical for attenuating the cobalt hydride bond strengths, thereby enabling catalysis using a weaker base.

While heterogeneous catalysts based on copper and copper oxide are quite effective for the reduction of  $\text{CO}_2$ , homogeneous complexes of copper have had very little use in the hydrogenation of  $\text{CO}_2$ . This scarcity of copper complexes stems



**Figure 18.** A cobalt tetraphosphine catalyst was developed to hydrogenate  $\text{CO}_2$  to formate using weaker organic bases than previous cobalt hydride complexes.



**Figure 17.** Catalytic performance can be improved by removing energy mismatches between catalytic intermediates, which are quantified using thermochemical studies.

from the inability to regenerate the active hydride complexes using mild reagents and conditions. To understand the potential for regeneration of copper hydride complexes using  $\text{H}_2$ , we have isolated and characterized a series of copper hydrides starting from a single



complex, and we have determined the thermodynamic hydricity of one of the isolated hydrides (Figure 19). The resulting copper hydride complex can be generated from hydrogen and a base, and the hydride is sufficiently hydridic to reduce CO<sub>2</sub> to formate.

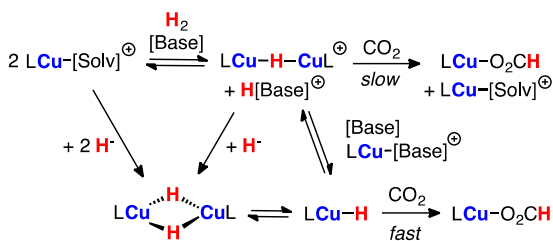


Figure 19. A catalyst system based on copper for the hydrogenation of CO<sub>2</sub> has been designed starting from copper-solvento complex (L = CH<sub>3</sub>C(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>).

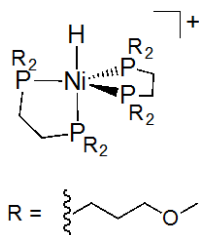


Figure 20. By controlling the free energy for H<sup>-</sup> transfer, a catalyst system was designed for hydrogenation of CO<sub>2</sub> in water.

In organic solvents, nickel hydride complexes are not catalytically active for the hydrogenation of CO<sub>2</sub>, essentially because the hydricities of these complexes are inadequate to transfer H<sup>-</sup> to CO<sub>2</sub>. However, the choice of condensed phase has now been shown to have a huge impact on the reactivity. Specifically, while nickel hydride complexes are thermodynamically incapable of transferring H<sup>-</sup> to CO<sub>2</sub> in organic solvents, the same complexes undergo favorable H<sup>-</sup> transfer in water. Based on this impact, a new catalyst system was designed (Figure 20), which is catalytically active for hydrogenation of CO<sub>2</sub> in water.

For many catalytic reactions, including hydrogenation of C=O bonds, controlling the heterolytic cleavage of the H-H bond of dihydrogen is critically important. We determined how the rate of reversible heterolytic cleavage of H<sub>2</sub> can be controlled, spanning four orders of magnitude at 25 °C, from 2.1 × 10<sup>3</sup> s<sup>-1</sup> to ≥10<sup>7</sup> s<sup>-1</sup> (Figure 21). Bifunctional Mo complexes, [CpMo(CO)(κ<sup>3</sup>-P<sub>2</sub>N<sub>2</sub>)]<sup>+</sup> (P<sub>2</sub>N<sub>2</sub> = 1,5-diaza-3,7-diphospha-cyclo-octane diphosphine ligand with alkyl/aryl groups

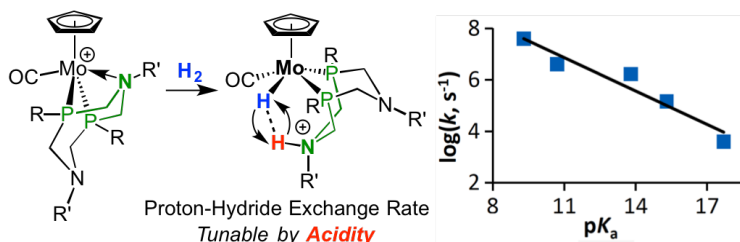


Figure 21. Splitting of H<sub>2</sub> in multifunctional complexes resulted in formation an amine protonated metal hydride, in which the exchange of the proton and hydride was observed to occur at high rates that depend upon the acidity of the protonated pendant amine.

on N and P), were developed for heterolytic cleavage of H<sub>2</sub> into a proton and a hydride. The heterolytic cleavage of the H-H bond is enabled by the basic amine in the second coordination sphere, giving Mo hydride complexes bearing protonated amines, [CpMo(H)(CO)(P<sub>2</sub>N<sub>2</sub>H)]<sup>+</sup>. Variable temperature <sup>1</sup>H, <sup>15</sup>N, and 2D <sup>1</sup>H-<sup>1</sup>H Rotating frame Overhauser Effect NMR spectra indicated rapid exchange of the proton and hydride. The pK<sub>a</sub> values determined in acetonitrile range from 9.3 to 17.7 and show a linear correlation with the logarithm of the exchange rates. The proton-hydride exchange appears to occur by formation of a molybdenum dihydride or dihydrogen complex resulting from proton transfer from the pendant amine to the metal hydride. The exchange dynamics are controlled by the relative acidity of the [CpMo(H)(CO)(P<sub>2</sub>N<sub>2</sub>H)]<sup>+</sup> and [CpMo(H<sub>2</sub>)(CO)(P<sub>2</sub>N<sub>2</sub>)]<sup>+</sup> isomers, providing a design principle for controlling heterolytic cleavage of H<sub>2</sub>.

## Thermodynamic Linear Scaling Relationships to Optimize Catalytic Reactions in Molecular Complexes

*Tom Autrey, Bojana Ginovska, Abhi Karkamkar, Gregory Schenter*

We have used a combination of experimental and computational methods to determine the thermodynamic parameters of the key intermediates leading to the catalytic reduction of CO<sub>2</sub> to formate. Our operating hypothesis is that a balance in the energy landscape minimizes energy sinks in the catalytic cycle leading to optimized rates. This section illustrates how concepts successfully utilized in heterogeneous catalysis can be used to test this hypothesis. Given the linear free energy scaling relationships established between H<sub>2</sub> addition, proton abstraction, and hydride transfer in previous work, we should be able to predict the best homogeneous catalysts. The volcano plot shown in Figure 22 predicts that the cobalt P<sub>2</sub> complex using dmpe as the ligand (green square) should be the best catalyst in the series given the energy balance. The free energy driving force for (1) dihydride formation (orange line), (2) proton abstraction from the dihydride to form the cobalt hydride (grey line) and (3) hydride transfer to CO<sub>2</sub> to form formate (blue line) is shown as a plot of ΔG<sub>pds</sub> vs. ΔG<sub>rrs,3</sub>, confirming the hypothesis that

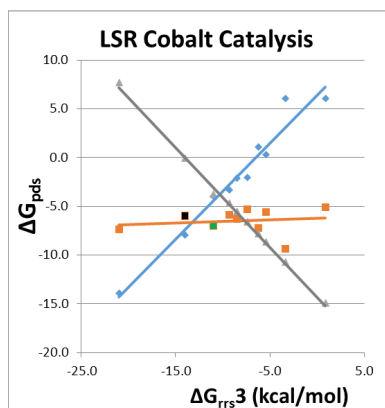


Figure 22. Linear scaling relationships predict that Co(dmpe)<sub>2</sub> at the top of the volcano plot should be one of the most efficient catalysts in a series of cobalt P<sub>2</sub> complexes in agreement with experimental rate comparisons.

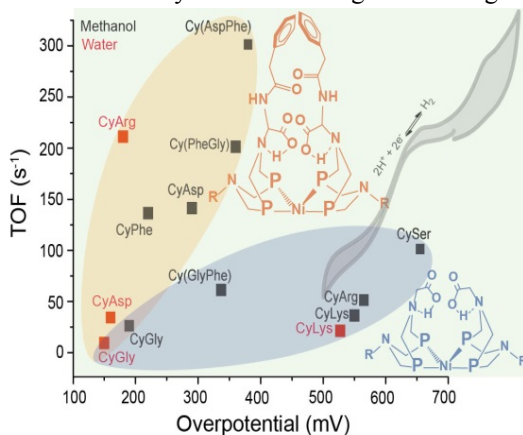
balance thermodynamics play a crucial role in optimizing rates of catalytic reactions.

## Modulating Catalysts with an Enzyme-like Outer Coordination Sphere

*Bojana Ginovska, John Linehan, Gregory Schenter, Wendy Shaw*

This research focuses on introducing the principles in enzymes that result in superior catalytic performance into molecular catalysts. The protein scaffold surrounding the active site in an enzyme has been demonstrated to contribute significantly to the performance of the enzyme. Unlocking this contribution is challenging in enzymes because of the complex interplay between features. Ultimately, we will have all of these features in molecular complexes. To understand how each of them works, and what contribution they have, we need to understand each of them individually. We have been approaching this by introducing amino acids and peptides into molecular complexes to capture the features of enzymes into molecular catalysts and probe how each function contributes to catalysis. We are focused on three aspects of the outer coordination sphere: (1) the unique environment created by the functional groups around the active site; (2) the transfer of substrates such as protons into and out of the active site; (3) controlled structural movements that dictate activity. Each of these goals is being pursued within the context of our research program.

In the past year, we have made several key advancements in our understanding of the outer coordination sphere. We have achieved an electrochemically reversible room temperature catalyst for  $H_2$  oxidation/production. This was achieved by introducing key attributes into the outer coordination sphere of a molecular complex. First, the first and second coordination sphere of the molecular complex,  $Ni(P^{Cy_2N^{amino}}$



**Figure 23.** A series of amino acid and dipeptide-substituted complexes demonstrates the sensitivity of the performance to both the presence of the COOH group, and the side chain interactions. The data provide design principles for molecular complexes that are inspired by enzymes.

$\text{acid}_2$ ), were thermodynamically matched, based on extensive work done within the CME Energy Frontier Research Center. However, this alone was not enough to achieve reversibility. Features in the outer coordination sphere were essential to lower the overpotential, while maintaining fast rates (Figure 23). Specifically, a COOH group enabled fast proton transport to and from the active site, enabling proton-coupled electron transfer (PCET). Further, interactions between the side chains altered the active site structure to facilitate  $\text{H}_2$  addition and electron transfer. We further investigated a series of complexes with different side chains and with COOH or amide groups. We found the amides were able to transfer protons, but those complexes did not result in reversible complexes, even though they were faster than those with COOH groups. Of interest is the complexes in water are all faster and more efficient than in methanol.

We also worked with collaborators to understand the implications of binding these complexes to surfaces. This information will be essential as these complexes are transferred to more practical applications in fuel cells. In one study, we demonstrated that the complex with phenylalanine amino acids that was reversible in methanol, but not soluble in water in solution, was functional in water on the surface. In a second study, with the amino acid arginine attached to the complex, putting the complex onto carbon nanotubes and then putting this into a fuel cell shows performance within an order of magnitude of a fully Pt fuel cell. A scientific outcome of this study was that that relative performance of the glycine-substituted complex and the arginine-substituted complex were the same as in solution. This implies that binding these complexes to solution did not alter the active site, one of the first demonstrations of non-intrusive binding.

Further, we have been developing synthetic strategies to attach full peptides to any type of ligand, including a phosphine protection strategy and click chemistry to attach the ligand to nearly any point in a peptide that is appropriately substituted. These approaches should provide significant flexibility to use these ligands with a multitude of peptides so we can evaluate the impact of the outer coordination sphere with relative ease by including systematic changes.

## High Surface Area Model Catalysts: Controlling Selectivity through Mechanistic Understanding

*Janos Szanyi*

The catalytic reduction of  $\text{CO}_2$  requires bifunctional catalysts as both  $\text{CO}_2$  and  $\text{H}_2$  need to be activated before their reaction. We have shown that in oxide-supported metal catalysts, the metal component dissociated  $\text{H}_2$ , while the oxide support activated  $\text{CO}_2$  by binding it as bicarbonate. The focus of our work has been

understanding what governs product selectivity in CO<sub>2</sub> hydrogenation over Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. To this end, we have conducted SSITKA/*operando* FTIR measurements on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts to identify the nature and the kinetics of surface species present on the catalysts under steady-state conditions.

We found (Table 1) that at low temperature (533 K), the real mean surface residence time of the intermediate leading to CO formation was shorter (107 sec) than that of the intermediate leading to CH<sub>4</sub> production (134 sec). However, at 573 K, the real mean surface residence time of the intermediate leading to CO formation was longer (55 sec) than that leading to CH<sub>4</sub> formation (41 sec). Interestingly, the activation energies of CO and CH<sub>4</sub> formation estimated from the real mean surface residence times were identical to those determined from the IR intensities of alumina-bound bidentate formates and Pd-adsorbed CO, respectively. These results let us conclude that the key intermediate in CO formation is formate, while in CH<sub>4</sub> formation it is strongly adsorbed CO. The selectivities toward CO and CH<sub>4</sub> productions were governed by the balance between the reaction rate of adsorbed formate reduction to CO, and the rate of strongly held CO hydrogenation to CH<sub>4</sub>. At low reaction temperatures, the methanation rate is low, while the formate hydrogenation rate is relatively high. Therefore, the Pd particles are populated with both strongly and weakly adsorbed CO, and most of the weakly held CO desorbed into the gas phase. This results in a high selectivity toward CO, and low selectivity toward CH<sub>4</sub> formations. In contrast, at high temperatures where the methanation rate is higher than the formate reduction rate, most of the CO produced in the formate reduction will adsorb strongly on the Pd particles, and it will further be reduced to CH<sub>4</sub>. Under these conditions, the pool of weakly adsorbed CO is only partially full, or empty. This results in high CH<sub>4</sub> formation, but low CO formation selectivities.

