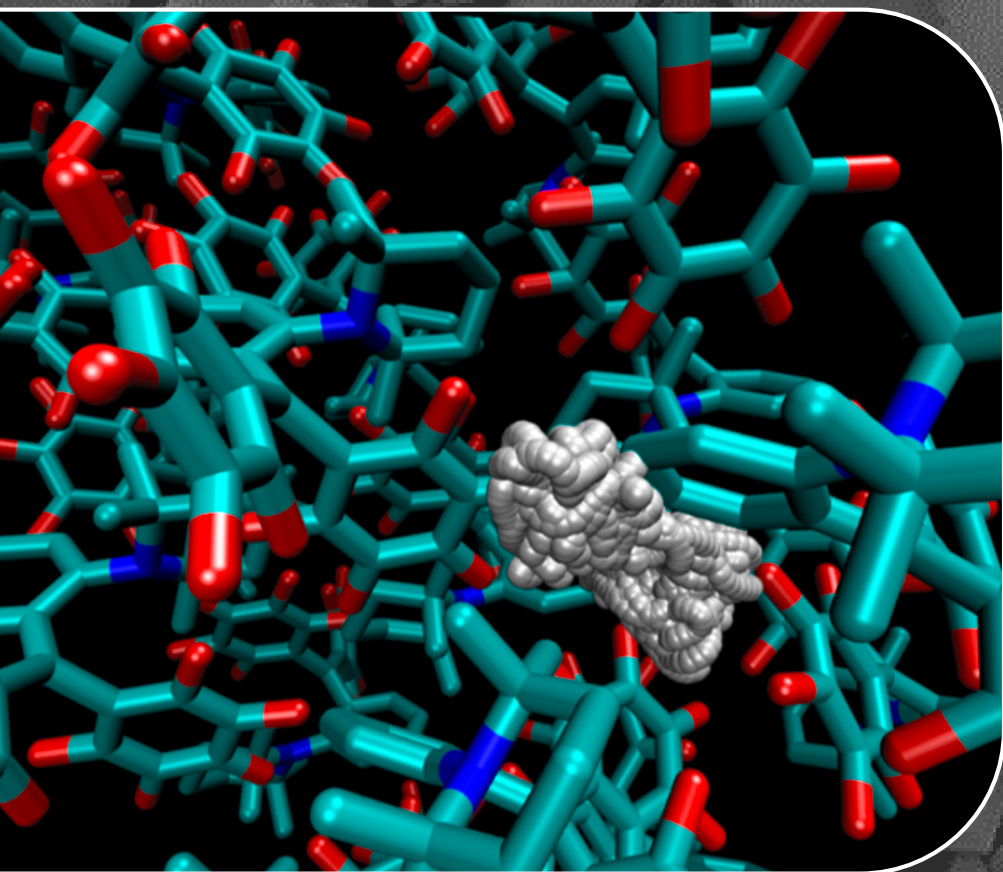


INSTITUTE FOR INTEGRATED CATALYSIS

2016 Program Briefing



Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by **Battelle** Since 1965

U.S. DEPARTMENT OF
ENERGY

Office of Science

ABBREVIATIONS

AIMD	Ab initio molecular dynamic
APS	Advanced Photon Source
ATP	Adenosine triphosphate
BAS	Brønsted acid sites
BES	Basic Energy Sciences
BETO	Bioenergy Technologies Office
CME	Center for Molecular Electrocatalysis
DBU	Diazabicyclo[5.4.0]-undec-7-ene
DFT	Density functional theory
DOE	U.S. Department of Energy
DRIFT	Diffuse reflectance infrared Fourier transform
EERE	Office of Energy Efficiency & Renewable Energy
EFRC	Energy Frontier Research Center
EMSL	Environmental Molecular Sciences Laboratory
EXAFS	Extended X-ray absorption fine structure
FLP	Frustrated Lewis pair
FTIR	Fourier transform infrared spectroscopy
HDO	Hydrodeoxygenation
IIC	Institute for Integrated Catalysis
INS	inelastic neutron scattering
KP	Key personnel
MAS	Magic angle spinning
MS	Mass spectrometry
NH ₃ SCR	Selective catalytic reduction of NO _x with ammonia
NMR	Nuclear magnetic resonance
ODH	Oxidative dehydrogenation
ORR	Oxygen reduction reaction
PI	Principal Investigator
PNNL	Pacific Northwest National Laboratory
POSS	Polyhedral oligomeric silsesquioxane
SSITKA	Steady State Isotopic Transient Kinetic Analysis
SSRL	Stanford Synchrotron Radiation Lightsource
STM	Scanning tunneling microscopy
SWIL	Switchable ionic liquid
THF	Tetrahydrofuran
TMA	Trimethyl acetate
TOF	Turnover frequency
XAS	X-ray absorption spectroscopy

Table of Contents

INTRODUCTION	1
Institute for Integrated Catalysis	1
CORE BES CATALYSIS PROGRAM: Low-temperature Catalytic Routes for Energy Carriers via Spatial and Chemical Organization.....	3
Thrust 1: Conversion of Biogenic Molecules in the Presence and Absence of Water	4
Subtask 1.1: Enhancing Activity of Acid-Base and Metal Sites through Ordering in Nanospace – A Novel Approach toward Conversion of Complex Biogenic Feedstocks (Lignin) to Energy Carriers	4
Subtask 1.2: Fundamentals of Acid/Base and Redox Reactions on Metal Oxide Catalysts	9
Thrust 2: Conversion of CO ₂ to Energy Carriers.....	13
Subtask 2.1: Designing Catalysts Using an Energy-Based Approach: Molecular Catalysis for CO ₂ Reduction	13
Subtask 2.2: Multifunctional Catalysts for CO ₂ Activation and Reduction.....	16
Thrust 3: Generation and Conversion of H ₂	20
Subtask 3.1: Fundamental Studies of Water Splitting on Model Multifunctional Photocatalysts	21
Subtask 3.2: Activation of Small Molecules with Bifunctional Ambiphilic Catalyst Complexes.....	23
Subtask 3.3: Modulating Catalysts with an Enzyme-Like Outer Coordination Sphere.....	25
Recognitions and Honors.....	28
Publications and Presentations	30
Journal Covers (2013-2016).....	31
ASSOCIATED BASIC ENERGY SCIENCES PROGRAMS	32

Energy Frontier Research Center: Center for Molecular Electrocatalysis	32
Physical Biosciences Program: Enzymatic Energy Conversion	36
Early Career Program: Combined Capture and Conversion of CO ₂	39
CONNECTIONS TO APPLIED PROGRAMS	42
Catalyst Development for Efficient Biomass Conversion to Fuels	42
Electrochemical Upgrading of Pyrolysis Oil.....	43
Chemical Transformations Initiative	44
Using Theory to Accelerate the Development of CO ₂ Capture Solvent Systems.....	45
Vehicle Emission Control Research	46
STAFF BIOS.....	49

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 CO₂ in the atmosphere. Nearly all these chemicals and energy

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

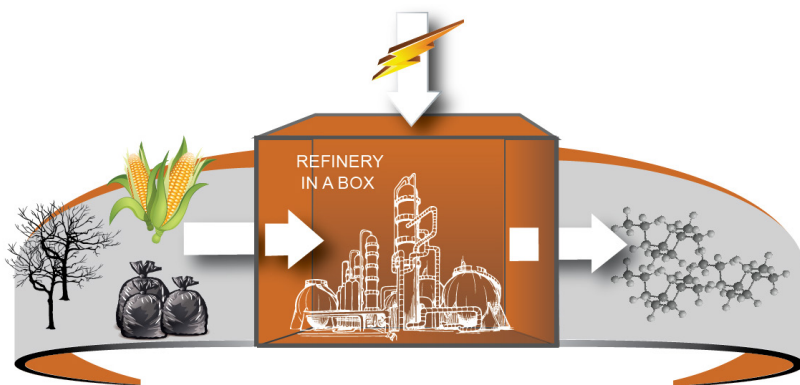
carriers are made using catalysis in at least one of the processing steps. Catalysis is, therefore, not only key to sustainable development, characterized by transition from the current fossil carbon-based energy carriers to a zero-carbon footprint energy future, but it will also secure energy independence.

Institute for Integrated Catalysis

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

Several critical boundary conditions dictate the catalytic chemistries that have to be achieved to develop new technologies that can operate at lower temperatures and pressures, and with higher selectivities. The lower temperatures require (1) operation mostly in condensed phase, (2) catalysts that enable the transformation of molecules with lower energy barriers and higher transition entropies, and (3) efficient transport and separation of molecules. Hydrogen from renewable energy is the critical reactant required to achieve the goal of a carbon-neutral synthesis of hydrocarbon energy carriers.

While the input for these boundary conditions certainly comes from applied problems, new catalysts can hardly be developed through empirical trial-and-error approaches – the space to be explored is simply too large, even when applying the most advanced parallelization technologies. Central to the strategy



of the IIC is, therefore, development of a principal understanding of the catalytic chemistries in three distinctive areas, which lay the basis for breakthroughs toward a zero-carbon-footprint future. These areas are:

- ▶ Storing electric energy in hydrogen (H_2 production takes up 40 percent of direct energy requirements in many reductive petrochemical processes, a chemistry which is a focus of the Center for Molecular Electrocatalysis (CME), an Energy Frontier Research Center (EFRC) at PNNL)
- ▶ Adding hydrogen to oxo-functionalized carbon resources (*i.e.*, biomass components or CO_2 , which store in essence the solar energy in chemical bonds and allow use of existing chemistry and infrastructure)
- ▶ Cleaving and manipulating carbon-carbon and carbon-heteroatom bonds (*i.e.*, ensuring the cleanest energy carriers possible and optimally produced chemicals).

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

CORE BES CATALYSIS PROGRAM:

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

This program focuses on the fundamental understanding of catalytic transformations that utilize common carbon resources, such as bioderived molecules (Thrust Area 1) and CO₂ (Thrust Area 2), and access and activate H₂ (Thrust Area 3) (Figure 1). Our strategy is to explore and understand the molecular and atomistic pathways of selected reactions on catalysts spanning from single-crystal surfaces to molecular complexes. Such fundamental understanding of the elemental steps of reaction sequences enables the knowledge-based design of novel catalysts that operate at lower temperatures and with higher rates than practiced today.