Temp.	$\tau_{0\_ICH}$	$\tau_{0\_ICO}$	$E_{CH_4}$	$E_{CO}$	$E_{*CO_s}$	$E_{HCOO^*}$
K	s		kJ mol <sup>-1</sup>			
533	134	107				
543	92	85	75	53	73	52
563	49	57				
573	41	55				

Table 1. Real mean surface residence times for ICH ( $\bar{\tau}_{0\_ICH}$ ) and ICO ( $\bar{\tau}_{0\_ICO}$ ), and activation energies for CH<sub>4</sub> ( $E_{CH_4}$ ) and CO ( $E_{CO}$ ) formation and adsorbed \*CO<sub>s</sub> ( $E_{*CO_s}$ ) and HCOO\* ( $E_{HCOO^*}$ ) conversions in CO<sub>2</sub> reduction at 533-573 K. Uncertainties in activation energies are  $\pm 2$  kJ mol<sup>-1</sup>.

To test this hypothesis, we prepared three Pd/Al<sub>2</sub>O<sub>3</sub> catalysts with Pd loadings of 2.5, 5, and 10 wt%, with very similar particle size distribution (estimated from TEM analysis). The changes in CO and CH<sub>4</sub> selectivities at comparable CO<sub>2</sub> conversion levels as a function of metal loadings are displayed in Figure 24. The catalyst with the lowest Pd loading exhibited the highest CO selectivity, while the catalyst with the highest metal content showed the highest CH<sub>4</sub> selectivity. The pool of the key intermediate to adsorbed CO formation (formate) is full in all three cases. However, the pool of sites that can hold adsorbed CO (sites on Pd clusters) varies strongly with metal loading. At low Pd loading, the pool of adsorbed CO is small, so lot of the CO from the reduction of adsorbed formates ends up at weak adsorption sites, and desorbs into the gas phase (high CO selectivity). On the other hand, at high metal loading, due to the large pool of adsorption sites on Pd clusters, most of the CO from formate reduction is bound to strong adsorption sites and can be further reduced to CH<sub>4</sub>. As a result, this catalyst produces CH<sub>4</sub> with high selectivity.

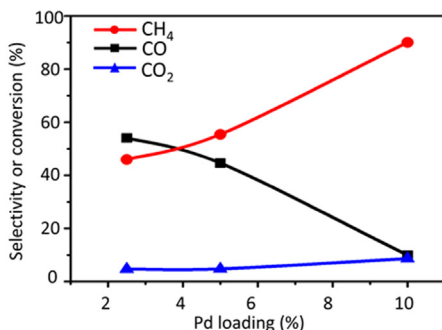


Figure 24. Controlling selectivities in CO<sub>2</sub> reduction by tailor-made catalysts through mechanistic understanding: CH<sub>4</sub> and CO selectivities and CO<sub>2</sub> conversion as a function of Pd loading at 573 K.

## Recognitions and Honors

**PNNL Hydrogen Catalysis Team:**  
*R. Morris Bullock, Aaron Appel, Monte Helm, Molly O'Hagan, Eric Wiedner, Wendy Shaw, Simone Rauei*

- ▶ ACS Catalysis Lectureship for the Advancement of Catalytic Science, 2015

**Aaron Appel**

- ▶ Pathways to Excellence Award, PNNL, April, 2016
- ▶ Invited panelist, Basic Research Needs: Catalysis Science to Transform Energy Technologies workshop, 2017



**Thomas Autrey**

- ▶ Affiliate Professor of Chemistry University of Hawaii, 2016 – present



**R. Morris Bullock**

- ▶ AAAS Fellow, 2016
- ▶ Advisory Board, *Chemical Society Reviews*, 2016 – present
- ▶ Panel lead, Basic Research Needs: Catalysis Science to



Transform Energy Technologies workshop, 2017

**Miroslaw Derewinski**

- ▶ Full Professor, Polish Academy of Sciences, 2014



**Zdenek Dohnálek**

- ▶ Guest Editor, Special Issues of *Surface Science* “Insights into Surface Phenomena: In Honor of John T. Yates Jr.”
- ▶ Associate Editor, *Progress in Surface Science*, 2016 – present
- ▶ Joint Appontment, Voiland School of Chemical Engineering and Bioengineering, Washington State University, 2016
- ▶ Fellow, American Vacuum Society, 2017



**Feng Gao**

- ▶ Recognition of Innovation by DOE Office of Energy Efficiency and Renewable Energy, 2015



### David Heldebrant

- ▶ Associate Editor, *RSC Advances*, 2015 – present
- ▶ Joint Appointment, Voiland School of Chemical Engineering and Bioengineering, Washington State University, 2015 – present



### Johannes Lercher

- ▶ R. B. Anderson Award, Canadian Catalysis Society, 2015
- ▶ Member of European Academy of Sciences, 2016
- ▶ Eni Award, New Frontiers in Hydrocarbons-Downstream Prize, 2016
- ▶ David Trim and Noel Cant Lectureship, Catalysis Society of Australia, 2016
- ▶ Co-chair, Basic Research Needs: Catalysis Science to Transform Energy Technologies workshop, 2017



### Jian Zhi Hu

- ▶ R&D100 Award on Pressurized Magic Angle Spinning Technology for NMR Spectroscopy, 2015



### Bruce Kay

- ▶ Adjunct Professor, Department of Chemistry, University of Alabama, 2014 – present
- ▶ Program Chair, 2016, and Division Chair, 2017, American Vacuum Society Surface Science Division



### Roger Rousseau

- ▶ Exceptional Scientific Achievement Award, PNNL, 2016
- ▶ Invited panelist, Basic Research Needs: Catalysis Science to Transform Energy Technologies workshop, 2017



### Gregory Kimmel

- ▶ Fellow, American Vacuum Society, 2016



### Wendy Shaw

- ▶ Editorial Board, *Biophysical Society Journal*
- ▶ Pathways to Excellence Award, PNNL, April 2015

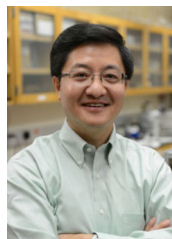




- ▶ Invited panelist, Basic Research Needs: Catalysis Science to Transform Energy Technologies workshop, 2017

*Yong Wang*

- ▶ Invited panelist, Basic Research Needs: Catalysis Science to Transform Energy Technologies workshop, 2017



## Publications and Presentations

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

- ▶ Total of 228 peer-reviewed publication (January 2014 – June 2017)
  - ▶ *Nature* (1), *Nature Energy* (1), *Nature Communications* (5), *Proceedings of the National Academy of Sciences* (PNAS) (2), *Journal of the American Chemical Society* (JACS) (16), *Angewandte Chemie International Edition* (11).
  - ▶ 9 review articles (*Chemical Reviews*, *Accounts of Chemical Research*, *Chemical Society Reviews*, and others).
  - ▶ 3 book chapters.
- ▶ 213 invited lectures at conferences, universities, and other professional venues.
- ▶ 10 symposia organized at scientific meetings.

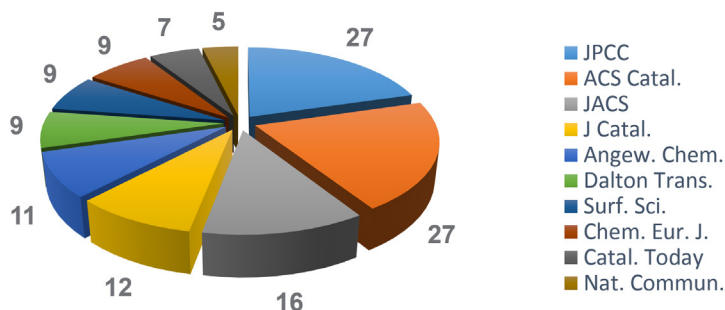


Figure 25. 132 publications (out of 228) in the journals with the highest occurrence (January 2014 – June 2017).

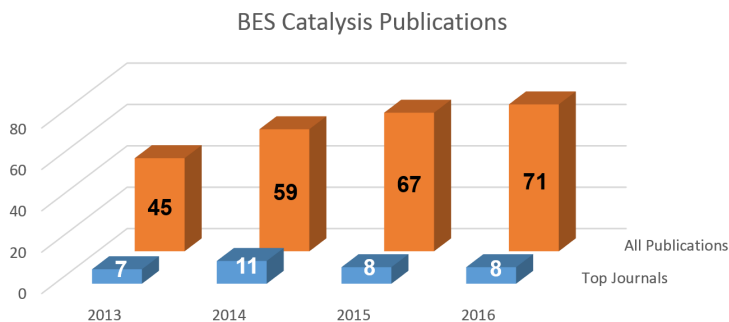
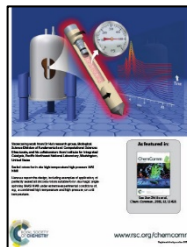
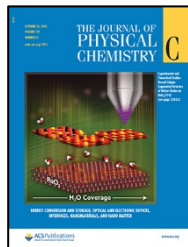
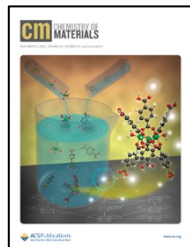
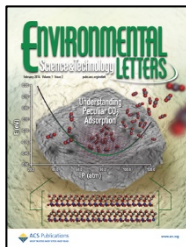
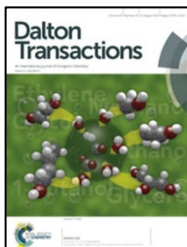
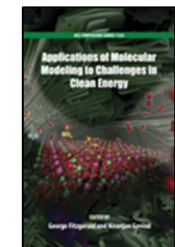
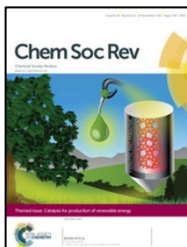
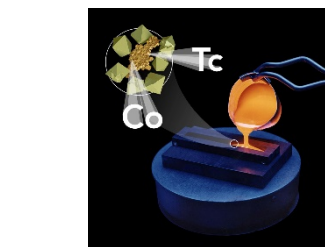
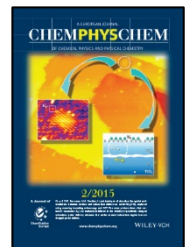
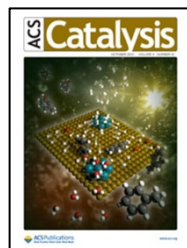
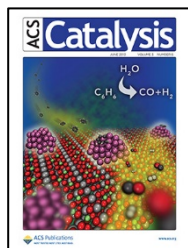
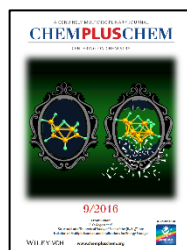
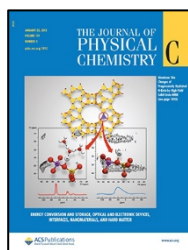
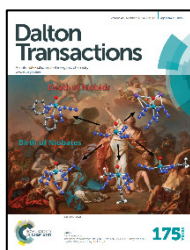
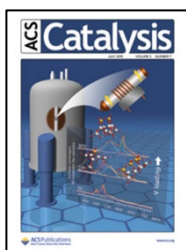


Figure 26. Total number of publications (orange) and publications in top journals (blue, includes *Science*, *Nature* journals, *PNAS*, *Angewandte Chemie International Edition*, and *JACS*).