Thrust 1	Thrust 2	Thrust 3
Catalytic conversion of biogenic molecules	Conversion of CO₂ to energy carriers	Generation and conversion of H₂
Subtask 1.1 – Enhancing activity of acid-base and metal sites through ordering in nanospace – A novel approach towards conversion of complex biogenic feedstocks Subtask 1.2 – Fundamentals of acid/base and redox reactions on metal oxide catalysts	Subtask 2.1 – Designing catalysts using an energy-based approach: Molecular catalysis for CO ₂ reduction Subtask 2.2 – Multifunction catalysts for CO ₂ activation and reduction	Subtask 3.1 – Fundamental studies of water splitting on model multifunctional photocatalysts Subtask 3.2 – Activation of small molecules with bifunctional ambiphilic catalyst complexes Subtask 3.3 – Modulating catalysts with an enzyme-like outer coordination sphere

Figure 1. Program Structure showing the three thrust areas and seven subtasks.

We believe we can make rapid progress on our research objectives using an integrated approach enabled by the synergy within our large multidisciplinary team that is created by focusing on the *four crosscutting research themes* that bridge our research areas:

- ▶ Multifunctional catalytic sites or catalytic sites acting in concert
- ▶ Spatially constrained, chemospecific environments of active centers
- ▶ Use of condensed phase to stabilize reactants, intermediates, and products along the catalytic pathway
- ▶ Dynamics and kinetics of charge transfer and the availability of charge-carrying species.

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

Our aim is to address individual reactions of the multistep conversion of polar molecules on surfaces and in the pores of metal oxides as well as on metal nanoparticles arranged to enable reaction cascades. The aim is to develop a better understanding of the role of the metal as well as the acid/base and redox functions as they interact with polar bioderived molecules. The relative stabilization of reactants, intermediates, and products as well as the impact of the local environment; that is, the nature of the sites of the catalyst as well as the steric environments around those sites is being explored. Our goal is to obtain insight into reactions at surfaces in condensed phase as well as their quantitative relation to the analogous reactions at a gas-solid interface. Hydrodeoxygenation and hydroalkylation are the reactions used to exemplify potential routes from lignocellulosic biomass to alkane energy carriers requiring several catalytic functions acting sequentially.

This thrust consists of two subtasks:

- ▶ *Enhancing Activity of Acid-Base and Metal Sites through Ordering in Nanospace – A Novel Approach toward Conversion of Complex Biogenic Feedstocks (Lignin) to Energy Carriers*
- ▶ *Fundamentals of Acid-Base and Redox Reactions on Metal Oxide Catalysts*

Subtask 1.1: Enhancing Activity of Acid-Base and Metal Sites through Ordering in Nanospace – A Novel Approach toward Conversion of Complex Biogenic Feedstocks (Lignin) to Energy Carriers

PI – Johannes Lercher

Co-PIs – Donald M. Camaioni, Donghai Mei

KPs – Nigel Browning, Mirek Derewinski, John Fulton, Jian Zhi Hu, Andreas Jentys (Technical University of Munich), 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 hydrodeoxygenation (HDO) 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. We emphasize understanding of the principal chemistry, and we are gradually deepening that by studying more complex representatives of the principal monomers, as well lignin itself, in the envisioned chemistries and to synthesize new generations of catalysts, basing the directions on the physicochemical insight realized by these studies.

Hydrogenation and hydrodeoxygenation of lignin components.

Concertedly acting catalysts containing acid and metal functions are being explored in aqueous and apolar phases to understand the elementary steps of hydrogenation and HDO of phenol. It has been shown that the rate-determining step is the dehydration of the intermediately formed cyclohexanol. The dehydration of alcohols catalyzed by hydronium ions in zeolites with sufficiently large pores to adsorb the alcohols is faster than in the homogenous aqueous phase, whereas dehydration is slower in mesoporous solids. As an example, Figure 2 shows an Arrhenius plot of the turnover frequencies (TOFs) for dehydration of aqueous cyclohexanol. They span more than three orders of magnitude and are seen to increase with decreasing size of the zeolite pores, except chabasite for which the pores are too small for cyclohexanol to enter. The lower activation barrier in tighter confines is partly offset by a concomitantly smaller entropy gain. While the intrinsic activation barrier for dehydration by aqueous hydronium ion is very similar to the intrinsic barrier for zeolite HBEA, the entropy of activation is less. This is due to the favorable adsorption of cyclohexanol molecules in HBEA pores leading to pore saturation with approximately 5 cyclohexanol and 20 water molecules per unit cell at reaction temperatures (160–200 °C). This effectively increases the probability for hydronium ion to associate with the alcohol in the pore compared to in the open solution. H/D kinetic isotope effects show that the cleavage of a C_β-H bond in the carbenium-ion intermediate is partly rate

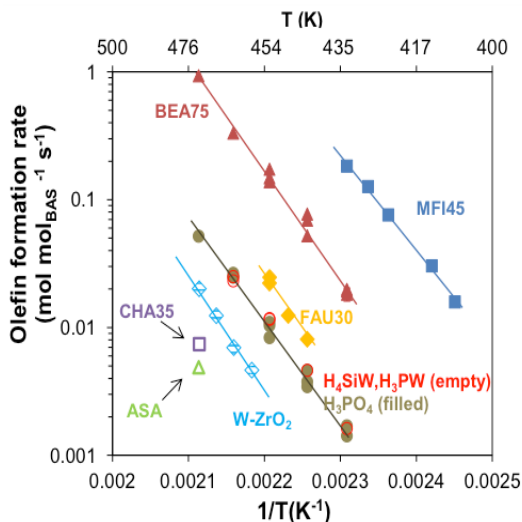


Figure 2. Temperature dependence of the TOFs for dehydration of aqueous cyclohexanol on different acid catalysts. H₃PW₁₂O₄₀ (H₃PW), H₄SiW₁₂O₄₀ (H₄SiW), amorphous silica-alumina (ASA), zeolites (BEA, CHA, FAU, MFI).

limiting both in the aqueous phase and in the confines of the micro- and mesoporous acids. However, isotopic exchange experiments using H_2^{18}O demonstrate that the dehydration occurs predominantly by an E1-type elimination path via formation of a metastable carbenium-ion-like intermediate.

The state of supported metal during catalysis in water. The impact of water on the supported metal has been explored using X-ray absorption spectroscopy (XAS). We followed the state of Pd and Ni catalysts under reaction conditions. We have shown that both metals interacted only weakly with water in the presence of 30 bar H_2 . We showed that under typical operating conditions with temperatures up to 200 °C, the metal surfaces were in equilibrium with H_2 . The high partial pressure under H_2 kept the metals in a reduced state even in acidic solutions (0.5 wt% HP_3O_4 or 15 wt% $\text{CH}_3\text{CO}_2\text{H}$) at 200 °C. In the case of Pd, the lack of the influence of water is best demonstrated in the Pd-Pd distances, indicating the presence of sorbed hydrogen and Pd hydrides. Extended X-ray absorption fine structure (EXAFS) of carbon-supported Pd nanoparticles were indistinguishable in the presence or absence of liquid water at 200 °C (30 bar H_2). It has also been shown that the concentration of H in Pd subtly depends on the presence of organic reactants competing for H_2 . This demonstrates that neither the Pd particles nor the H_2/Pd ratio in the nanoparticle are influenced by water, but dynamically adapt to reaction conditions. Similarly, Ni on sulfonated carbon and zeolite (HZSM-5) supports was rapidly reduced from its oxidized state after the onset of the reaction and remained reduced even after substantial concentrations of acid had been admitted. In contrast, Ni supported on SiO_2 was not stable in a fully reduced Ni^0 state. The presence of liquid water enables the formation of Ni^{II} phyllosilicate, which is more stable, *i.e.*, difficult to reduce, than either $\alpha\text{-Ni}(\text{OH})_2$ or NiO .

Effect of liquid water on zeolite framework sites and lattice stability and catalytic activity. The degree of substitution of Si^{4+} by Al^{3+} in zeolite framework determines the concentration of BAS. As the location of these Al-tetrahedral sites will influence the subtle steric requirements for the catalyzed reactions, quantitative information about location of Al T-sites in the framework is critical to rationalize catalytic properties and to design new catalysts. Using a combination of EXAFS analysis and ^{27}Al *in situ* magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) spectroscopy supported by density functional theory (DFT) based molecular dynamics simulations, a first quantitative distribution of Al^{3+} in the HBEA zeolite framework has been attained. This combination of spectroscopies, in particular NMR and EXAFS, as well as transmission electron microscopy, showed that water damaged the zeolite, producing structural defect sites; *i.e.*, Si-O and Al-O bond cleavage leading to a loss of lattice integrity. We determined that hot liquid water

treatment decreased the framework crystallinity primarily via hydrolysis of siloxane (Si–O–Si) groups. The combined data suggest a three-step mechanism in which initially, the framework crystallinity is decreased via cleavage of Si–O bonds along polymorph stacking faults and intergrain boundaries. With prolonged exposure, amorphization occurs via hydrolysis of surface Si–OH groups propagating inward through the zeolite lattice. In parallel, cracks propagate within the crystalline microdomains along paths through specific T–O–T groups. The exposure to hot water reduced the concentration of BAS, but the activity of the sites remained unchanged (see Figure 3). This suggests that while water treatment does not remove Al from its coordination in a local silica matrix, access to the catalytic Al sites is reduced.

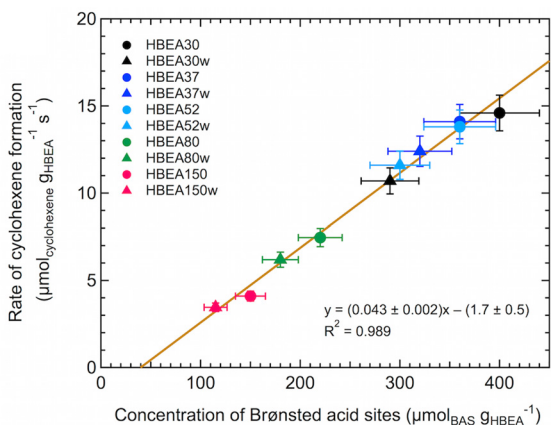


Figure 3. The rate of dehydration of aqueous cyclohexanol over HBEA at 160 °C as a function of the concentration of BAS. Names with a “w” suffix denote the HBEA sample was contacted with 160° C water for 48 h before using for catalysis.