# Journal Covers (January 2014 – June 2017)



## ASSOCIATED BASIC ENERGY SCIENCES PROGRAMS

### Energy Frontier Research Center: Center for Molecular Electrocatalysis

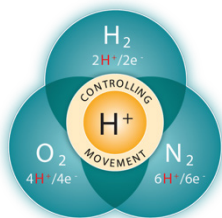
*Director – R. Morris Bullock*

*Deputy Director – Shannon Stahl*

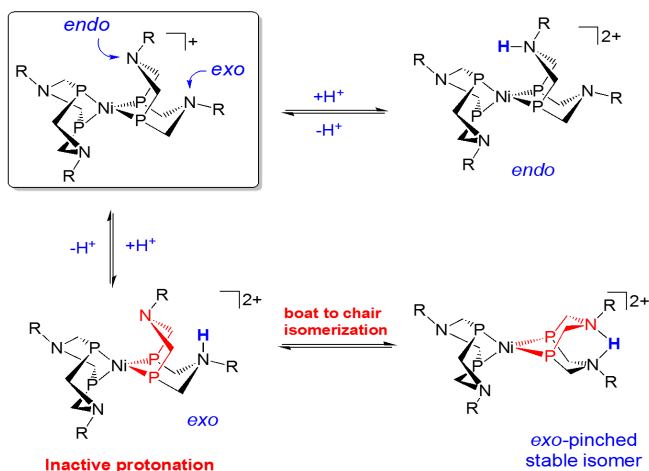
*Co-PIs – Aaron Appel, Michael Mock, Molly O’Hagan, Simone Raagei, Eric Wiedner*

*University Collaborators – James Mayer (Yale University), Sharon Hammes-Schiffer (University of Illinois – Urbana-Champaign), Shannon Stahl (University of Wisconsin – Madison)*

The CME seeks to achieve a transformative impact on the **design of molecular electrocatalysts for the interconversion of electricity and fuels**. The ability to understand, predict, and control the intramolecular and intermolecular transfer of protons provides the basis to achieve this goal. These concepts are being pursued in the context of electrocatalytic multi-electron, multi-proton processes of critical importance to a secure energy future: the production and oxidation of  $\text{H}_2$  ( $2\text{e}^-/2\text{H}^+$ ), the reduction of  $\text{O}_2$  ( $4\text{e}^-/4\text{H}^+$ ), and the interconversion of  $\text{N}_2$  and  $\text{NH}_3$  ( $6\text{e}^-/6\text{H}^+$ ). Catalyst design strategies include the incorporation of proton relays that facilitate intramolecular proton transfer steps, which are often coupled to electron transfer steps, and the use of electron-proton-transfer mediators (EPTMs), such as quinones, that can facilitate challenging electrochemical transformations. Our strategies have led to the development of some of the best molecular catalysts to date, with excellent rates, efficiencies, and lifetimes. The breadth of expertise in the CME enables the Center to complement the catalyst development by a rigorous mechanistic foundation that continues to enable major future advances in the field.



Over the past year, the CME has made outstanding progress toward our overarching goal of elucidating and demonstrating the principles of design of molecular catalysts for electrochemical interconversion of chemical fuels and electricity. Research progress includes development of the fastest molecular electrocatalyst for  $\text{H}_2$  production *and* the fastest molecular electrocatalyst for  $\text{O}_2$  reduction to water. Key insights into the mechanistic basis for these accomplishments have been obtained, including characterization of relationships between rates (turnover frequencies) and overpotentials



**Figure 27.** Branching of the catalytic cycle occurs because of protonation at the inactive *exo* site or active *endo* site. Only *endo* protonation results in H<sub>2</sub> formation (top pathway). The *exo* protonation is stabilized by a boat to chair isomerization of the ligand and to form a hydrogen bond (lower pathway), giving a conformer that is thermodynamically and kinetically stabilized to the deprotonation required to resume catalytic activity.

for different sets of catalysts and the elucidation of principles that will guide the development of catalysts that deviate from linear scaling relationships.

Expansion on the use of proton relays showed that control of the structural dynamics of catalysts containing these relays enables orders-of-magnitude improvements in the rate of H<sub>2</sub> production, without incurring a significant increase in the overpotential. Demonstration of our ability to **implement catalyst design principles** is exemplified by our design of the fastest molecular electrocatalyst for production of H<sub>2</sub>, with a turnover frequency of  $4.5 \times 10^7 \text{ s}^{-1}$ . Our biologically inspired approach emulates features of the active site of hydrogenases in nature. The crucial role of structural dynamics in many enzymes, including hydrogenases, is widely recognized, but this feature is seldom considered in the design of synthetic catalysts. For a series of [Ni(P<sup>Ph</sup><sub>2</sub>N<sup>C<sub>6</sub>H<sub>4</sub>-R</sup>)<sub>2</sub>]<sup>2+</sup> catalysts (for cyclic P<sub>2</sub>N<sub>2</sub> ligands, the first superscript is the substituent on P, and the second indicates the organic group on N), we demonstrated that the dynamic processes involved in proton delivery can be controlled through modifications of the outer coordination sphere, similar to the role of the protein architecture in many enzymes. Such modifications enable an increase in the H<sub>2</sub> production rates by three orders of magnitude with minimal increase in overpotential (Figure 27).

Our **mechanistic understanding** of molecular cobalt electrocatalysts for H<sub>2</sub> production was advanced through the use of electrochemical techniques to detect transient Co<sup>III</sup>H and Co<sup>II</sup>H intermediates of electrocatalytic H<sub>2</sub> production by

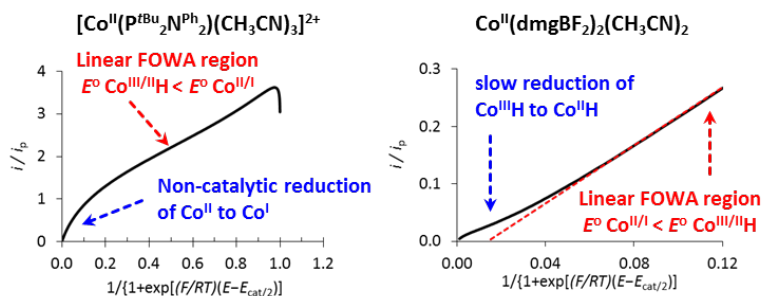


Figure 28. Foot-of-the-wave analysis detects the presence of closely spaced redox couples under electrocatalytic conditions for H<sub>2</sub> production.

[Co<sup>II</sup>(P<sup>t</sup>Bu<sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(CH<sub>3</sub>CN)<sub>3</sub>]<sup>2+</sup> and Co<sup>II</sup>(dmgBF<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>. Whereas many molecular cobalt catalysts are known, the key cobalt hydride intermediates are frequently difficult to detect, owing to their high reactivity. DFT provided Co<sup>III</sup>-H and Co<sup>II</sup>-H bond strengths for both catalysts. Our mechanistic analysis indicates reduction of a Co<sup>III</sup>H complex to Co<sup>II</sup>H, then protonation to generate H<sub>2</sub> (Figure 28). These results demonstrate the power of simple, yet valuable, methods to analyze electrochemical pathways.

Important **fundamental principles of catalyst design** were obtained from our characterization of a series of iron porphyrin complexes for the electrochemical oxygen reduction reaction (ORR), leading molecular iron catalysts that exhibit unprecedented turnover rates ( $2 \times 10^6 \text{ s}^{-1}$ ) (Figure 29). Rates obtained for the series of iron catalysts span six orders of magnitude, and revealed the first demonstration of a correlation between catalyst rate and overpotential for molecular ORR catalysts. These results reveal that fast rates are a consequence of the high overpotential. Joint experimental and computational studies clarified the origin of the rate/overpotential correlation and provided rare atomistic insights into the origin of the scaling relationships for the ORR, which will guide the design of improved catalysts that bypass these constraints.

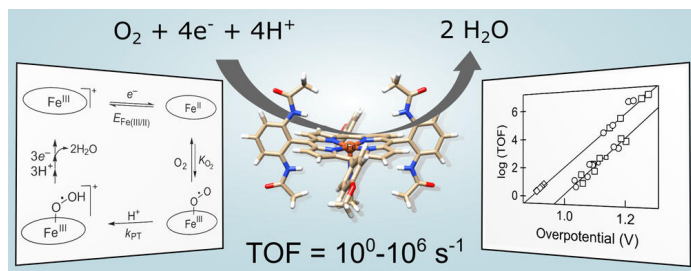


Figure 29. The overpotential for the fastest molecular electrocatalyst for reduction of O<sub>2</sub> is understood in terms of the correlation between rate and overpotential.

In a strategy that is complementary to the use of proton relays, the CME has begun to demonstrate how molecular EPTMs can have a large impact on electrocatalytic reactions. Efforts have been initiated to **evaluate EPTMs as a new catalyst design principle** within the context of electrocatalytic  $O_2$  reduction. Much of this effort has focused on the use of quinones as EPTMs.

Upon undergoing efficient reduction at an electrode, the quinones diffuse into the bulk solution, where they can serve as  $2e^-/2H^+$  reducing agents. Experimental and computational studies characterized the mechanism of  $O_2$  reduction by hydroquinone catalyzed by molecular cobalt catalysts (Figure 30). Spectroscopic, kinetic and computational studies highlight the role of both H atom and PCET steps in this process. This new direction in CME research is complemented by extensive computational efforts directed toward understanding the relationship between  $1e^-$  vs.  $2e^-/2H^+$  reduction potentials of diverse quinone structures. This effort aligns with our goal of **advancing computational methodology needed for the design of new catalysts**. More than 130 quinones were analyzed by DFT methods to probe the basis for linear scaling relationships among the different redox potentials and  $pK_a$  values. These results enable effective prediction of reduction potentials and  $pK_a$  values of quinones, and this ability will play an important role in designing new EPTMs and associated

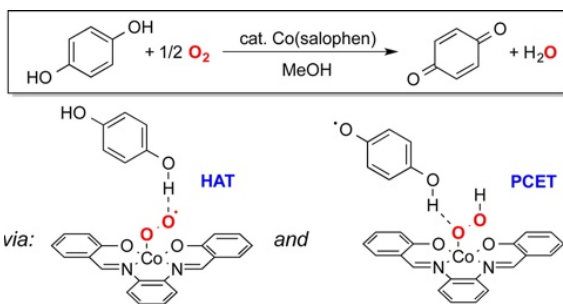


Figure 30. Transition states associated with the key HAT and PCET processes involved in the reduction of  $O_2$  by *para*-hydroquinone, catalyzed by Co(salophen).

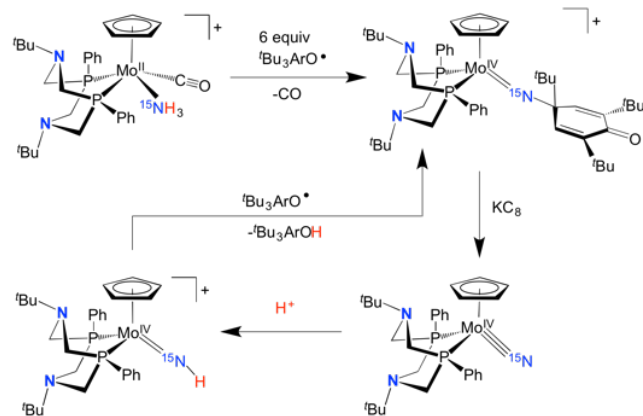


Figure 31. Oxidation of  $NH_3$  on a Mo complex by removal of all three hydrogen atoms.

new catalytic systems for energy conversion reactions.

We implemented a new approach for the oxidation of  $NH_3$  that is conceptually linked to our work on EPTMs, whereby a metal-bound  $NH_3$  molecule undergoes transfer of all three

H atoms to a H atom acceptor (Figure 30). Electrocatalysts to lower the environmental impact of  $\text{NH}_3$  synthesis are needed, and catalysts for the reverse reaction,  $\text{NH}_3$  oxidation, will be essential to utilize energy stored in N-H bonds. Yet molecular catalysts for the oxidation of  $\text{NH}_3$  to  $\text{N}_2$  remain unknown, and fundamental studies of N-H bonds in metal complexes are needed. We discovered  $\text{NH}_3$  oxidation by homolytic cleavage of all three H atoms from a  $[\text{Mo-NH}_3]^+$  complex using an organic radical, producing a  $[\text{Mo=NR}]^+$  complex. Computational analysis describes the energetic profile for the stepwise removal of three H atoms from  $[\text{Mo-NH}_3]^+$  and formation of  $[\text{Mo=NR}]^+$ . Our results demonstrate that transition metal complexes can mediate N-H cleavage of multiple  $\text{M-NH}_x$  species.

Collectively, our Center's progress has resulted in increasingly strong collaborations throughout the Center, coupling experimental and computational efforts to enable the development of new catalysts as well as the elucidation of fundamental principles of catalytic reactivity. The combination of new catalyst synthesis, kinetic and electrochemical measurements, and thermochemical analyses will have long-lasting impacts on energy science beyond the specific accomplishments in the CME.



# Physical Biosciences Program: Enzymatic Energy Conversion

*PIs – Lance Seefeldt, Simone Raagei*

*Co-PIs – James Evans, Wendy Shaw*

The Physical Biosciences program at PNNL aims to define core principles used by enzymes that catalyze energy-relevant reactions, such as H<sub>2</sub> production and oxidation, CO<sub>2</sub> reduction, and N<sub>2</sub> reduction. The suite of enzymes that catalyze these reactions operate with high efficiency at ambient conditions. The activities carried out within this program leverage the current state of knowledge using our team's wide-ranging capabilities, including biochemistry, kinetics, advanced computational methods, single-molecule imaging, and molecular catalyst functionalization, to significantly advance our understanding of how energy is efficiently utilized by these enzymes. The understanding provided by such a biocatalysis research activity will be essential to translating catalytic principles to advance the design of next-generation synthetic molecular catalysts. This effort is connected to the PNNL BES catalysis programs.