Hydroalkylation to adjust the size of alkanes. Zeolites are effective in forming C–C bonds when the pore size allows the transition state. Phenol and substituted phenols were hydroalkylated and hydrodeoxygenated to bicycloalkanes; for example, in a tandem reaction over metal nanoclusters supported on HBEA below 523 K in the presence of water. The HBEA-supported Pd catalyst (metal-acid ratio: 1:22 mol/mol) optimally balances the competing rates of metal catalyzed hydrogenation as well as of solid acid-catalyzed dehydration and carbon-carbon coupling to combine HDO and alkylation dimerization of phenol derivatives to C₁₂–C₁₈ bicycloalkanes in a single reaction sequence. Phenol selectively reacts with the in-situ-generated cyclohexanol or cyclohexene on BAS (see Figure 4). The acid-catalyzed alkylation of phenol with alcohol intermediates and alcohol dehydration are parallel reactions, which are subtly influenced by the competing hydrogenation reactions as well as by the presence of water as solvent. MAS NMR of absorbed species and molecular modeling indicate that phenol and cyclohexanol enrichment in the large pores of zeolite HBEA is critical for high activity and hydroalkylation selectivity of large-pore

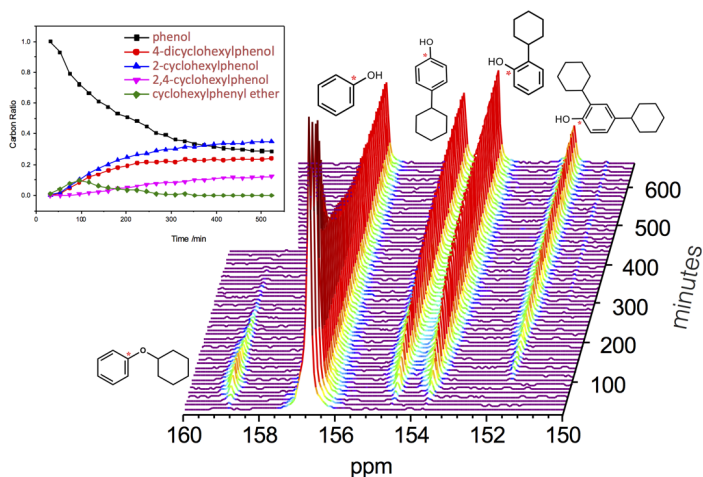


Figure 4. *In situ* ^{13}C MAS NMR spectra of the alkylation of phenol-1- ^{13}C by cyclohexanol in decalin catalyzed by HBEA at 415 K.

zeolitic materials, which is absent with other solid acids such as heteropoly acids.

Cleavage of ether bonds. Ni-catalyzed routes to selectively cleave ether bonds of (lignin-derived) aromatic ethers and to hydrogenate the oxygen containing intermediates have been mechanistically explored. The C–O bonds of α -O-4 and β -O-4 linkages are cleaved by hydrogenolysis on Ni, while the C–O bond of 4-O-5 is cleaved via parallel hydrogenolysis and hydrolysis. The difference is attributed to the fact that the $\text{C}_{\text{aliphatic}}$ -O-4 linkages can be further hydrogenolyzed, while phenol (hydrolysis from 4-O-5 linkage) is hydrogenated to produce cyclohexanone and cyclohexanol under conditions investigated. The apparent energies of activation vary proportionally with the bond dissociation energies, e.g., $E_a(\alpha\text{-O-4}) < E_a(4\text{-O-5})$. In the α -O-4 and 4-O-5 ether bonds, C–O bond cleavage is the rate-determining step with the reactants competing with hydrogen for active sites, leading to a maximum reaction rate as a function of the H_2 pressure. For the very fast rate of C–O bond cleavage for the α -O-4 linkage, increasing H_2 pressures increases the rate-determining product desorption under conditions tested. The substitution of the aromatic ring induces remarkable differences indicating that the local arrangement of the ether bonds at the metal surface depends subtly on steric effects of the substituents and controls reactivity and selectivity.

Deconstruction and HDO of lignin. Mechanistic aspects of deconstruction and hydrodeoxygenation of an organosolv lignin were explored using zeolite (HZSM-5 and HBEA) and SiO_2 supported Ni catalysts. The lignin, consisting of

seven to eight monolignols (mainly guaiacyl, syringyl and phenylcoumaran), randomly interconnected through ether bonds was deconstructed and converted to substituted alicyclic and aromatic hydrocarbons with 5 to 14 carbon atoms. Full conversion was achieved at 593 K and 20 bar H₂ in hexadecane solvent. In-situ IR spectroscopy was used to follow the changes in lignin constituents during reaction. The reductive catalytic deconstruction of organosolv lignin started with the hydrogenolysis of aryl alkyl ether bonds, followed by hydrogenation of the aromatic rings to cyclic alcohols. Oxygen was removed from the alcohols via dehydration on Bronsted acid sites to cyclic alkenes that were then further hydrogenated. Thus, using Ni supported on zeolites (HZSM-5 and HBEA), which have strong BAS, gave the highest selectivity to alkanes. The HBEA supported catalyst showed increased selectivity to alkanes with carbon numbers in excess of C₉ due to alkylation reactions being favored in pores that are sufficiently large to accommodate the transition state of the reaction.

Subtask 1.2: Fundamentals of Acid/Base and Redox Reactions on Metal Oxide Catalysts

PI – Zdenek Dohnálek

Co-PIs – David Dixon (University of Alabama), Enrique Iglesia (University of California, Berkeley), Bruce Kay, Roger Rousseau, Yong Wang (Washington State University)

KPs - Feng Gao, Jian Zhi Hu, Jun Liu, Huamin Wang

A primary goal of this subtask 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, thus allowing 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. This approach involving model systems of different complexity as illustrated in Figure 5. Several recent examples highlighting this approach are summarized below.

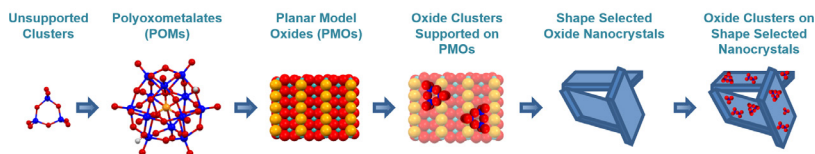


Figure 5. Subtask 1.2 focuses on the acid/base and redox chemistry of structurally well-defined model oxide systems. The investigators involved in different parts of this project are listed below each panel and illustrate the collaborative efforts of this team.

Structure/function of redox-active supported VO_x ODH catalysts. We have been studying supported VO_x/TiO_2 -Rod catalysts using ^{51}V MAS NMR at high field using a sample spinning rate of 55 kHz. The superior spectral resolution allows for the observation of at least five vanadate species (Figure 6). The assignment of these vanadate species was carried out by quantum chemical calculations of ^{51}V NMR chemical shifts of model V-Surface structures. Methanol oxidative dehydrogenation (ODH) was used to establish a correlation between catalytic activity and the various surface V-Sites. It is found that monomeric V-Species are predominant at low vanadium loadings with two ^{51}V NMR peaks observed at about -502 and -529 ppm. V-Dimers with two bridged oxygens result in a peak at about -555 ppm. Vanadate dimers and polyvanadates connected by one bridged oxygen atom between two adjacent V atoms resonate at about -630 ppm. A positive correlation is found between the V-Dimers giving rise to the -555 ppm peak and the ODH rate, and an even better correlation is obtained by including V-Monomer contributions (Figure 6). This result suggests that surface V-Dimers related to the -555 ppm peak and monomers are the primary active sites for the methanol ODH reaction. Furthermore, a portion of the V-Species is found to be invisible to NMR and the level of such invisibility increases with decreasing V-Loading levels, suggesting the existence

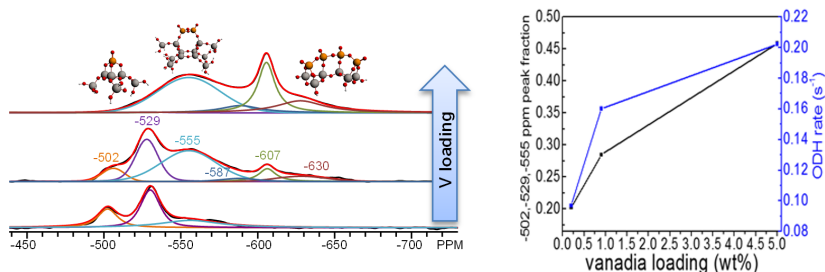


Figure 6. (Left) Quantification of V species using ^{51}V MAS NMR assisted by quantum chemical calculations; (Right) A positive correlation between surface V-dimers/monomers and methanol oxidative dehydrogenation.

of paramagnetic V-Species at the surface. These paramagnetic V-Species are also found to be much less active in methanol ODH.

Cerium oxide-induced intercalation of oxygen on supported graphene.

Cerium oxide is an important catalytic material known for its ability to store and release oxygen, and as such, it has been used in a range of applications, both as an active catalyst and as a catalyst support. Here, we investigate the growth of ceria nanoclusters and their oxygen storage/release properties on single-layer graphene (Gr) on Ru(0001) with a view towards fabricating a stable system for model catalysis studies. We find that the ceria nanoparticles are of the $\text{CeO}_2(111)$ -type and are anchored at the intrinsic defects of the Gr surface. The ceria clusters on Gr display a remarkable stability against reduction in ultrahigh vacuum up to 900 K, but some sintering of clusters is observed for temperatures > 450 K. The evolution of the cluster size distribution suggests that the sintering proceeds via a Smoluchowski ripening mechanism, *i.e.* diffusion and aggregation of entire clusters.