**Nitrogenase as a paradigm.** Our current focus is mostly dedicated to understanding the energetics of electron and proton delivery for N<sub>2</sub> reduction catalyzed by the metalloenzyme nitrogenase. Our studies suggest that one key to deciphering this enzyme's mechanism is the large-scale protein conformational changes that control electron delivery (Figure 32). The reduction of N<sub>2</sub> to NH<sub>3</sub> is a reaction fundamental to all life and is one of the most energy-consuming reactions. Bacteria catalyze this reaction using the adenosine triphosphate (ATP)-regulated metalloenzyme nitrogenase at room temperature and atmospheric pressure using electrons and protons. In contrast, the industrial Haber-Bosch reaction demands high pressures (200 atm), high temperatures (500°C), and H<sub>2</sub>, whose

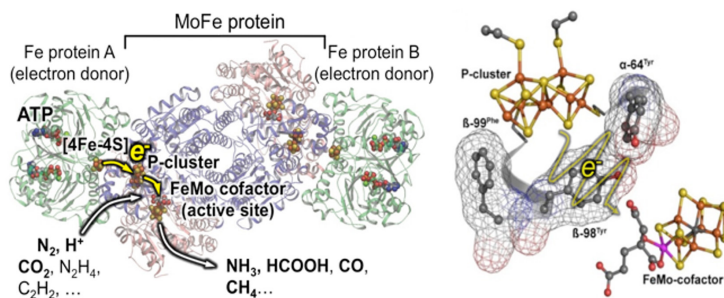


Figure 32. Nitrogenase and metal clusters. Left: Structure of the nitrogenase complex. Right: The three amino acid residues relevant to the Fe protein-independent reduction of the substrates (N<sub>2</sub>H<sub>4</sub>, N<sub>2</sub>, and H<sup>+</sup>) by the MoFe protein are shown, along with the P cluster and FeMo-co.

production from fossil fuels represents a majority of the feedstock costs and energy demands.

In addition to reducing  $N_2$  and protons, nitrogenase can reduce a number of small, multiply bonded compounds. In particular,  $CO_2$  can be catalytically reduced by 2 or 8 electrons/protons to CO or  $CH_4$  at low rates. A better understanding of the mechanism by which nitrogenase catalyzes  $CO_2$  reduction would provide insight into the challenging and environmentally important reduction of  $CO_2$ .

**Electron delivery.** Nitrogenase is a multi-subunit metalloenzyme comprising the electron-donor Fe protein and a MoFe protein complex. The Fe protein is the natural electron donor supporting  $N_2$  reduction. Electron accumulation at the catalytic center (the seven iron [7Fe-9S-Mo-homocitrate] FeMo cofactor, FeMo-co) is key for the efficient  $N_2$  activation. A major effort is dedicated to elucidate how protein structure and dynamics control the delivery of electrons in the nitrogenase system. We performed a series of combined computational and experimental investigations aimed at understanding how the association between the biological electron donor (the ATP-dependent Fe protein) and the MoFe protein allosterically regulates some aspects of catalysis. Specifically, we investigated intramolecular electron transfer and/or substrates binding and reducing. Our studies added to previous findings that substitution of amino acid residues buried inside the MoFe protein within the FeMo-co and the P-cluster allow for fewer substrates without the Fe protein and ATP. Computational analysis showed that the Fe protein and this region of the MoFe protein are mechanically coupled, suggesting a possible mechanism for how the Fe protein communicates with the MoFe protein.

Taking this work a step further, using kinetic measurements of electron transfer, ATP hydrolysis and  $P_i$  release, along with normal modes analysis of the nitrogenase complex motions, we also showed that the two halves of the nitrogenase complex do not undergo the electron transfer cycle independently. Rather, the electron transfer within one-half of the nitrogenase dimer induces conformational changes that allow for ATP hydrolysis and subsequent steps, while allosterically suppressing (partially) the electron transfer in the other half [*PNAS* **113** (2016) E5783].

**Characterization of key catalytic intermediates.** Early kinetic studies indicated that FeMo-co must accumulate four electrons and protons (the  $E_4(4H)$  state in the Lowe and Thorneley kinetic model) before the first step of  $N_2$  reduction. The electrons are delivered one at a time by the nitrogenase Fe protein, before  $N_2$  can be reduced. The  $N_2$  binding coincides with the reversible reductive elimination of one equivalent of  $H_2$ . By employing spectroscopic methodologies

and quantum chemical calculations, we proposed that reductive elimination takes place from  $E_4(4H)$  via an unprecedented dihydrogen  $E_4$  adduct, denoted  $E_4(H_2; 2H)$ , which is thermally populated under catalytic conditions.  $N_2$  reacts with this complex to complete the activated conversion of  $[E_4(4H) + N_2]$  into a  $E_4$  diazene-bound intermediate  $[E_4(N_2H_2) + H_2]$  [*Inorg. Chem.* **56** (2017) 2233].

**CO<sub>2</sub> reduction by nitrogenase.** In a parallel effort, we investigated possible channels for CO<sub>2</sub> reduction to HCOO<sup>-</sup>, CO, and CH<sub>4</sub> (Figure 33). We demonstrated that nitrogenase preferentially reduces CO<sub>2</sub> by two electrons/protons to formate (HCOO<sup>-</sup>) at rates more than 10 times higher than rates of CO<sub>2</sub> reduction to CO and CH<sub>4</sub>. Quantum mechanical calculations on the doubly reduced FeMo cofactor with a Fe-bound hydride and S-bound proton ( $E_2$  state) favor a direct reaction of CO<sub>2</sub> with the hydride (direct hydride transfer reaction pathway), with facile hydride transfer to CO<sub>2</sub> yielding formate. In contrast, a significant barrier is observed for reaction of Fe-bound CO<sub>2</sub> with the hydride (associative reaction pathway), which leads to CO and CH<sub>4</sub>. Importantly, computations revealed that protein residues above the reactive face of the FeMo-co limit the CO<sub>2</sub> access to the hydridic H, introducing a barrier for the direct hydride transfer favoring the competitive elimination of H<sub>2</sub> over HCOO<sup>-</sup> formation. Consistently with this finding, MoFe proteins with amino acid substitutions near FeMo cofactor ( $\alpha$ -70<sup>Val→Ala</sup>,  $\alpha$ -195<sup>His→Gln</sup>) are found to significantly alter the distribution of products between formate and CO/CH<sub>4</sub> [*Inorg. Chem.* **55** (2016) 8321].



## Early Career Program: Combined Capture and Conversion of CO<sub>2</sub>

PI – David J. Heldebrant

Collaborators – Leo Bañuelos (University of Texas at El Paso), Tom Heading (ISIS, UK), Robert Dalgliesh (ISIS, UK), John Linehan, Vassiliki-Alexandra Glezakou, Roger Rousseau, Xiao-Ying Yu, Juan Yao, Steven Saunders (Washington State University)

The goals of this project are to use a combined experimental/theoretical approach to explore in depth a unique heterogeneous, micro-domain solvent molecular structure found in switchable ionic liquids and determine how this structure impacts CO<sub>2</sub> diffusion, CO<sub>2</sub> complexation, and subsequent catalytic conversion of CO<sub>2</sub> into energy carriers. This program aims to determine the correlation between the solvent's mesoscopic structure, *i.e.*, defining CO<sub>2</sub>'s diffusion and complexation pathways and relate that knowledge to a catalyst's location and solvation sphere inside the ionic domains. Later program goals are to perform evaluations of the hydride affinity (electrophilicity) of "captured" CO<sub>2</sub> as alkyl-carbonates or carbamates. This program is synergistic with CO<sub>2</sub>-centric subtasks in the BES Catalysis program.

**3D characterization of molecular-level solvent heterogeneity using time-of-flight secondary ion mass spectrometry (SIMS) and inelastic neutron scattering and small angle neutron scattering.** IPADM-2-BOL, a binding organic liquid (BOL), a molecule currently under investigation as a CO<sub>2</sub> capture solvent (Figure 34), is an energy-efficient solvent that rapidly binds and releases CO<sub>2</sub> at rates faster than aqueous solvents albeit at viscosities an order of magnitude higher. It is unclear as to why a viscous fluid exhibits such high diffusion rates of CO<sub>2</sub>. The molecular structure of this fluid (and other switchable ionic liquids) is hypothesized to account for this.

IPADM-2-BOL was subjected to time-of-flight SIMS analysis to provide 2D and 3D chemical mapping of the speciation of ions in the fluid at various CO<sub>2</sub> loadings. The 2D liquid SIMS images showed dissimilar concentrations of protonated IPADM-2-BOL ( $m/z$  172) and protonated IPADM-2-BOL with CO<sub>2</sub> ( $m/z$  216) in the positive and negative ion modes. Chemical mapping of the speciation of ions in the fluid was performed at various CO<sub>2</sub> loadings (0, 15, 25, 35, 45 mol%). The normalized intensities were then plotted into 3D images with overlaid images constructing a cuboid with 2  $\mu\text{m}$   $\times$  2  $\mu\text{m}$   $\times$  100 seconds of

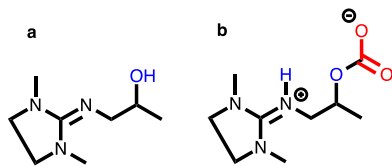
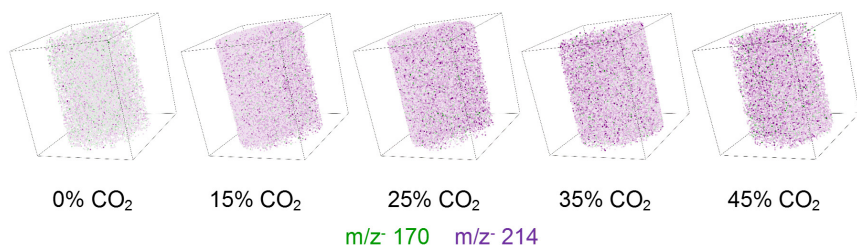


Figure 34. Structure of (a) IPADM-2-BOL, (b) IPADM-2-BOL + CO<sub>2</sub>.



**Figure 35.** Extended 3D chemical mapping of IPADM-2-BOL as a function of CO<sub>2</sub> loading in the negative mode. IPADM-2-BOL (m/z 170), IPADM-2-BOL + CO<sub>2</sub> (m/z 214).

scanning (Figure 35). The 2D and the 3D mappings matched the proposed heterogeneous solvent structure predicted by our simulations (Figure 35), confirming a unique solvent structure of coexisting disparate regions of high and low CO<sub>2</sub> concentration. The observed rapid diffusion of CO<sub>2</sub> in and out of the liquid is attributed to the segregation of non-ionic regions in the fluid allowing for regions of low-polarity where CO<sub>2</sub> would readily move through. This molecular structure is different from water-based solvents or ionic liquids that do not have such a structure.

Deuterium-enriched IPADM-2-BOL molecules were synthesized and subjected to total neutron scattering and small angle neutron diffraction at the ISIS neutron facility in Oxford, United Kingdom, to observe solvent structure as a function of temperature. Total elastic and inelastic scattering experiments on NIMROD indicated that the disparate ionic domains were composed of non-spherical 2-5 nm clusters of zwitterions. Discrete changes at intermediate and high  $q$  were observed, indicating there were changes at both the large and small length scales with heating (CO<sub>2</sub> release) or cooling (CO<sub>2</sub> fixation). Dynamic changes in the low  $q$  were observed, while there was no change in the high  $q$ , indicating that the small clusters (composed of CO<sub>2</sub> containing ions) never changed size or shape at any temperature or CO<sub>2</sub> loading (except for 0 percent). Clusters were then observed to aggregate at a lower temperature (Figure 3), forming spherical aggregates that ranged between 100 and 500 nm. Interestingly, the smaller clusters did not combine to make larger clusters, rather the aggregate was composed of increasing numbers of the 2- to 5-nm clusters. The aggregate was found to break apart at higher temperatures, suggesting the reversible aggregation and formation of long-range order in solution may be analogous to a glass transition. This observation provides valuable insight into the dynamic molecular structure of these liquids, notably how solution viscosity is changed by cluster and aggregate orientation, how CO<sub>2</sub> readily diffuses between the ionic clusters in solution and where catalysts would reside (low-temperature aggregates) during catalytic conversion of CO<sub>2</sub> captured in solution.

### Understanding the reactivity of captured CO<sub>2</sub> (carbamates) in solution.

Carbamates have been claimed to be catalytically active as “captured CO<sub>2</sub>,” yet there are no definitive observations of a direct coordination followed by carbamate insertion into a M-H bond. A known

Ru(pnp)<sub>2</sub>H<sub>2</sub> complex was used to study the hydrogenation of the carbamate of monoethanolamine (MEA) and compared the reactivity to that of (free) CO<sub>2</sub> or (captured CO<sub>2</sub>) alkylcarbonates. Reductions were performed at room temperature at 600 psi H<sub>2</sub> with equivalents of MEA-carbamate dissolved in 1,2-dimethylimidazolidinone solvent at room temperature (to prevent the contribution of free CO<sub>2</sub> that could be released from the carbamate at higher temperatures). The low (single digit) turnover frequency and turnover number suggested (but not yet conclusively) that the carbamate was likely being reduced, as our own control experiments have shown free CO<sub>2</sub> has a turnover number and turnover frequency over two orders of magnitude higher than what was observed for the carbamate. The slower rate and conversion of the carbamate were hypothesized to be due to a reduction via an inner-sphere mechanism (Figure 36, left) in contrast to free CO<sub>2</sub>, which is reduced in an outer sphere reduction (Figure 36, right).

To probe a possible inner-sphere mechanism, a molar equivalent of DBU:hexylamine-carbamate was added to the *cis*-Ru(PNP)<sub>2</sub>H<sub>2</sub> complex in tetrahydrofuran at standard temperature and pressure. The carbamate was observed to add to the Ru, forming a *cis*-hydrido carbamate, which then inserted into the metal-hydride bond producing [DBUH<sup>+</sup>] HCO<sub>2</sub><sup>-</sup> product. This result marked the first observed inner-sphere reduction where a negatively charged amine-carbamate inserted into a metal hydride. The finding also opens new doors for catalyst design focused on controlling hydride donation strength for inner-sphere insertions into a M-H bond rather than the conventional outer sphere reduction.

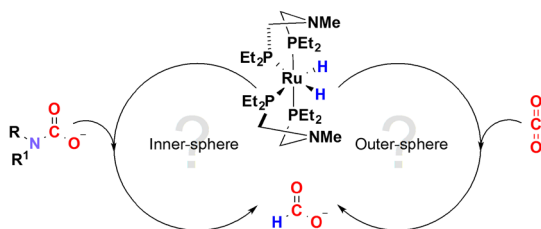


Figure 36. Proposed reactive pathways of carbamates via inner or outer sphere reduction with a representative *cis*-Ru(PNP)<sub>2</sub>H<sub>2</sub> complex.

## CONNECTIONS TO APPLIED PROGRAMS

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.

## Chemical Transformations Initiative

*John Holladay, Johannes Lercher, Roger Rousseau, Robert Weber*

**Overview.** Carbon-containing feedstocks that can be transformed into zero-carbon footprint products, either liquid fuel or valuable chemical intermediates, are abundant in the U.S. but highly decentralized. This initiative has been launched to develop the science and engineering needed to create the technology for the requisite transformations, recognizing that underlying reactions require energy input. Moreover, they will be affected at a small scale (typically less than the equivalent of 200 barrels of oil per day) in the absence of the infrastructure that supplies conventional refineries and chemical plants with utilities such as steam, cooling water, pollution abatement, valorized sinks for waste heat, and a cohort of trained 24/7 operators. Consequently, the reactions need to be performed at temperatures and pressures close enough to ambient that the reactants and products will remain in the liquid phase and so that the processes require minimal safety or environmental controls. Therefore, we seek new catalysts that are very

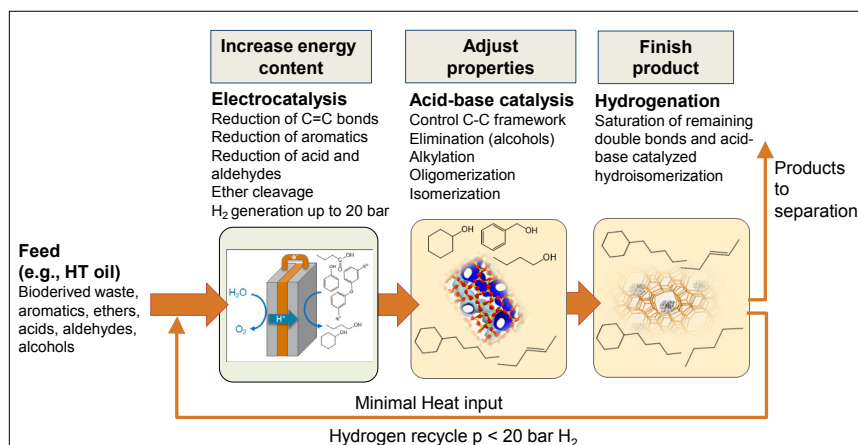


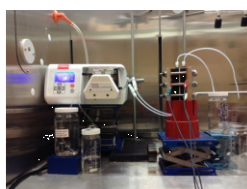
Figure 37. Chemical Transformation Initiative’s staged roadmap that combines electrochemical reductions with dehydration reactions, alkylation reactions, and other critical reactions for low-temperature catalysis that produce carbon energy carriers.



active, selective, and durable when confronted with liquid-phase reaction media, likely rich in water and high concentrations of corrosive chemical species.

**Research themes.** The Initiative is organized into three themes that complement other DOE-funded projects: electrocatalysis of hydrocarbon transformation, low-temperature acid catalysis, and system design. The first two themes are being explored with an eye toward kinetically coupling them to reduce oxygen atoms from carbonyls to alcohols, to cleave O-C bonds through dehydrations, and to control C-C bond connectivity as seamlessly as possible (Figure 37). To that end, we recognize that novel reactor design will be required to orchestrate the heat and mass transfer as well as the kinetics of multiple and simultaneous catalytic conversions into an overall process that is both efficient and commercially viable. Synthesis of fuels from oxygenates requires large quantities of hydrogen to increase the H/C ratio in distillate fuels. Direct, electrocatalytic hydrogenation achieves a number of desired outcomes as it (1) affords economical scaling to the required small sizes, (2) reduces the inefficiencies (overpotential) associated with producing high-pressure H<sub>2</sub>, (3) achieves efficiency and durability at low temperatures, (4) provides a means for oxidative cleanup of produced water, and (5) utilizes renewable electrons by storing the electrical energy in chemical bonds. While electrocatalytic reduction allows effective use of the available protons and electrons to create a product stream that is richer in hydrogen, the product will still be undesirable as a fuel because it will contain a high content of oxygen. Kinetically coupled acid-base functionalities are required for further dehydration, and carbon bond manipulation is required to provide a quality diesel or kerosene. The challenge is developing acid-base catalysts that are sufficiently active at the mild temperatures favored by the redox catalyst system.

The Initiative has been organized to approach the ultimate goal (high quality fuels and chemicals) in stages that will produce interim results and promote effective communication with other, ongoing work. Over the past year, we have adapted both batch and continuous flow reactors (Figure 38), developed a series



Bench: 2.4 cm × 4.2 cm  
~ 1 g/day



Pilot: 5.7 cm × 10 cm  
~50 g/day



Demo: 10.7 cm × 18.7 cm  
1500 g/day

Figure 38. Three scales of flow electrolysis cells have been adapted for use in the Chemical Transformations Initiative to electrochemically upgrade biomass-derived feedstocks.

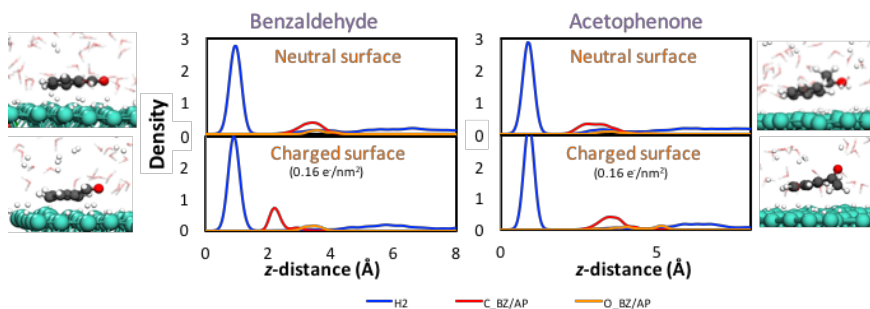


Figure 39. The Chemical Transformations Initiative is developing multiscale atomistic models to understand the kinetics of heterogeneous electrocatalysis.

of scalable, tunable catalysts (metals supported on carbon felts), and characterization techniques, including X-ray absorption spectroscopy and the quantitative determination of active metal sites.

These studies and theoretical method capability development will allow us to build a multi-scale model for heterogeneous electrocatalysis (Figure 39) that explicitly accounts for (i) the solid-liquid interface; (ii) external bias on the electrode; (iii) transport of charge to substrates; and (iv) coupled reactivity and transport in a micro-kinetics ansatz.

The central piece of work was, however, the development of selective catalysis to reduce oxygenated feed molecules. Marked differences in the activity of supported metal catalysts for hydrogenation of aromatic rings and functional aldehyde groups were observed. Overall, two mechanisms of electrocatalytic hydrogenation have been identified. The first mechanism is one in which the rate depends largely on the chemical potential of H at the surface of the electrode (dominating with aromatic rings). The second mechanism is one in which proton transfer to a basic oxygen is accompanied by electron transfer (dominating with aldehyde groups). The efficiency to add hydrogen to an organic substrate in comparison to the evolution of  $H_2$  (Faradaic efficiency) has been related to the ability to add hydrogen (forward rate of hydrogen addition) compared to the recombination of H atoms at the surface. Substitution at the aromatic ring or the functional group leads surprisingly to a reduction of the rate of H addition enhancement, not only to lower hydrogenation rates, but also to lower Faradaic efficiencies. All preliminary results suggest that the reductive conversion of complex mixtures of organic substrates will require the presence of several catalysts simultaneously. We are exploring the impact of this increasing complexity on rates and selectivities of electrocatalytic conversions.

## Vehicle Emission Control Research

*Mirek Derewinski, Feng Gao, Donghai Mei, Ken Rappe, Mark Stewart, Chaitanya Sampara, Janos Szanyi, Diana Tran, Yilin Wang, Yong Wang*

**Overview.** The IIC supports DOE's Vehicle Technologies mission of advanced combustion engine research and development through its work on emissions controls technologies that enable improved engine designs. Expertise and capabilities for this work have been developed in large part by programs funded by DOE's Office of Science. For example, our work in efficient particulate controls, hydrocarbons/CO oxidation, and NO<sub>x</sub> reduction catalysts involves the use of sophisticated surface science techniques, advanced computational chemistry, modeling and simulation, and systems optimization. We also employ state-of-the-art characterization tools at the Environmental Molecular Sciences Laboratory, a DOE Office of Biological and Environmental Research user facility, as well as BES-funded facilities within the IIC. Our work focuses on reducing efficiency losses in emissions controls devices with improved catalyst materials and processes, by minimizing regeneration penalties, systems optimization, and enabling new combustion strategies.

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

**Recent highlights.** Lean combustion gasoline and diesel engines provide substantially higher fuel efficiency, reduced CO<sub>2</sub> emissions, and equivalent performance compared to stoichiometric gasoline engines. However, meeting stringent TierIII and LEVIII emissions standards using these higher efficiency engines has been a major challenge. Scientists at the IIC have been developing new catalysts for the selective catalytic reduction (SCR) of NO<sub>x</sub>, coupled with either upstream urea injection or passive NH<sub>3</sub> generation, which is a promising innovation for controlling NO<sub>x</sub>.

In addition to regulating emission levels, current standards also mandate that aftertreatment systems must be durable up to 150,000 miles of use for commercialization. Discovering and developing materials and emissions systems that are able to attain these in-use requirements is a daunting task. IIC researchers conducted systematic research to elucidate reaction mechanisms and site requirements for SCR and catalyst designing principles, to provide guidelines to the

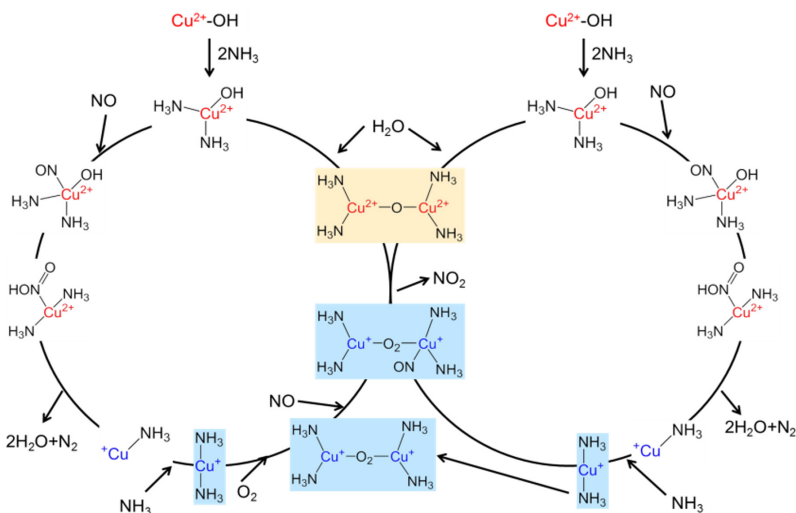


Figure 40. Complete redox cycling of low-temperature  $\text{NH}_3$ -SCR derived from DFT calculations that involves two Cu(I) centers in the oxidation half-cycle. Replotted from Gao, et al., *JACS* 2017, 139, 4935–4942.

synthesis of SCR catalysts with optimized balance in low-temperature activity, selectivity, and long-term durability.

In a recent kinetics and theoretical work, they demonstrated, as shown in Figure 40, that the low-temperature oxidation half-cycle of the SCR reaction cannot be achieved on isolated Cu ions;  $\text{O}_2$  activation requires participation of a pair of mobile  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  sites with the formation of a  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+ - \text{O}_2 - [\text{Cu}^{\text{I}}(\text{NH}_3)_2]^+$  intermediate. This chemistry occurs homogeneously within the SSZ-13 pores and is the rate-limiting step at low Cu loadings. At high temperatures, isolated Cu ions anchor on the SSZ-13 framework and become immobilized. In this case, the oxidation half-cycle occurs on isolated Cu(I) sites with rather high activation barriers. They further demonstrated that not all active sites in Cu/SSZ-13 have the same hydrothermal stability, and certain Cu-containing moieties formed during hydrothermal treatment are rather detrimental to long-term stability of Cu/SSZ-13. Based on which, IIC researchers have provided “optimized” Si/Al and Cu/Al ratios for the design of this catalyst.