To follow the oxygen store and release properties of the CeO_x clusters, we examined their interaction with oxygen at elevated temperatures (550 – 700 K). Under oxidizing conditions ($\sim 10^{-7}$ Torr of O_2), oxygen intercalation under the Gr layer is observed (Figure 7). Time dependent studies demonstrate that the intercalation starts in the vicinity of the CeO_x clusters and extends until a completely intercalated layer is observed. Atomically resolved images further show that oxygen forms $p(2 \times 1)$ structure underneath the Gr monolayer. Temperature dependent studies yield an apparent kinetic barrier for the intercalation of 1.2 eV. This value correlates well with the theoretically determined value for the reduction of small CeO_2 clusters reported previously. At higher temperatures, the intercalation is followed by a slower etching of the intercalated Gr. Vacuum annealing of the intercalated Gr leads to the formation of carbon monoxide, causing etching of the Gr film, demonstrating that the

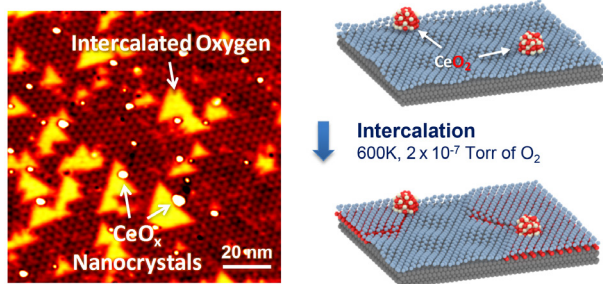


Figure 7. (Left) High resolution scanning tunneling microscopy image of ceria nanoclusters supported on Gr monolayer on Ru(0001) illustrating the oxygen intercalation underneath the Gr film in O_2 background of 2×10^{-7} Torr at 600 K. (Right) Schematic view of the O_2 intercalation process.

spillover of oxygen is not reversible. In agreement with previous studies, no intercalation is observed on a complete Gr monolayer without CeO_x clusters, even in the presence of a large number of point defects. These studies demonstrate that the easily reducible CeO_x clusters act as intercalation gateways capable of efficiently delivering oxygen underneath the Gr layer. Our future studies will focus on catalytic studies on this model catalytic system.

Theoretical studies of strong metal support interactions. Reducible oxides, such as titanium dioxide and cerium dioxide, can play a critical role in catalysis either directly taking part in reactivity or by modulating the reactivity of metal particles supported on these oxides.

We have undertaken ambitious theoretical studies to clarify the role of reducible oxides in catalysis with a specific goal of understanding how excess charge carriers, generated by defects such as oxygen vacancies, impact surface reactivity. In a recent series of studies, we probed the metal particle/reducible oxide interactions, by employing DFT-based AIMD on Au_{20} - Au_{50} supported on reducible oxide (rutile $\text{TiO}_2(110)$ and $\text{CeO}_2(111)$) to explicitly account for finite temperature effects and the role of excess surface charge in the metal oxide.

It was found that the reduction level of the support has a strong influence on the charge of the metal nanoparticle and the nature of the catalytic active sites. On strongly oxidized supports such as CeO_2 on oxidized TiO_2 single Au^+ cations can form and be active for reactions like CO oxidation. These Au^+ -cations are catalytic only when they act as transient species that extrude from the nanoparticle onto the support, perform the reaction, and subsequently reintegrate back into the nanoparticle, see Figure 8.

On the other hand, these species can also serve as a route for catalyst deactivation under reducing conditions, such as partially reduced TiO_2 where they can inhibit access to either oxygen vacancy or adatoms sites. Contrary to the ubiquitous picture of a statically charged metal cluster performing catalysis, while the oxide being only a passive spectator, we find that charge transfer occurs dynamically throughout the catalytic cycle with electrons shuttling back and forth between the metal and the support. Due to this fact, the redox state of the support has a surprising influence

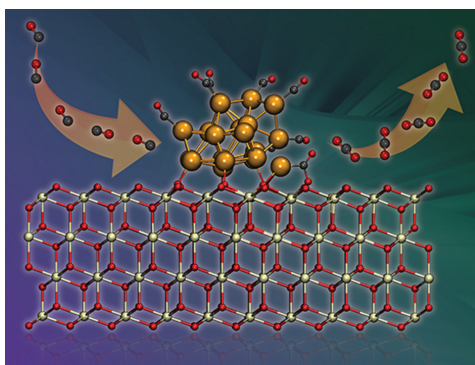


Figure 8. In situ CO oxidation on CeO_2 induces single Au^+ sites that catalyze the reaction.

on reaction barriers for redox reactions and leads to a rich phase diagram of mechanistic pathways as a function of temperature and pressure. The overall result is that the same reaction can be catalyzed by either single atoms, and/or a cluster perimeter site, depending on the reduction level of the support.

Thrust 2: Conversion of CO₂ to Energy Carriers

Carbon-neutral fuels are essential to the environmental sustainability, and, as such, the utilization of carbon dioxide as a renewable resource in a carbon-neutral economy is highly desirable. To address these challenges, research in this thrust focuses on carbon dioxide conversion to viable energy carriers such as methanol. The primary objective is to develop a fundamental understanding of homogeneous and heterogeneous carbon dioxide conversion on structurally well-defined catalytic systems and to design novel catalysts that take synergistic advantage of the mechanistic insights acquired from homogeneous and heterogeneous catalysis. The thrust consists of two subtasks.

This thrust consists of two subtasks:

- ▶ *Designing Catalysts Using an Energy-Based Approach: Molecular Catalysis for CO₂ Reduction*
- ▶ *Multifunctional Catalysts for CO₂ Reduction*

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 and electrocatalytic carbon dioxide reduction in homogeneous and heterogeneous environments.

Subtask 2.1: Designing Catalysts Using an Energy-Based Approach: Molecular Catalysis for CO₂ Reduction

PI – Aaron Appel

Co-PIs – Morris Bullock, John Linehan, and Eric Wiedner

The aim of Subtask 2.1 is to develop the fundamental understanding of how to design catalysts for the reduction of CO₂ to fuels, such as methanol. Towards this goal, the overall conversion is broken down into steps consisting of each net H₂ addition as illustrated in Figure 9, and the critical design principles for these steps are investigated using molecular complexes as catalysts. Our approach is based upon minimizing energy mismatches between catalytic intermediates by

understanding the free energies for fundamental bond-forming and bond-breaking reactions and controlling those energies through synthetic modification as schematically shown in Figure 10.

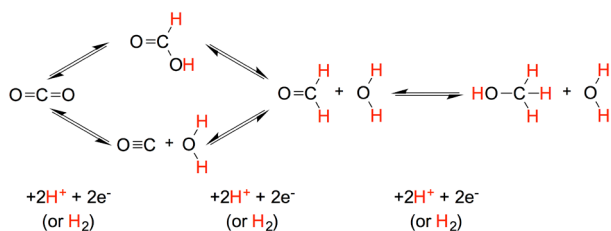


Figure 9. Subtask 2.1 focuses on molecular catalysis for the individual steps in the production and utilization of fuels from CO_2 .

For the hydrogenation of CO_2 to formate, we have previously demonstrated that cobalt hydride complexes are capable efficient hydride transfer to CO_2 , however, regeneration of these complexes is challenging due to the extremely low acidity of the H_2 addition product. Alternate nonprecious metal complexes are needed to develop an understanding of fundamental design principles to overcome this limitation. Two recent areas of investigation include the use of catalysts based on nickel or copper.

In organic solvents, many metal hydrides are incapable of transferring H^- to CO_2 to generate formate due to having an inadequate hydricity, or an insufficiently weak $\text{M}-\text{H}$ bond towards liberation of H^- . However, the relative hydricities change substantially from organic solvents to water. To quantify the effects of the change in solvent upon the hydricities for different complexes and formate, we developed improved estimates of the thermochemical constants that describe the free energy of formation of the hydride ion in aqueous solution. Previous estimates were based upon a variety of different assumptions and standard state conditions, and therefore they varied remarkably. By publishing a self-consistent set of constants to describe the stabilities of H^+ , H^\bullet , and H^- in aqueous solution, we aimed to enable greatly simplified prediction of reactivity based on reported data from multiple research groups.

Using our updated thermochemical constants, results with $\text{HNi}(\text{dmpe})_2^+$ in water show that the hydride-donating power of this

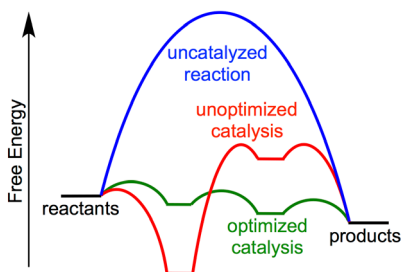


Figure 10. Catalytic performance can be improved by removing energy mismatches between catalytic intermediates, which are quantified using thermochemical studies.

complex changes dramatically between an organic solvent and water, improving from 7 kcal/mol unfavorable in acetonitrile to 8 kcal/mol favorable in water for transferring a hydride to CO₂ to generate formate (Figure 11). These results have paved the way for developing catalysts for the hydrogenation of CO₂ in water.

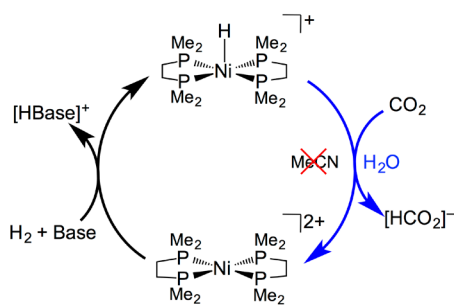


Figure 11. A nickel complex, $\text{HNi}(\text{dmpe})_2^+$, was used in the reduction of CO₂ by exploiting the increased hydricity in water relative to organic solvents.

Catalysts based on copper are of interest for CO₂ reduction, but few effective molecular systems have

been designed. Copper hydride complexes have been used for stoichiometric reactions with CO₂, as well as many other catalytic transformations, but no well-defined complexes have been used for the hydrogenation of CO₂. We have now reported the hydrogenation of CO₂ using a triphosphine-copper complex (Figure 12). One unusual aspect of the catalytic transformation with this complex is that base coordination appears to facilitate catalysis, rather than hinder it. Ongoing experimental and theoretical studies are aimed at addressing the role of the base coordination as well as the mechanism for the activation of H₂.

The catalytic hydrogenation of C=O bonds, such as those in formaldehyde and ketones, represents a critical step in the reduction of CO₂ to MeOH. By using multifunctional complexes of molybdenum, we aim to control the heterolysis of H₂ to generate complexes with tunable acidity and hydricity. In one recent

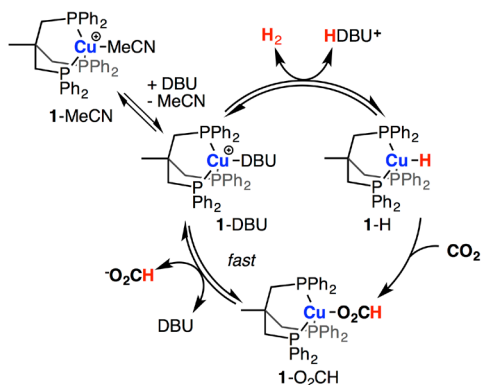


Figure 12. We have reported the first well-defined copper complex for the hydrogenation of CO₂ to formate.

report, the reactivity of a multifunctional molybdenum complex was shown to be substantially influenced by the incorporation of the additional functionality, relative to the monofunctional analog.

While the majority of the focus of Subtask 2.1 is on the formation of fuels from CO₂, the efficient use of these fuels is equally important. The energy stored in alcohols can be efficiently recovered using fuel cells, but widespread

implementation will require the development of inexpensive electrocatalysts. In our research, we have shown that nickel complexes containing pendant amines are effective for the oxidation of formate, and we have now extended the use of this series of catalysts to the oxidation of alcohols (Figure 13). These complexes are the first nonprecious metal molecular electrocatalysts for this transformation.

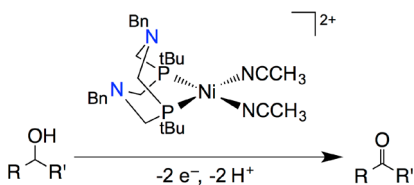


Figure 13. The electrocatalytic oxidation of alcohols has been demonstrated for the first time with a molecular complex of a nonprecious metal.

Subtask 2.2: Multifunctional Catalysts for CO₂ Activation and Reduction

PI – Roger Rousseau

Co-PIs – Zdenek Dohnálek, Vassiliki-Alexandra Glezakou, David J. Heldebrant, Abhijeet Karkamkar, Janos Szanyi

Experimental and theoretical capabilities are combined to investigate in quantitative detail the mechanistic chemistry of catalytic carbon dioxide conversion to value-added fuels (methane, methanol, and C₂ oxygenated hydrocarbons) by well-characterized multifunctional catalysts in media including vapor phase, liquid phase, and ionic liquid environments. The overall structure of this Subtask is summarized in Figure 14.

The primary goals of this project are:

- ▶ Identify the chemical functionalities required by a catalyst to perform the desired transformations of carbon dioxide.
- ▶ Determine how these functionalities can be tuned by change of catalyst structure or support to optimize catalyst activity and selectivity.

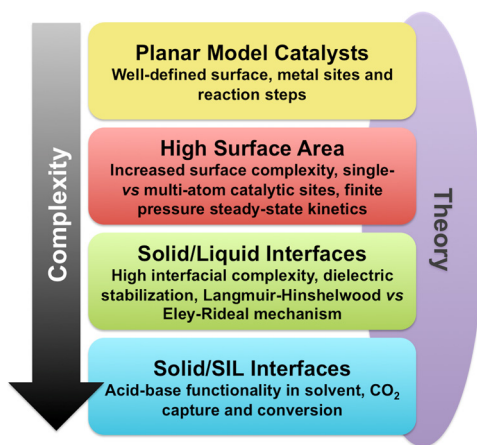


Figure 14. Relationships between activities in Subtask 2.2.

- ▶ Evaluate the role of chemical environment on the mechanistic pathways.
- ▶ Systematically, build catalysts using this information and test them towards carbon dioxide conversion.

High surface area model catalysts. Experimental and theoretical capabilities are combined to investigate in quantitative detail the mechanistic chemistry of catalytic CO₂ conversion to value-added fuels (methane, methanol, and C2 oxygenated hydrocarbons) by well-characterized multifunctional catalysts in media including vapor phase, liquid phase, and ionic liquid environments.

The catalytic reduction of CO₂ requires bifunctional catalysts as both CO₂ and H₂ need to be activated prior to their reaction. We have shown that in oxide-supported metal catalysts (Pd/- and Ru/ γ -Al₂O₃) the metal component was responsible for the activation (dissociation) of H₂, while the oxide support activated CO₂ by binding it as bicarbonate. The focus of our work has been the understanding of the mechanistic consequences of metal dispersion in the heterogeneous catalytic CO₂ reduction over Pd/- and Ru/ γ -Al₂O₃ catalysts. To this end we have carried out detailed kinetic and transient DRIFT spectroscopy studies. We also conducted SSITKA/operando FTIR measurements on Pd/ γ -Al₂O₃ catalysts in order to identify the nature and the kinetics of surface species present on the catalysts under steady state conditions. Transient DRIFTS measurements showed when hydrogen was present on the metal, adsorbed CO formed on the metal while the oxide remained saturated with bicarbonates. This was explained by the ready reaction between bicarbonates (on the oxide) and atomic H (on the metal) that initially formed formate species at the metal/oxide interface and was further reduced to CO. When H₂ was introduced into the CO₂/He gas mixture bicarbonates were rapidly converted to formates, and the formates to CO, and some of the CO to CH₄ (Figure 15a).

The key difference that ultimately seems to control the product selectivity is the amount of available activated hydrogen. At high metal dispersion the availability of H is limited, therefore the product selectivity is shifted toward CO. On the other hand, on large metal particles large pool of active H is available, allowing further reduction of the initially formed CO to produce CH₄ with high selectivity.

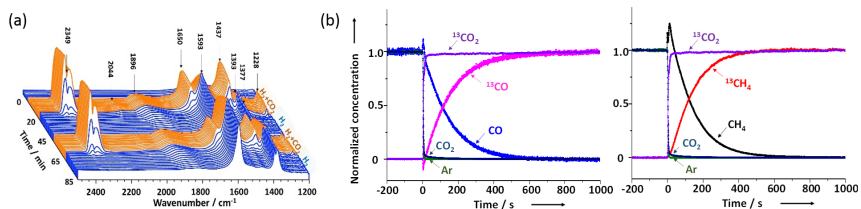


Figure 15. a. DRIFT spectra collected during alternate switching between H₂ and CO₂+H₂ over 0.5% Pd/Al₂O₃ at 513 K. b. Normalized product concentrations during SSITKA experiments as the ¹²CO₂+H₂ flow is switched to ¹³CO₂+H₂ over a 5% Pd/Al₂O₃ catalyst at 523 K.

The analysis of the SSITKA/operando FTIR data shows (Figure 15b) that the disappearance rate of $^{12}\text{CH}_4$ from the reactor (measured by MS) is identical to the disappearance rate of adsorbed ^{12}CO from the metal surface after the $^{12}\text{CO}_2+\text{H}_2$ gas mixture was switched to $^{13}\text{CO}_2+\text{H}_2$, clearly substantiating the role of CO as an intermediate in the path to CH_4 formation. The rate-determining step in the CH_4 formation was determined to be the C-O bond breaking, which was hydrogen assisted, as evidenced by the inverse H/D kinetic isotope effect. Modulation excitation experiments identified monodentate formates and formyl species as key intermediates in CH_4 formation.

In summary, our current understanding is that CO_2 conversion on single site catalysts in the vapor phase proceeds via bi-carbonates eventually leading to CO, which can be hydrogenated to methane.

Synthesis and evaluation of single-site catalysis for CO_2 conversion. We synthesized stable homotopic, single-site catalysts supported on MCM-41 by a combination of sol-gel and surface organometallic chemistry (SOMC). These systems are ideal for the study of CO_2 and H_2 reactivity toward a metal site as a function of the environment. We synthesized several versions of MCM-41-supported ligands and characterized them by multinuclear NMR, FTIR, and MS.

We demonstrated that a variety of metal atoms (Ni, Cu, Ru, and Pd) could be anchored on these ligands. In addition to incorporation of single metal sites we have been able to incorporate multi-nuclear clusters of metals. We have devised and synthesized monomeric, dimeric, trimeric, and tetrameric clusters that have been incorporated in high surface area mesoporous silica with high degree of control. Structural characterization of these catalytic materials has shown desirable properties such as high surface area, high degree of porosity, and high thermal stability. In tetrahydrofuran (THF), for example, catalytic reduction studies show that CO_2 conversion proceeds to formate at low temperature (60°C) with activity comparable to that of the unsupported organometallic catalyst alone. This demonstrates *that we are able to design and synthesize homotopic catalysts by wet chemical means, which can preserve the functionality of an organometallic analogue.*

Reactivity in liquids. The concept and preliminary results that led to the BES Early Career Award for Heldebrant were a component of Subtask 2.2. Key findings in Subtask 2.2 were that switchable ionic liquids (SWILs) could be used to not only capture CO_2 , but also to aid the reduction of captured CO_2 in solution using molecular catalysts used in Subtask 2.1, and functionalized poly-sesquioxane (POSS) clusters designed to mimic the homogeneous catalysts, see Figure 16. Key findings were that alkylcarbonates (made from the reaction of diazabicyclo[5.4.0]-undec-7-ene (DBU), and an alcohol) could be hydrogenated to alkylformate in one pot. This result is only a single hydrogenation reaction short of achieving a low-temperature methanol synthesis; a reaction

which can be performed under mild conditions but requires distillation of methylformate. Conditions for the reductions were 140 °C and 20 atm of H₂ with no added CO₂ pressure. Here, it was discovered that C-O cleavage could be promoted by esterification of the produced DBU formate (with the liberated alcohol from the hydrogenation step), yielding alkylformate and water, releasing the base.

Our current hypothesis is that alkylcarbonate is more likely to be reduced in solution provided that a cationic single hydrogenation catalyst be used. As such, these conversions are ideal for single metal sites and we were able to synthesize novel catalysts to reproduce these conversions based on several classes of POSS-based complexes which consisted of POSS tethered organometallics, and supported single atom Ru₂⁺ on amorphous silica, Figure 17.

In this way, we have translated knowledge directly from homogeneous catalysts to design homotopic heterogeneous analogues.

Simulation and theory. Modern methods for computing reaction energetics at the *ab initio* level of theory are on the cusp of being able to address reactivity in chemically complex environments taking into account both energy and entropy beyond simple harmonic models.