**Future directions.** In recognition of the need for high risk/highly efficient stoichiometric and lean combustion strategies to achieve superior performance, DOE and domestic automotive manufacturers through U.S. DRIVE are developing advanced engine technologies. However, before these advancements can be introduced into the U.S. market, they must be able to meet stringent emissions requirements. A significant roadblock to this implementation is the inability of current catalyst and aftertreatment technologies to provide the required activity

at the much lower exhaust temperatures that will accompany highly efficient combustion processes and powertrain strategies. PNNL's IIC is investigating a number of novel approaches to this "low-temperature challenge" such as nano-phase catalysts and catalyst supports that participate in the catalytic chemistry, including passive NO<sub>x</sub> adsorption, and CO and hydrocarbon oxidation. These fundamental studies, which include mechanistic determinations of elementary reactions that limit reactivity at low temperatures, are aimed at providing revolutionary new materials and processes.

## STAFF BIOS

- ▶ Aaron Appel
- ▶ Tom Autrey
- ▶ Nigel Browning
- ▶ R. Morris Bullock
- ▶ Donald Camaioni
- ▶ Herman Cho
- ▶ Miroslaw Derewinski
- ▶ David Dixon
- ▶ Zdenek Dohnálek
- ▶ John Fulton
- ▶ Feng Gao
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- ▶ Gregory Kimmel
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- ▶ Johannes Lercher
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- ▶ Nikolay Petrik
- ▶ Simone Raugei
- ▶ Roger Rousseau
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- ▶ Wendy Shaw
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My research is focused on the catalytic and electrocatalytic interconversion of energy and chemical fuels with an emphasis on thermodynamic considerations for both the individual reaction steps and the overall process. My approach is focused on the coupling of synthetic chemistry with thermochemical studies to understand the limiting factors in catalytic systems, thereby identifying and controlling high-energy steps. I have incorporated bifunctionality into catalysts to avoid high-energy species and to increase catalyst performance through improved rates and energy efficiency.

I am leading the subtask entitled Designing Catalysts Using an Energy-Based Approach: Molecular Catalysis for CO<sub>2</sub> Reduction, which is focused on developing an understanding of how to design new catalysts for the production and utilization of carbon-based fuels. In addition to leading the subtask on the reduction of carbon dioxide, I am involved in the Center for Molecular Electrocatalysis. Specifically, I work on thermochemical and electrochemical studies of molecular catalysts, especially for transformations related to the production and utilization of hydrogen.



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My research interest is focused on measuring the thermodynamic properties of catalytic intermediates with a goal of providing insight for the development of new catalyst materials designed for small molecule activation. Using a combination of experimental and computational approaches, we study how environmental factors such as electrostatic interactions, spatial confinement, and solvent effects enhance the kinetics and modify the thermodynamics of catalytic hydrogenation reactions. This insight provides a rational approach to understand how the reaction environment can be tuned to control selectivity and enhance reactivity in chemical

transformations. Given our focus on the catalytic reduction of polar and polarizable substrates, the heterolytic activation of molecular hydrogen, which provides a catalyst-based complex containing both hydridic and protonic hydrogen, is of special interest. My colleagues and I have shown how to use *in situ* reaction calorimetry to obtain both kinetic and thermodynamics data simultaneously. We collaborate with the theory group to better understand the relationships between the structure and dynamical properties in these molecular complexes. These research studies will provide the foundation for the development of new catalyst materials.





## Nigel Browning

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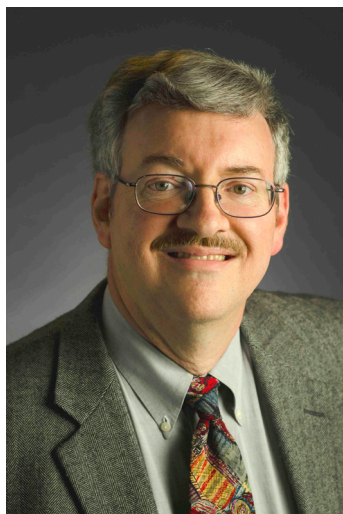
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My research is focused on the design and implementation of novel high spatial, temporal, and spectroscopic resolution methods in the (scanning) transmission electron microscope (STEM) to study catalytic materials *ex situ* and catalytic processes *in situ*. This work is principally aimed at directly imaging the atomic-scale behavior of metal cluster interactions with supports under various synthesis and functional conditions. By observing clusters that vary in size from a single atom up to several nanometers

in size, my colleagues and I can understand how changes in the support and cluster chemistry change the location and type of interactions with porous materials such as zeolites and metal-organic frameworks. In more recent work on MoVTaNb oxide catalysts used for alkane oxidative dehydrogenation, we evaluated the different activity associated with the different facets of the material, and by using *ab initio* simulations, we identified unique atomic interactions that could potentially be responsible for the activity of the system.



## R. Morris Bullock

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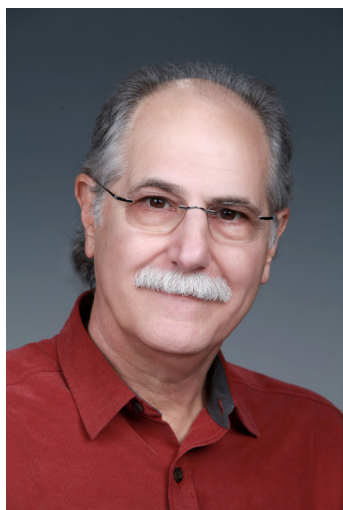
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My research is focused on fundamental studies of the reactivity of molecular inorganic complexes and development of catalysts. Much of our research involves metal hydrides and related catalytically active complexes. A long-term interest has been cheap metals for noble tasks. Most fuel cells are based on platinum, an expensive, precious metal. Our goal is to use the insights of reactivity and thermodynamics to design electrocatalysts based on inexpensive, earth-abundant metals.

I am the Director of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center. The Center includes partners at Yale University, the University of Illinois at Urbana-Champaign, and the University of Wisconsin-Madison. In the Center, we use combined experimental and

theoretical approaches to understand, predict, and control the intra- and intermolecular flow of protons in electrocatalytic multi-proton, multi-electron processes of critical importance to energy transformation reactions.

We focus on the production of hydrogen, oxidation of hydrogen, reduction of oxygen, reduction of nitrogen, and oxidation of ammonia. We study how proton relays regulate the movement of protons and electrons within and between molecules to enhance rates of electrocatalysis. Our research includes synthesis, mechanistic studies, electrochemistry, determination of thermochemical properties, evaluation of catalysis performance, and close connections of experiments with theory.



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My research interests center on reaction mechanisms, the activation of molecules, and theoretical correlation of reactivity with structure, solvation, and surface interactions. My areas of expertise include physical organic chemistry, thermochemistry, kinetics, spectroscopy, and computational chemistry. In relation to the catalysis research thrusts, I am investigating the catalysis of routes from lignin to hydrocarbon energy carriers and the use of Lewis acid-base pairs to activate hydrogen and catalyze reduction of unsaturated molecules. In the first thrust, I am working on the team to examine the catalysis of reduction and deoxygenation reactions of lignin-derived molecules in water and apolar phases by combinations of metal and acid functions. We focus on monitoring the state of the reacting

molecules by spectroscopic methods, in combination with first-principles theory to interpret and simulate the states and reaction mechanisms. This combined experimental and computational approach potentially allows understanding of the reaction pathways for the purpose of designing new catalysts and improving existing catalysts with respect to activity and selectivity. In the second thrust, we are elucidating the mechanism of activation of molecular hydrogen by non-metal Lewis pairs for use in catalysis. We are using experimental methods with computational electronic structure methods to develop thermodynamic and kinetic models of these novel systems for catalytic hydrogenation and small molecule activation.



## Herman Cho

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

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



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

Substituting metal cations into zeolite lattices helps not only to create local structures, but also introduces controlled locations in a framework where thermal and solvothermal degradation as well as reformation of

bonds allows the generation of new and periodic structures. Using kinetic methods, I synthesize such structures in nanometric dimensions, *i.e.*, in sizes below the periodic detectability of the framework structure, yet these materials have the complete local properties that would be seen in such microporous materials. Structural features of crystalline microporous solids of various length scales—responsible for reduced thermal and hydrothermal stability—are explored in the quest to synthesize materials with unprecedented stability. In addition, I am working on stabilizing zeolites used in conversion of bio-derived compounds in liquid water environment via post-synthetic selective removal of structural defects.



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My group's research is focused on developing and using computational electronic structure chemistry approaches to tackle a broad range of problems of interest to the DOE. The focus of the current effort is on the study heterogeneous and homogeneous catalysts. In addition, we are developing and applying reliable electronic structure prediction methods at the correlated molecular orbital theory level for model catalytic systems that can serve as benchmarks for more approximate methods such as density functional theory. Our applications in catalysis cover a broad range and our work is in close collaboration with experimental efforts. We have completed extensive studies on alcohol and water reactions on transition metal oxide nanoclusters, the most recent on  $(\text{RuO}_2)_n$ . We are exploring the interactions of organics on  $\text{TiO}_2$  nanoclusters to better understand the role of entropy in terms of

the binding energies. We are investigating the role of bulky ligands at transition metal sites for homogeneous catalysis for  $\text{CO}_2$  hydrogenation and for C-C bond formation and cross-coupling reactions. A goal of this effort is to study the role of the ligand in controlling not only the energetics of the reaction but also the selectivity. In addition, this effort is providing insights into enthalpic vs. entropic effects on catalytic processes and the role of the local environment on catalytic reactions. We are also studying systems that allow us to explore and develop common themes between homogeneous and heterogeneous catalysts, especially from the use of site-isolated metals in heterogeneous environments. We are also generating thermodynamic and electronic structure datasets for the development of correlations across a broad range of catalytic properties.



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My research centers on experimental studies of fundamental model systems that are prerequisite for understanding complex processes that take place in heterogeneous catalysis and the environment. The catalytic chemistry of interest focuses on reactions that are critical for achieving a zero-carbon-footprint economy such as biomass conversion and CO<sub>2</sub> hydrogenation. The primary goal of the surface science approach used in my lab is to achieve a detailed, site-specific, molecular-level understanding of the kinetics and dynamics of elemental reaction steps on well-defined surfaces and monodispersed clusters. Comprehensive experimental studies involve

both atomically resolved imaging and ensemble averaged spectroscopies to determine the catalyst structure and identify reaction intermediates and products. Novel deposition methods are developed and employed to prepare clusters and films of model metal and metal oxide catalysts with tailored chemical properties. Studies are complemented by collaborative theoretical investigations to achieve detailed generalizable structure-reactivity relationships. Systems recently investigated include anatase(101) and rutile(110) TiO<sub>2</sub> and RuO<sub>2</sub>(110) surfaces and supported WO<sub>3</sub>, MoO<sub>3</sub>, CeO<sub>2</sub>, and TiO<sub>2</sub> clusters.



## John Fulton

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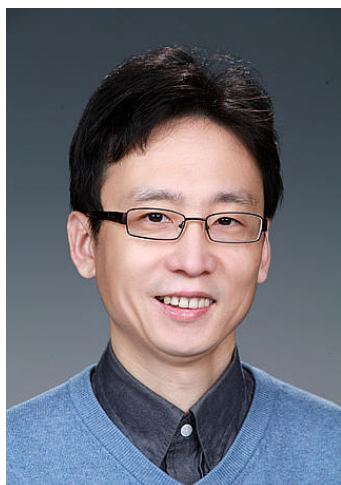
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My research focuses on describing the details of molecular structure, dynamics, and chemical state of various species in fluids such as water, under extremely non-ideal conditions. The goal is to gain a molecular-level understanding of species such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

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





## Feng Gao

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My research interest is in heterogeneous catalysis, specifically the understanding of structure-function relationships on well-defined catalytic systems using (*in situ*) spectroscopies and reaction kinetics. In Thrust 1 of the BES program, my role is to lead the research on synthesis of facet-specific early transition metal oxide catalysts, and their use in the conversion of bio-derived molecules to value-added chemicals and/or energy carriers through solid-gas catalytic reactions. Our current focus is utilizing facet-specific  $\text{CeO}_2$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$  as catalysts or catalyst supports for oxygen removal, C-C coupling, and oxidative dehydrogenation reactions.

My research team also conducts research associated with diesel engine exhaust cleaning, supported by DOE Energy Efficiency and Renewable

Energy, Vehicle Technologies Office. We work on developing novel zeolite-based catalysts for use in selective catalytic reduction (SCR) and passive  $\text{NO}_x$  adsorber processes, and on understanding fundamental catalytic chemistries involved in these processes. Our research group was the first to suggest two catalytic centers in Cu/SSZ-13, an industrial SCR catalyst and to prove the mobile nature of catalytic active centers under reaction conditions. In 2015, our group contributed to the first comprehensive overview of small pore materials as SCR catalysts in *Chemical Society Reviews*. We also collaborate with industrial partners, including Cummins, Inc., Johnson Matthey Inc., Fiat Chrysler Automotive, and PACCAR, to provide solutions to their practical problems.



## Bojana Ginovska

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My research interests focus on theory-based investigation and modeling of enzymes and biomimetic catalysts for energy applications using a variety of methodologies, including quantum mechanical calculations, classical and quantum mechanics/molecular mechanics simulations, and enhanced sampling techniques. Specifically, my work focuses on understanding the role of the outer coordination sphere on catalysis in enzymes and biomimetic metal-based molecular catalysts. I am exploring the effects of structural flexibility, allosteric regulation, and mutations on the thermody-

namic and kinetic properties of biocatalysts, as well as accurate characterization on reaction pathways. The work extends to modeling synthetic molecular catalysts with peptide outer coordination sphere, and probing the structure-function relationships. My research on the biocatalysts focuses on fundamentally understanding the mechanism of enzymatic interconversion of small molecules and extracting design principles from enzymes that can be applied to development of bioinspired catalysts.