We have examined, via *ab initio* molecular dynamics, the free energy associated with the reactivity of a complex solid/multicomponent liquid interface: anorthite (100) surfaces with water-bearing supercritical CO₂, Figure 18. From this study, we determined that even trace amounts of water in sc-CO₂, ~10⁻⁴ % mol, can

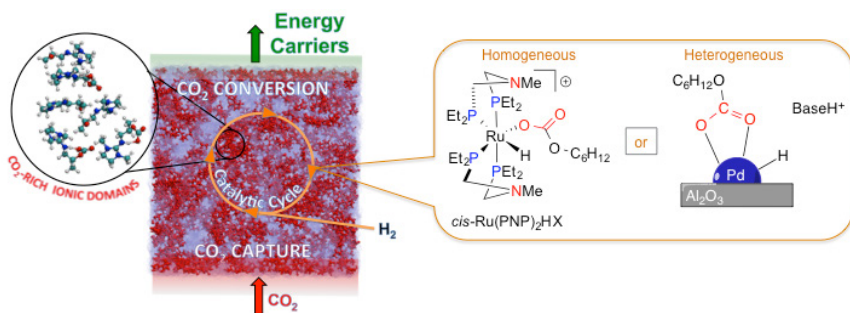


Figure 17. Working hypothesis for alkylcarbonate reduction in solution using novel single metal catalysts (Pd, Ru).

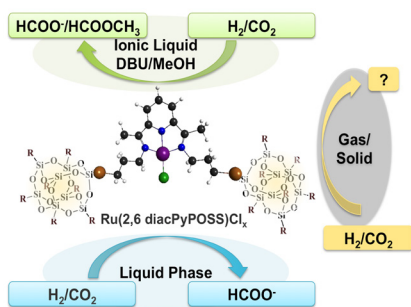


Figure 16. Integration of Subtasks 2.1 and 2.2 will be realized by coupling CO₂ capture and conversion in SWILs bearing functionalized POSS clusters.

lead to formation of a stable water layer on even a weakly hydrophilic surface. The formation of this layer radically changes the surface, leading to the facile formation of cation vacancies and carbonates via direct CO_2 reaction with the surface.

These results underscore *the complexity of reactivity at solid-liquid interfaces, where species concentrations radically differ from the bulk leading to unique reaction environments. CO_2 hydrogenation will produce water, and even in “dry solvents” this can result in a wet environment at the interface where catalysts are anchored and carbonate formation is highly favorable.*

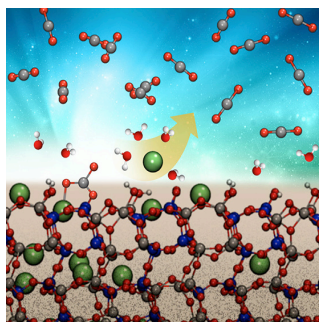


Figure 18. Free-energy requirements for vacancy formation of a silicate support as a function of water concentration.

Thrust 3: Generation and Conversion of H_2

This thrust explores fundamental aspects of the synthesis and use of H_2 as a key component of sustainable synthesis of energy carriers. The three subtasks span from photocatalytic water cleavage via the heterolytic cleavage of molecular hydrogen by multifunctional catalysts to a bioinspired H^+ reduction and oxidation using bioinspired catalysts. Hydrogen formation from water notably in the absence of bulk water as well as the activation by sterically well-defined Lewis acid/base pairs (frustrated Lewis acid/base pairs) and the use of H^- and H^+ for hydrogenation reactions. As a special aspect, we explore the role of H^+ carriers and of the local peptide environment (outer coordination sphere) on the activity of a central site.

This thrust consists of three subtasks:

- ▶ *Fundamental Studies of Water Splitting on Model Multifunctional Photocatalysts*
- ▶ *Activation of Small Molecules with Bi-functional Amphiphilic Catalyst Complexes*
- ▶ *Modulating Catalysts with an Enzyme-Like Outer Coordination Sphere*

Subtask 3.1: Fundamental Studies of Water Splitting on Model Multifunctional Photocatalysts

PI – Michael Henderson

Co-PIs – Zdenek Dohnálek, Gregory Kimmel, Igor Lyubintsev, Roger Rousseau

KP – Vassiliki-Alexandra Glezakou, Nikolai Petrik

The goal of this subtask is to provide fundamental insight into multifunctional heterogeneous catalysts used for water splitting. We focus on determining the interplay between a photocatalyst that converts light into charge carriers and a supported co-catalyst that uses the charge carriers to catalytically convert water into H_2 and/or O_2 . Ruthenium dioxide has emerged as a model co-catalyst material in the water-splitting literature. Using ultrahigh vacuum model systems and theoretical modeling, we follow the kinetics and energetics of key mechanistic steps in water splitting are affected by a spectrum of redox conditions on model single-crystal $RuO_2(110)$ surface. Our recent advances towards mechanistic understanding of thermal and photochemical transformations on $TiO_2(110)$ and $RuO_2(110)$ surfaces are highlighted below.

Water reactions with reduced, stoichiometric, and oxidized $RuO_2(110)$ surfaces. In these studies we employed stoichiometric (s-), reduced (r-), and oxidized (o-) $RuO_2(110)$ surfaces and studied water adsorption, dissociation, and diffusion, Figure 19, using time-lapsed scanning tunneling microscopy and DFT calculations. Our studies on s- $RuO_2(110)$ show that water monomers become mobile above ~ 240 K and form dimers which are immobile below 273 K. More importantly, we find that the mobile water dimers dissociate readily to form Ru-bound H_3O_2 and hydroxyl species (HO_b) on O_b rows, $(H_2O)_2 + O_b \rightarrow H_3O_2 + HO_b$. The onset for diffusion of H_3O_2 on s- $RuO_2(110)$ is observed at ~ 273 K, indicating a significantly higher diffusion barrier than that for water monomers. The experimentally determined diffusion barriers are in agreement with those obtained from the DFT calculations. The observed behavior is compared and contrasted with that observed for water on isostructural rutile $TiO_2(110)$ where both molecularly-bound monomers and dimers are in equilibrium with their

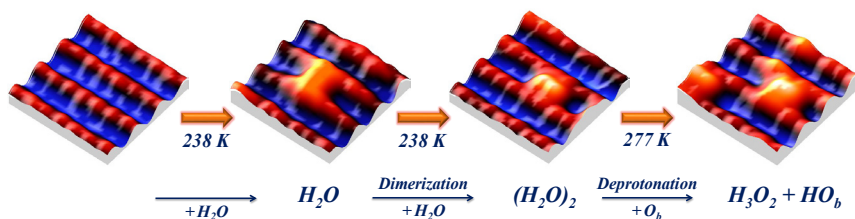


Figure 19. A sequence of high-resolution scanning tunneling microscopy images illustrating the water dimerization-induced deprotonation on $RuO_2(110)$ surface.

deprotonated configurations. In contrast with $\text{TiO}_2(110)$, the larger separation of Ru atoms induces the segmentation of water chains at high water coverages. On slightly oxidized o- $\text{RuO}_2(110)$, water molecules react with oxygen adatoms (O_a 's) on Ru rows and form pairs of Ru-bound terminal hydroxyl (HO_t) groups which can reversibly dissociate back to a water molecule and O_a , $\text{H}_2\text{O} + \text{O}_a \rightleftharpoons 2\text{HO}_t$. We have also followed along- and across-row diffusion of isolated water molecules on both slightly, and heavily oxidized o- $\text{RuO}_2(110)$ by following the position of hydroxyl pairs. On r- $\text{RuO}_2(110)$, we find that water molecules readily dissociate at bridging oxygen vacancies (V_O 's) and form HO_b groups, $\text{H}_2\text{O} + \text{V}_\text{O} + \text{O}_b \rightarrow 2\text{HO}_b$. The atomically-detailed, quantitative assessment of binding and diffusion of the surface species formed upon water adsorption on $\text{RuO}_2(110)$ represent a critical step in achieving fundamental understanding of the role RuO_2 plays as H_2 and O_2 evolution co-catalysts in photocatalytic water splitting reactions.

Energy dispersal during photocatalytic charge transfer on $\text{TiO}_2(110)$.

The well-accepted model for photocatalytic transformations of molecules at surfaces is that of charge carrier transfer between the valence and conduction bands in a semiconductor and donor/acceptor states in adsorbed species. Very little is known about the fate of the energy resulting from these transfer events. For example, to what extent is it available to carry out secondary reactions? We show that various atomic and molecular forms of oxygen chemisorbed on $\text{TiO}_2(110)$ surface, when excited by charge carrier transfer, distribute energy to neighboring molecules leading to their desorption. Figure 20 illustrates this effect for a variety of coadsorbates with different adsorption energies. If the binding energy of the adsorbate is low enough, the energy transfer results in desorption. With this method, photoactivity of oxygen adatoms on $\text{TiO}_2(110)$ was discovered for the first time. The inset in Figure 20 illustrates this effect with Kr. This unique photochemical effect provides a useful approach to observing and characterizing otherwise undetectable electron transfer events between the photocatalyst and an adsorbate.

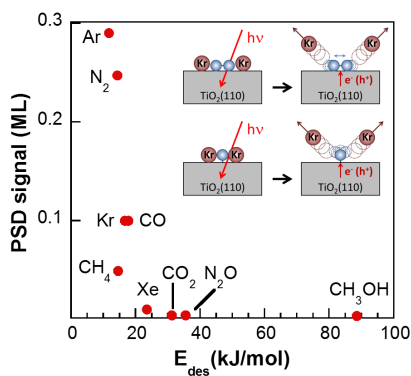


Figure 20. Photo-stimulated desorption (PSD) of molecules coadsorbed with O_2 on $\text{TiO}_2(110)$ versus their adsorption energies (E_{ads}). Inset: models of energy sharing from O_x photochemistry (blue balls) leading to Kr PSD.

Hindering photoreactivity of carboxylate on $\text{TiO}_2(110)$ by charged coadsorbed hydroxyls. Employing scanning tunneling microscopy and ultraviolet photoelectron spectroscopy, we have observed a strong nonlinear decay of the rate constant with coverage for the photolysis of trimethyl acetate (TMA) on $\text{TiO}_2(110)$. This inhibition stems from a buildup of the coadsorbed hydroxyl (HO_b) species, taking into account that upon (thermal) dissociative adsorption of trimethylacetic acid, the equal amount of TMA and HO_b species is generated concurrently. Confirmation of the inhibiting influence of HO_b groups was obtained by dissociating H_2O at O-vacancy sites, resulting in an additional hindering effect on TMA photochemistry. While hydroxyl species are not highly photoreactive, they are not merely spectators, functioning as trap sites for photoexcited electrons. We postulate that these trapped electrons attract and neutralize photoexcited holes, adversely affecting the hole-mediated photochemistry of TMA as schematically shown in Figure 21. In this sense, the photochemical rate dependence on TMA coverage correlates with the affinity of HO_b species to trap negative charge. The rate constants for the hole-mediated TMA depletion and electron trapping both depend similarly on HO_b coverage, follow the first-order kinetics, and have comparable absolute values, as anticipated for the photo-processes enabled by opposite charge carriers. This study provides new fundamental insights into the roles of surface defects and coadsorbates on oxide photochemistry. Because hydroxyl formation is a common phenomenon resulting from dissociative adsorption of numerous species (water, carboxylic acids, alcohols, etc.), a similar negative influence on hole-mediated photochemistry should be expected on other reducible oxides.