## Vassiliki-Alexandra Glezakou

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A computational chemist by training with experience in correlated methods and transition metal chemistry, I have expanded my research portfolio to include condensed systems relevant to materials and carbon capture, sequestration, and conversion. The focus of my recent work is the structure, vibrational spectroscopy, and structure/activity correlations in a diverse ensemble of systems that commonly include carbon dioxide. These studies have enabled an intimate knowledge of carbon dioxide chemistry that is transferrable to other research problems, including the following:

- ▶ Catalytic activity of metal clusters on various oxide supports

- ▶ Catalyst design for transmetalation reactions
- ▶ Mechanistic studies for secondary methane recovery
- ▶ Studies of CO/CO<sub>2</sub> sorption mechanism on oxides
- ▶ Solvent transformation for post-combustion carbon dioxide separation
- ▶ Mechanistic studies for metal organic framework nucleation and growth
- ▶ Solvatochromic effects in surface-supported chromophores.

I work closely with experimental groups and provide insights regarding mechanistic details, as well as guide synthesis of novel catalytic systems.



## Oliver Y. Gutierrez

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### Co-principal Investigator

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My research aims to build a bridge between molecular description of catalytic reactions and rational design of novel catalysts and catalytic processes. Thus, my work focuses on fundamental aspects of heterogeneous catalysis covering topics in industrial and emerging processes for the production of chemical energy carriers. Specifically, catalytic target reactions have included hydrodefunctionalization and hydrogenation of hydrocarbons, bio-oil conversion and photocatalytic H<sub>2</sub> generation. Accordingly, I have mainly investigated bulk and supported transition metal sulfides, and supported metal nanoparticles. The properties of these materials, in stages of preparation and during/after sorption and catalysis, have been

studied making use of rigorous kinetics and advanced characterization methods, *e.g.*, *in situ* infrared, Raman, and X-ray absorption spectroscopy, X-ray diffraction, and temperature-programmed reactions. Currently, my work centers on the phenomena at the interface between electrocatalysis and thermal catalysis for the transformation of oxygenated molecules. Another topic of my current research is the cooperative effects between metal sites and acid sites and the associated reaction mechanisms for the conversion of polar molecules to fuels. We aim at structure-activity correlations for designing new catalysts and catalytic routes with enhanced activity and selectivity.



## David Heldebrant

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Energy and Environment Division

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My research focuses on applying the principles of green chemistry to improve atom and energy efficiency and reduce toxicity of chemical processes. Focus areas are on developing materials that can perform multiple tasks to reduce waste and improve energy efficiency in the fields of chemical separations and chemical conversions, applying these principles in areas of industrial gas separations, liquid/liquid separations and catalysis. The work focuses on the development of organic gas-separating liquids that can chemically remove  $\text{CO}_2$ ,  $\text{SO}_x$ , and  $\text{H}_2\text{S}$  from combustion, gasification or natural gas streams through applied and fundamental studies of gas absorption kinetics, thermodynamics and mechanistic studies.

My research areas also include chemical fixation/catalytic conversion of alkylcarbonates ( $\text{CO}_2$  surrogates) into chemicals such as fuels ( $\text{CH}_3\text{OH}$ ) and polymers. My experimental approach of these systems includes design and fabrication of catalysts and kinetic/thermodynamic testing of catalytic systems to study mechanisms, catalyst structure and selectivity/reactivity. My current focus combines catalytic conversions of alkylcarbonates with  $\text{CO}_2$ -activating/concentrating solvents to develop catalytic systems to provide renewable energy storage or value-added products from  $\text{CO}_2$ .



## John Holladay

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As a scientist, I have spent more than fifteen years in catalysis focused on condensed phase processing of renewable carbon for production of fuels and chemicals. These processes have led to 18 U.S. patents, numerous commercial licenses, including one practiced at the full commercial scale. At the Pacific Northwest National Laboratory (PNNL), I am responsible for shaping the strategic direction of our transportation portfolio, which includes bioenergy, vehicles, and fuel cell technologies. I am active in co-managing multi-laboratory consortia, including co-leadership of Energy Efficiency and Renewable Energy's Co-Optimization of Fuels and Engines cross-cut. As Associate Director of the Institute for Integrated Catalysis, my role is to build on PNNL's fundamental science base to help solve applied energy challenges. As a team, we have focused our applied catalyst programs on production of distillate

and mid-distillate fuels. The science focus is improving catalyst activity allowing for operation at lower processing temperatures and catalyst robustness allowing the conversion of carbon-rich waste streams, including complex wet sludges and aqueous oxygenates from industrial waste gases, forest and agriculture residues. To further our focus on low temperature processing, beginning in 2016, I will be leading a new initiative at PNNL, with Johannes Lercher and Roger Rousseau that combines electrocatalysis and acid-base catalysis in novel reactor designs that address challenges in distributed carbon energy production. I have served as Chief Scientific Officer for the National Advanced Biofuels Consortium, Chief Operations Officer for the National Alliance for Biofuels and Bioproducts, and the Chair of the Organic Reactions Catalysis Society.



## Jian Zhi Hu

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I have extensive research experience in solid-state and liquid-state nuclear magnetic resonance (NMR) spectroscopy and magnetic resonance imaging with about 190 peer-reviewed publications, h-index of 35 and nearly 4000 web of science citations. I have developed or originated a range of slow and ultra-slow magic angle spinning or magic angle turning NMR techniques for enhanced spectral resolution in solids, semi-solids and biological materials. Recently, I have developed the combined high-temperature and high-pressure magic angle spinning NMR for *in situ* studying of the reaction mechanisms associated with catalytic reaction and materials synthesis.

My current research interests and expertise include the following:

- ▶ *In situ* and *ex situ* NMR characterization of heterogeneous solid

catalyst materials, surface functional groups and active sites, molecular dynamics at the interface, reaction mechanisms and pathways.

- ▶ Development and application of *in situ* constant flow and the combined high temperature and high-pressure magic angle spinning NMR capabilities.
- ▶ Ultrahigh field (850-MHz) NMR and computational modeling of NMR parameters.

Development of unique high-resolution slow magic angle spinning NMR metabolomics tools for biosignature discovery in biological tissues with sample volume from less than about 0.2  $\mu\text{l}$  to more than 1  $\text{cm}^3$  using a single probe.



## Enrique Iglesia

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### Co-principal Investigator

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Enrique Iglesia is the Theodore Vermeulen Chair in Chemical Engineering at the University of California at Berkeley. He joined Berkeley in 1993 after twelve years in research and management at the Corporate Research Labs of Exxon. He has served as Editor-in-Chief of *Journal of Catalysis* (1997–2010) and President of the North American Catalysis Society (NACS) (2009–2017) and serves as Vice President and President-Elect of the International Association of Catalysis Society. He has been elected to the National Academy of Engineering, the American Academy of Arts and Sciences, and the National Academy of Inventors. He is a Fellow of the American Chemical Society (ACS) and the American Institute of Chemical Engineers (AIChE).

His group addresses the synthesis and the structural and functional characterization of solids used as catalysts for production of fuels and petrochemicals, for conversion of energy carriers,

and for improving the energy and atom efficiency and the sustainability of chemical processes. His work combines synthetic, spectroscopic, theoretical, and mechanistic techniques to advance novel concepts and applications in heterogeneous catalysis. He has co-authored more than 340 publications and 40 U.S. patents.

He is the recipient of 2012 Eni Research Prize, the Somorjai and Olah ACS Awards, the Wilhelm and Alpha Chi Sigma AIChE Awards, the Emmett and Burwell NACS Awards, the Cross Canada Lectureship of the Chemical Institute of Canada, and the François Gault European Federation of Catalysis Societies Award. He has also received the Award for Excellence in Natural Gas Conversion, the Tanabe Prize in Acid-Base Catalysis, a Humboldt Senior Scientist Award, and the Noyce Prize, the highest teaching honor in the sciences in the Berkeley campus.





## Abhi Karkamkar

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My research is focused on the synthesis of multifunctional catalysts that are created by an approach based on surface organometallic chemistry.

This approach is being developed to provide a pathway to bridge molecular catalysts and heterogeneous catalysts as model single site catalysts for conversion of carbon dioxide to fuels

and activation of hydrogen on amphiphilic surfaces. My research interests are primarily in the area of synthesis and modification of these multifunctional catalysts and supports. I am also involved with calorimetric studies of hydrogen storage materials and synthesis and characterization of zeolites, mesoporous materials, oxide nanoparticles, and nano-alloy materials.



## Bruce Kay

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

deposited supported clusters. This experimental work is performed in collaboration with Zdenek Dohnálek and is strongly coupled with Roger Rousseau's and David Dixon's theoretical work. Recent activities have focused on studying the adsorption, desorption, and reaction of hydrocarbons and polar molecules such as alcohols and polyols on  $\text{TiO}_2(110)$  and supported oxide catalysts based on cyclic  $(\text{WO}_3)_3$  and  $(\text{MoO}_3)_3$  clusters.



## Gregory Kimmel

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

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



## Libor Kovarik

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My research is focused on understanding the oxidation-reduction properties of supported transition metal (TM) nanoparticles. TM catalytic nanoparticles supported on oxide or non-oxide substrates can undergo a number of surface/structural transformations during exposure to elevated temperatures and reactive gas environments, which has a significant effect on catalytic properties. The aim of this work is to develop an understanding of phase stability of nanoparticles surfaces and the mechanism of the oxidation/reduction transformation. Currently, my work is focused on establishing chemical and coherency effects from the support on stability of Pd nanoparticles using en-

vironmental transmission electron microscopy (ETEM). In addition, I am also involved in studying structural and surface properties of transition aluminas, which form a basis of important catalytic and catalytic support materials due to their unique surface acidity and high temperature structural stability. In our previous work, we used model system to derive the structural nature of several important transition alumina phases. More recently, this work involves studying their surface structure. Specifically, I use S/TEM, NMR and *ab initio* method to study the bonding environment of massively reconstructed low-index surfaces of  $\delta$ -Al<sub>2</sub>O<sub>3</sub> and  $\theta$ -Al<sub>2</sub>O<sub>3</sub>.



## Johannes Lercher

Director

Institute for Integrated Catalysis

**Principal Investigator**

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

metal oxide clusters. Advanced characterization methods (*in situ* X-ray diffraction; X-ray absorption spectroscopy; and infrared, Raman, and inelastic neutron scattering spectroscopy) are used to characterize these materials in stages of preparation and during/after sorption and catalysis. Catalytic target reactions are the low-temperature, acid-catalyzed activation, functionalization, and transformation of alkanes; the oxidative activation of light alkanes, including CH<sub>4</sub>; and the hydrogenation and hydrodefunctionalization of biogenic and fossil feedstocks (such as lignin and aromatic molecules containing oxygen, nitrogen, and sulfur). The elementary steps and selective control of sorption and diffusion in molecular sieves is another significant focus of my work outside the catalysis area.



## John Linehan

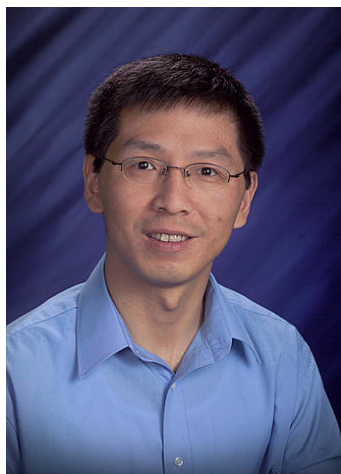
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My major research goal is to determine catalytic mechanisms and use the new understanding of how catalysts work to design and synthesize better catalysts. *In situ* and *operando* spectroscopies, including nuclear magnetic resonance (NMR), Fourier transform infrared, and X-ray absorption fine structure are used to interrogate the metal catalyst species prevalent during catalysis. Meanwhile, the substrates and products also are investigated so that catalytic rates can be correlated with the metal-containing catalytic species present in a time-dependent manner. In collaboration with my colleagues, we have developed the fastest first row transition

metal catalyst for CO<sub>2</sub> hydrogenation to formate using thermodynamic principles and *operando* spectroscopy. This new catalyst efficiently operates at room temperature and at 1 atm total pressure. Both properties are unusual for any CO<sub>2</sub> hydrogenation catalyst, including those made from precious metals. *Operando* NMR studies have revealed a more accurate picture of carbon dioxide to formic acid catalysts. Continuing work includes determining kinetics, thermodynamics, and mechanisms of small molecule interactions with other organometallic catalysts that are active in energy conversions.



## Donghai Mei

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

tween all elementary processes involved in the catalytic cycle, and at the macroscopic scale the effects of heat and mass transfer will be described by continuum theories, which ultimately scale up to reactor level. In the past year, I focused on the theoretical modeling of catalytic conversion of aqueous phase alcohol dehydration and alkylation in zeolites, as well as the selective C-O bond cleavage of model ether compound over transition metals. In addition, the stability of zeolite with steam pre-treatment and its effects on the selective catalytic reduction over Cu/SSZ13 catalysts were investigated with the explicit description of aqueous phase using *ab initio* molecular dynamics simulations.