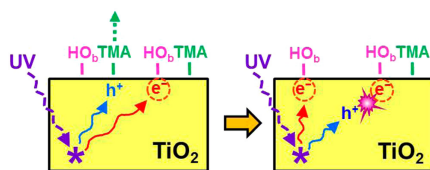


Figure 21. Schematic illustration of the hindering influence of surface hydroxyls on hole-mediated photochemistry of TMA on $\text{TiO}_2(110)$.

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

PI – Thomas Autrey

Co-PIs – Donald Camaioni, Bojana Ginovska, Abhijeet Karkamkar, Gregory Schenter

Our research interests are focused on the development of tools and approaches using a combination of theory and experiment to understand how molecular hydrogen is activated heterolytically without using metals in frustrated Lewis

pairs. Inelastic neutron scattering spectroscopy (INS) provides a unique approach to study both the energetics and dynamics of hydrogen interactions in condensed phase materials. Using the VISION spectrometer at the Spallation Neutron Source we were able to investigate the single crystal – single crystal transformation of solid KCAT, 1-{2-[bis(pentafluorophenyl)boryl]phenyl}-2,2,6,6-tetramethylpiperidine to the corresponding ion pair, KCATH2, quantitatively upon exposure to gaseous H₂. The reaction does not occur until temperatures exceeded 200 K. AIMD approaches (Figure 22) used to calculate the INS spectra are in excellent agreement with the experimentally measured spectra.

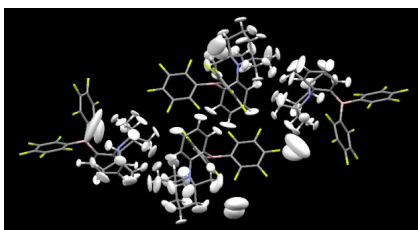


Figure 22. Thermal ellipsoids predicted from harmonic calculations of H₂ interacting with KCAT.

Optical microscopy (Figure 23) was used to follow the transformation of the colored KCAT crystals to form the colorless KCATH2 in the presence of H₂ gas at room temperature. The results show that some regions of the crystal react faster than other regions, but the boundaries between these regions are diffuse, showing there is not a clear preference for reactivity at surface or interior sites.

The chemical transformation of a crystalline FLP to the corresponding crystalline ion pair provides the first example of a “non-metal” activation of H₂ in the solid state. Insight from these studies will permit the development of a rational approach to “heterogenize” Lewis acid/base pairs on conventional catalyst supports. These ambiphilic centers activate H₂ heterolytically to provide a greater selectivity for the catalytic reduction of polar and polarizable substrates under investigation in this collaborative research effort.



Figure 23. Optical micrographs of KCAT crystals exposed to H₂ gas for a) 0 min., b) 55 min., c) 85 min., d) 112 min., e) 150 min. Scale bar = 100 μ m.

Subtask 3.3: Modulating Catalysts with an Enzyme-Like Outer Coordination Sphere

PI – Wendy Shaw

Co-PIs – David Baker (University of Washington), Garry Buchko, Bojana Ginovska, John Linehan

The goal of this research is to incorporate an enzyme-inspired outer coordination sphere onto molecular catalysts to capture the functionality of the protein scaffold for enhanced catalytic performance, while at the same time providing insight into the role of the enzyme scaffold. The enzyme scaffold is critical to achieving catalytic function and efficiency, but historically, only the first and, more recently, the second coordination spheres have been considered in building molecular catalysts. Research from our laboratory and others demonstrates that attaching a simple amino acid-based outer coordination sphere on molecular catalysts can have a significant impact on the performance of electrocatalysts and thermal catalysts, including enhanced rates, lower overpotentials, and reversibility. We seek to understand three aspects of the outer coordination sphere: 1) environment around the active site, 2) proton pathways, and 3) controlled structural switching. As complexes upon which to investigate the outer coordination sphere, we will use two molecular catalyst cores with well-understood first and second coordination spheres that operate at room temperature: Ni-based complexes that are active for H₂ production/oxidation, and Rh-based complexes that are active for CO₂ hydrogenation. We will use a combination of advanced synthetic, spectroscopic, and computational approaches to design and build complexes with structured peptide scaffolds and evaluate the mechanistic role of the outer coordination sphere. The goal of our research is to determine the minimal scaffold needed to achieve similar performance and to understand the scaffold's function at a mechanistic level to extract design principles. Establishing these design principles will dramatically alter the approach to developing molecular catalysts, with a possible paradigm shift in the field, transitioning from a focus on the first and second coordination spheres, to one in which all three coordination spheres are considered essential in replicating the performance of an enzyme with a molecular mimic. As we learn how the scaffold elements interact, we will build in the mesoscale complexity that drives the exceptional performance of enzymes.

The catalyzed conversion of lignin to hydrocarbon energy carriers requires a cascade of reactions for deconstructing and reducing the polymeric, highly oxofunctionalized material. While lignin is the most intractable component of lignocellulose, its conversion to useful products is particularly important, because the carbon in lignin is the most reduced fraction of lignocellulose. In the present phase, we are focused on understanding the properties of catalysts in an

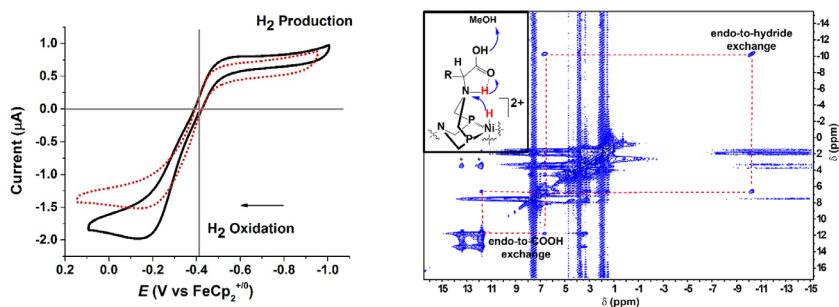


Figure 24. (Left) Electrochemical reversibility was achieved at room temperature for $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{Phe}}_2)_2]^{2+}$ (Cy=cyclohexyl, Phe=phenylalanine). This behavior is seldom observed in molecular catalysts and is reminiscent of the behavior in enzymes. (Right) NMR exchange spectroscopy data confirm that the -COOH groups in the outer coordination sphere enabling rapid proton transfer, a critical element in achieving reversibility.

aqueous environment and the catalytic chemistry of lignin fragments in the aqueous environment as well as the biphasic oil-water environment. In particular, we are studying ether hydrogenolysis and hydrolysis, the reduction of phenols, hydrodeoxygenation of alcohols, and the alkylation of (substituted) phenols in the aqueous phase using supported noble and base metals as well as zeolites. Hydrogenation, hydrogenolysis, and even hydrolysis were found to be effectively catalyzed by supported palladium and nickel catalysts allowing for higher reaction rates on these metal particles than observed previously by molecular catalysts.

Achieving room temperature reversibility for a molecular complex. The H_2 oxidation catalyst $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{Phe}}_2)_2]^{2+}$ (Cy=cyclohexyl, Phe=phenylalanine) was prepared. *Reminiscent of enzymes, electrochemical reversibility is achieved while fast rates are maintained (Figure 24, left), the first time this has been demonstrated for a molecular catalyst.* The influence of the amino acids on these catalytic properties is proposed to result from directly transferring protons via the carboxylic acid groups creating a three-membered proton pathway (Figure 24, right) as well as interactions between the side chain groups such as guanidinium or aromatic groups that result in structural modifications to facilitate H_2 addition and electron transfer. These observations demonstrate that outer coordination sphere amino acids work in synergy with the active site and can play an equally important role for synthetic molecular electrocatalysts as the protein scaffold does for redox active enzymes. Moving forward, the principles learned here will be applied to CO_2 hydrogenation catalysts, with some initial results demonstrating feasibility.

Structured peptide incorporated onto functional H_2 production complex. Recognizing the need for a structured outer coordination sphere and

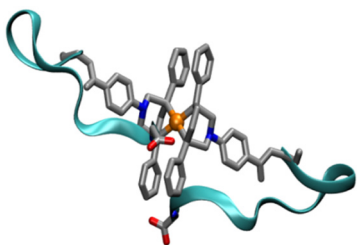


Figure 25. Incorporation and characterization of a complex with a structured β -hairpin outer coordination sphere. This complex enhanced the rate by a factor of two, but more important, provides a strong foundation for combined computational and experimental development of “bottom-up” molecular catalysts with an outer coordination sphere.

building on the success of the H_2 production catalysts with dipeptides, we developed a procedure for incorporating larger peptides onto an analogous H_2 production core catalyst. The result is a catalyst with a structured β -hairpin peptide (Figure 25) that not only maintains, but enhances its catalytic function by a factor of two. *This complex serves as a platform on which we can develop our proposed structured outer coordination sphere complexes, with controlled amino acid positioning to influence the environment and create a proton pathway.*

Stimulus-controlled catalysis. One hallmark of enzymes is their use of structural changes in response to stimuli to control reactivity. We have successfully mimicked this feature by introducing an azobenzene-based photoswitch onto the amino acid scaffold of one of our core complexes. Upon application of a stimulus, light of a defined frequency range, the azobenzene isomerizes and propagates structural changes in the complex (Figure 26). In our example, *switching the azobenzene from trans to cis causes reactivity to increase by 40% in a complex for CO_2 hydrogenation.*

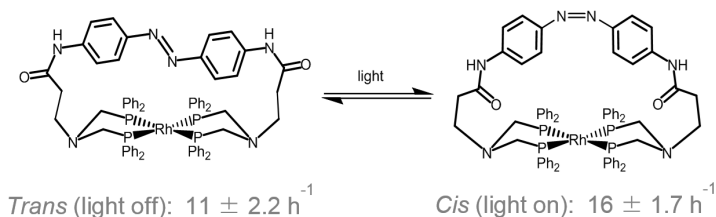


Figure 26. A trans-spanning azobenzene modulates catalytic activity, demonstrating the principle of stimulus controlled catalysis, similar to the catalytic control.