## Michael Mock

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My current research interests in the Center for Molecular Electrocatalysis (CME), an Energy Frontier Research Center, are focused on the synthesis and reactivity of homogeneous complexes for the catalytic reduction of dinitrogen to ammonia and hydrazine, and the oxidation of ammonia to dinitrogen. Developing efficient electrocatalysts for  $\text{NH}_3$  synthesis from  $\text{N}_2$ , and protons and electrons, could augment the energy intensive Haber-Bosch process and enable distributed facilities for on-demand  $\text{NH}_3$  production. Catalysts for the reverse reaction,  $\text{NH}_3$  oxidation, will be essential to utilize the energy stored in N-H bonds. This research combines experiment and theory, and uses transition metals such as chromium, molybdenum, iron, and ruthenium to study dinitrogen and ammonia complexes containing bidentate and tetradentate

phosphine ligands. These studies seek to develop strategies for making and breaking  $\text{N}\equiv\text{N}$  and N-H bonds by applying chemical kinetics and thermochemical approaches. Catalyst design strategies aim to modulate the reduction and oxidation potentials of metal complexes, promote H atom and proton-coupled electron transfer reactions, and facilitate proton transfer processes that are critical to develop electrocatalysts for the multi-proton, multi-electron reduction pathway of dinitrogen to ammonia, and to utilize energy storage in N-H bonds. Outside the work in the CME, my research interests focus on designing novel trimetallic systems for  $\text{N}_2/\text{NH}_3$  activation and catalysis; synthetic nitrogenase models with sulfur-based ligands; photocatalysis and flow-reactor design.





## Molly O'Hagan

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My research is focused on using biologically derived and inspired catalysts to develop a fundamental understanding of the function of metalloenzymes and how this can be applied to designing better molecular catalysts. Using nuclear magnetic resonance spectroscopy, we work to identify cat-

alytic intermediates, understand structural dynamics and study the mechanism of proton movement in bioinspired catalysts for H<sub>2</sub> oxidation and production. My efforts have been closely coupled with theoretical efforts to provide mechanistic details to develop design principles for improved catalysts.



## Nikolay Petrik

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My research is focused on fundamental experimental studies of thermal and non-thermal processes at surfaces and interfaces, including heterogeneous thermal- and photo-catalysis, adsorption, desorption, surface and bulk diffusion, defects and reactions induced by energetic electrons, and others. I am interested in kinetics and dynamics of reactions at interfaces, involving electronic excitations, such as electrons, holes, and excitons. The goal is to understand basic mechanisms of the interfacial non-thermal processes to optimize their efficiency. I use well-characterized metallic and metal oxide substrates (*e.g.*, Pt(111), rutile TiO<sub>2</sub>(110), anatase TiO<sub>2</sub>(101),  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001)) and a wide spectrum of inorganic and organic adsorbates, from simple molecules (CO<sub>2</sub>, CO, O<sub>2</sub>,

H<sub>2</sub>O, etc.) to more complicated organic alcohols, ketones, acids, and hydrocarbons. An experimental approach involves basic surface science techniques and ultra-high vacuum chambers equipped with sources of UV photons, low energy electron guns, reflection absorption FTIR, a mass spectrometer for angular- and time-resolved desorption measurements, a molecular beam doser, and other state-of-the-art capabilities. My current studies include understanding thermal and non-thermal processes effects in catalysis, the role of charged point-defects in adsorption, chemical transformation and photodesorption, the correlation of the structure of the adsorption complex with reactivity on metal oxide surfaces, the role of surface diffusion in surface reactions.



## Simone Raugei

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My activity focuses on the development and application of computational and theoretical methodologies for the study of chemical and biochemical processes using high-performance computing. I am the principal investigator (PI) of the Basic Energy Sciences Biophysical Sciences Program at PNNL. This is a highly interdisciplinary program that focuses on uniquely characterize key biochemical and biophysical features of enzymatic processes related to production of a suite of small sustainable energy carriers to drive the design of synthetic catalytic platforms with enhanced performances. Initial efforts

are directed toward understanding hydrogenase,  $\text{CH}_4$  coenzyme M reductase and nitrogenase using a variety of computational and experimental approaches. I am the PI for the crosscutting theory tasks in of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center (Director: R. Morris Bullock), where I am leading a theoretical effort for the design of electrocatalysts for energy storage and energy delivery. In particular, I am focusing on the theoretical characterization of novel electrocatalysts, based on inexpensive transition metals, for dihydrogen production/oxidation, dioxygen reduction, dinitrogen reduction and ammonia oxidation.



## Roger Rousseau

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### Co-principal Investigator

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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 study heterogeneous and homogeneous catalysis reaction mechanisms.

In the past few years, our team has contributed to theoretical studies of itinerant electrons in metal oxide catalytic materials, which provided novel insights into how these excess charge carriers influence the reactivity of surface adsorbates and supported metal clusters. We also contributed to studies of catalysts for  $C_2$ -oxygenate synthesis from syngas and

steam reforming of biomass-derived tars, thermal and electrochemical upgrading of bio-oils to fuel precursors; design of  $CO_2$  capture solvent systems for flue-gas cleanup; and the role of anharmonicity on the free energetics of confinement in zeolites and reactivity at solid-liquid interfaces. A hallmark of our team is that we develop and test modern simulation techniques on well-defined model systems in direct comparison with concurrent experiments as represented by our activities on the core Basic Energy Sciences program. These methods are then adapted and deployed on projects relevant to the U.S. Department of Energy's technology offices where we have active programs in applied catalysis and materials.



## Gregory Schenter

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My research focuses on the development of statistical mechanical techniques to better understand molecular interactions and processes in complex condensed phase systems. Development of new simulation capabilities that enhance the interpretation of experimental measurement is an important component of my work.

Teaming with Tom Autrey, we have studied chemical and physical properties of catalytic ambiphilic sites with a goal of providing fundamental insight into the development of new catalytic materials designed for small molecule activation. This research focused on the non-metal activation of molecular hydrogen in bifunctional molecular complexes. We are developing molecular simulation techniques to elucidate the role of steric hindrance, the nature of electronic states, and the role of dynamical fluctuations in the equilibrium between dative bonding and hydrogen activa-

tion in molecular complexes composed of Lewis acid-Lewis base pairs. We combine experimental and computational approaches to study how tunable environmental factors, such as electrostatic interactions, nano confinement, and pressure, enhance the kinetics and modify the thermodynamics of hydrogen release and uptake in condensed phases. 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. Our group uses experimental spectroscopy methods combined with computational methods to gain fundamental insight into relationships between the structure and dynamical properties of molecular complexes. These basic research studies will provide the foundation for the development of a rational approach in designing new catalyst matter.



## Wendy Shaw

Director  
Physical Sciences Division

### Co-principal Investigator

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My research focuses on learning from enzymes to develop a more mechanistic understanding of the outer coordination sphere of molecular catalysts. Together with my colleagues, we are building on well-understood molecular electrocatalysts and thermal catalysts and incorporating peptides into the outer coordination sphere to provide enzymatic features to molecular complexes. We are investigating:

- ▶ Role of proton pathways
- ▶ Stimulus-sensitive peptides as enzyme mimics
- ▶ Physical-chemical characteristics of the active site pocket

In the past year, our team has developed a catalyst that is electrochemically reversible at room temperature for  $H_2$  oxidation  $H_2$  reduction. The combination of both a COOH group and side chains that can interact to control the active site structure and

help move protons were found to be essential. In the absence of these features, reversibility is lost, indicating an increase in overpotential. The cooperativity of the individual features is reminiscent of enzymes and is resulting in design principles for the outer coordination sphere. We also worked with collaborators to evaluate complexes on surfaces and in fuel cells. Several interesting scientific insights resulted, including evaluating a non-water soluble complex in water when it was immobilized. Additionally, the properties of several complexes do not appear to be altered when bound to the surface, an essential observation for practical use. We are currently translating the outer coordination sphere understanding that we have to  $CO_2$  reduction, and are working with a computational collaborator to develop a good starting point for a structured outer coordination sphere.



## János Szanyi

Catalysis Science  
Physical Sciences Division

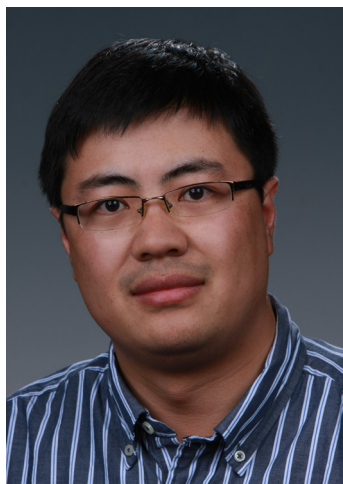
### Co-principal Investigator

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My research is aimed at understanding structure-reactivity relationships surface science, spectroscopy and kinetic studies on heterogeneous catalytic reaction systems. In particular, I am interested in understanding the mechanistic consequences of very high (atomic) metal dispersion on different support materials. Using a series of ensemble-averaged spectroscopy methods, we investigate the fundamental properties of metal atoms and small metal clusters prepared under well-controlled ultrahigh vacuum conditions. Our results provide information on the energetics of the interactions between highly dispersed metals and selected probe molecules. Applying *in situ* reflection absorption infrared spectroscopy, we study the binding configurations of adsorbates to metals and identify surface species present on the metal and support materials under elevated reactant pres-

ures. Simultaneously, we are conducting detailed kinetics and *operando* spectroscopy measurements on model high surface area supported metal catalysts using flow reactors and steady-state isotopic transient kinetic analysis/Fourier transform infrared/mass spectrometry techniques. These measurements provide detailed kinetic information together with surface speciation that allow us to greatly enhance our mechanistic understanding of heterogeneous catalytic systems, in particular the reduction of CO<sub>2</sub>. I am also involved in research related to the fundamental understanding of automotive emission control catalysis, and I am conducting research in selective catalytic reduction of NO<sub>x</sub> on zeolite-based catalysts, low temperature NO and CO oxidation on metal oxides, and low temperatures NO<sub>x</sub> and hydrocarbon storage in zeolites.



## Huamin Wang

Chemical and Biological Process Development

Energy Processes & Materials Division

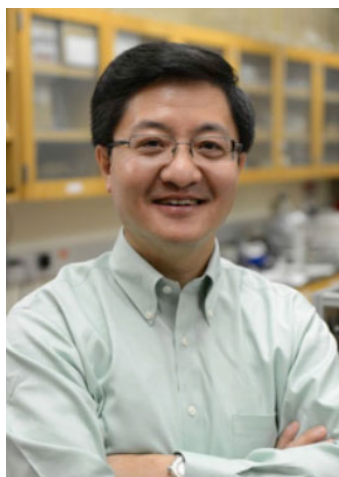
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My research interests include the catalyst and process development for the production of clean and renewable fuels and chemicals and fundamental understanding of catalytic reactions involved in the process by experimental approaches. My recent work in PNNL has two focuses:

- ▶ Developing efficient and cost-effective catalysts and catalytic processes for biomass conversion to renewable fuels and chemicals. Specifically, I am working on hydrotreating of intermediates produced by thermochemical processing of biomass into fuels, catalytic fast pyrolysis of biomass, and acid-base catalysis for converting biomass-derived oxygenates to fuels and chemicals
- ▶ Basic energy science research aimed at developing structurally well-defined transition metal oxide catalysts and understanding atomic-level structure/function relationships of these catalysts used in various catalytic reactions





## Yong Wang

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### Co-principal Investigator

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

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



## Robert Weber

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

Currently, my modeling efforts and experimental activities focus on reaction kinetics and transport in condensed media, where bulk and local polarizability can alter the energetics of charged and polar intermediates, compared with their stabilities in reaction media that have low dielectric

constants. The immediate applications are the upgrading reactions of the oxygen-containing intermediates produced by thermochemical processing of biomass into fuel precursors, and the electrochemical and photochemical transformations of organic molecules into active pharmaceutical ingredients.

The kinetics and transport models are used to devise improved catalysts, for process scaling, and to help diagnose maldistributions of flow in existing reactors.

The work is funded by the Energy Efficiency and Renewable Energy/Bioenergy Technologies Office and a multinational pharmaceutical company.



## Eric Wiedner

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

values and the ability to obtain parameters for reactive species. This work relies heavily on the synthesis of both new ligand platforms and potential catalytic intermediates. I am working on electrochemical hydrogen production and ammonia oxidation as part of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center, and the hydrogenation of carbon dioxide as part of the Designing Catalysts Using an Energy-Based Approach: Molecular Catalysis for Carbon Dioxide Reduction task, funded by the U.S. Department of Energy Basic Energy Sciences.





## About Pacific Northwest National Laboratory

Interdisciplinary teams at Pacific Northwest National Laboratory address many of America's most pressing issues in energy, the environment, and national security through advances in basic and applied science. PNNL employs 4,400 staff, has an annual budget of nearly \$955 million, and has been managed for the U.S. Department of Energy by Ohio-based Battelle since the laboratory's inception in 1965. For more information, visit the PNNL News Center, or follow PNNL on Facebook, LinkedIn and Twitter.

[www.pnnl.gov](http://www.pnnl.gov)

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