Recognitions and Honors

PNNL Hydrogen Catalysis Team:

R. Morris Bullock, Aaron Appel, Monte Helm, Molly O'Hagan, Eric Wiedner, Wendy Shaw, Simone Raugel

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

R. Morris Bullock

- ▶ Fellow, Royal Society of Chemistry, 2013
- ▶ Royal Society of Chemistry Homogeneous Catalysis Award, 2013
- ▶ Visiting Professor, Liebig-College of Justus-Liebig University, Gießen (Germany), 2015



Miroslaw Derewinski

- ▶ Full Professor, Polish Academy of Sciences, 2014



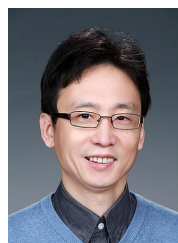
Zdenek Dohnálek

- ▶ Adjunct Professor, Department of Chemical Engineering, Washington State University, 2016



Feng Gao

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



David Heldebrant

- ▶ Associate Editor, RSC Advances, 2015 - present
- ▶ Adjunct Professor, Department of Chemical Engineering, Washington State University, 2015 - present



Jianzhi Hu

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



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



Gregory Kimmel

- ▶ Fellow, American Vacuum Society, 2016



Johannes Lercher

- ▶ Kozo Tanabe Award for Acid-Base Chemistry, 2013
- ▶ Francois Gault Lectureship Award, 2013
- ▶ R. B. Anderson Award, Canadian Catalysis Society, 2015
- ▶ Member of European Academy of Sciences, 2016



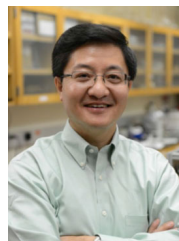
Wendy Shaw

- ▶ Pathways to Excellence Award, PNNL, 2013, 2015
- ▶ Panelist, Chemical Sciences Roundtable of the National Research Council: Workshop on Mesoscale Chemistry, 2014



Yong Wang

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



Publications and Presentations

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

- ▶ Total of 208 peer-reviewed publication
 - ▶ *Nature* (1), *Nature Chemistry* (1) *Nature Communications* (4), *Proceedings of the National Academy of Sciences* (1), *Journal of The American Chemical Society* (15), *Angewandte Chemie* (7).
 - ▶ 12 review articles (*Chemical Reviews*, *Accounts of Chemical Research*, *Chemical Society Reviews*, and others).
 - ▶ 3 book chapters.
- ▶ 205 invited lectures at conferences, universities, and other professional venues.
- ▶ 12 symposia organized at scientific meetings.

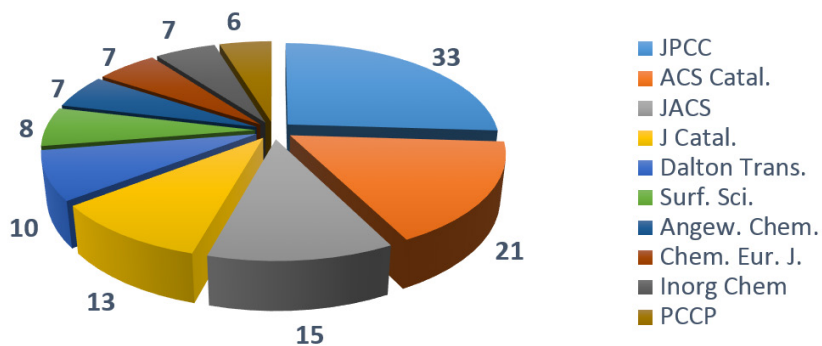
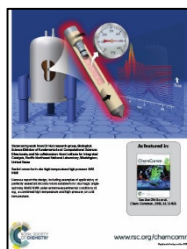
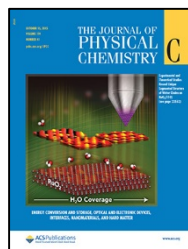
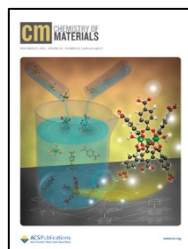
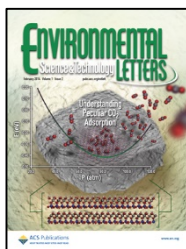
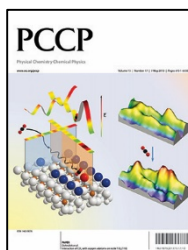
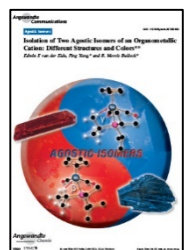
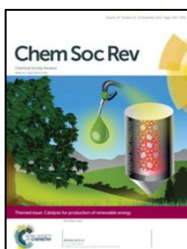
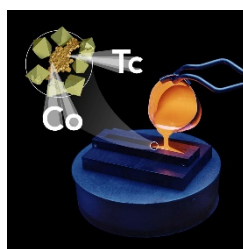
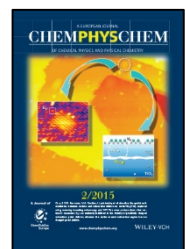
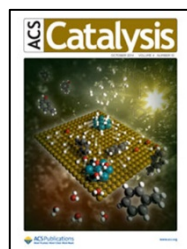
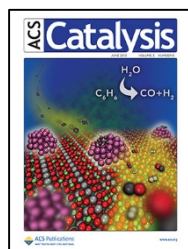
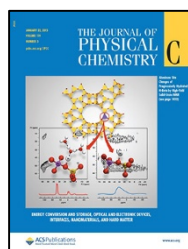


Figure 27. 127 publications (out of 208) in the journals with the highest occurrence.

Journal Covers (2013-2016)



ASSOCIATED BASIC ENERGY SCIENCES PROGRAMS

Energy Frontier Research Center: Center for Molecular Electrocatalysis

Director – Morris Bullock

Deputy Director – Aaron Appel

Co-PIs – Monte Helm, 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 vision of the Center for Molecular Electrocatalysis (CME) is to make transformational changes in our ability to design molecular electrocatalysts for the interconversion of electricity and fuels. Our overarching goal is to understand, predict, and control the intramolecular and intermolecular flow of protons in electrocatalytic multi-proton, multi-electron processes of critical importance to a secure energy future: the production of H₂, the oxidation of H₂, the reduction of O₂, the reduction of N₂, and the oxidation of NH₃. These targets provide increasingly demanding tests of our ability to design catalysts for precise proton delivery in reactions of rising complexity from 2 H⁺/2 e⁻ for H₂, 4 H⁺/4 e⁻ for O₂, to 6 H⁺/6 e⁻ for N₂. Our objectives are focused on identifying, understanding, and developing scientific principles that provide the basis for design of improved catalysts.

The CME is a synergistic research program focused on the design of fast, efficient electrocatalysts through understanding and precisely controlling proton movement. As a prominent example, an exceptional level of understanding and control has been achieved in the [Ni(P^R₂N^{R'}₂)₂]²⁺ family of catalysts for H₂ production, from insights gained through both theory and experiments. We now focus on controlling the relationship between overpotential and catalytic rate, as exemplified in Figure 28.

Our approach in the H₂ subtask focuses on *functional* models, which complements remarkable progress reported by many groups in *structural* models of [FeFe]-hydrogenases. We achieved progress by building on principles identified in the first funding period and, importantly, by exploiting a *new discovery* that

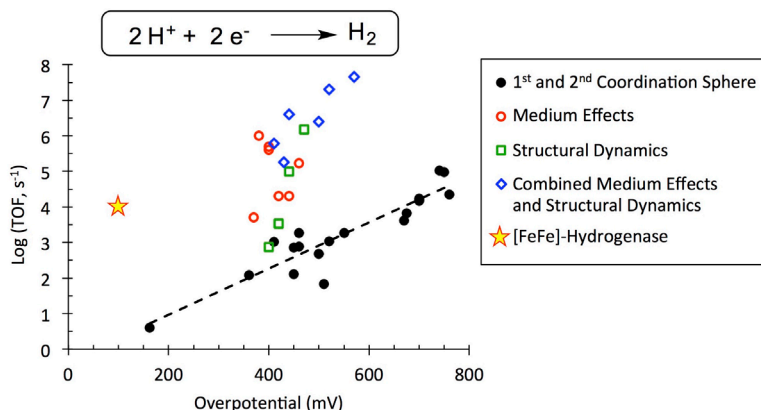


Figure 28. A focus of the CME is understanding and controlling the relationship between rate and overpotential. The individual data points represent different nickel catalysts, which vary by structural modifications and conditions for catalysis.

demonstrates how controlling ligand structural dynamics improves catalyst performance of $[\text{Ni}(\text{P}^{\text{R}}_2\text{N}^{\text{R}'}_2)_2]^{2+}$ for production of H_2 . In aqueous ionic liquid media, this recently discovered conformational control leads to $\text{TOF} > 10^7 \text{ s}^{-1}$. A microkinetic model based on extensive *ab initio* simulations provides an exquisitely detailed understanding that provides valuable information on the factors that promote or limit rates of catalysis.

In research on the electrocatalytic oxidation of hydrogen, we discovered new Fe catalysts with outer coordination sphere proton relays that increase the rates of H_2 oxidation by an order of magnitude *without* a significant increase in overpotential. Computations revealed that the addition of an outer coordination sphere amine provided a more suitably energy-matched pathway to transfer the proton from the Fe(III) to the periphery of the catalyst.

In the O_2 subtask, we demonstrated that rate constants correlate with the catalyst overpotential for a range of iron porphyrin catalysts, as illustrated in Figure 29. An Fe(porphyrin) catalyst that has a TOF of $1.7 \times 10^7 \text{ s}^{-1}$, which is the fastest rate ever observed for a molecular catalyst for the oxygen reduction reaction (ORR), albeit at a high overpotential. As with the H_2 subtask, synergistic experimental and computational efforts provide insights into the requirements for precise proton delivery. Our understanding of these systems has progressed from appending proton relays (CO_2H groups on the porphyrin ring) to a much more comprehensive evaluation of the mesoscale organization of solvent near the catalyst. Medium effects were evaluated using Fe(porphyrin) catalysts coated on electrodes and deposited with NafionTM. The selectivity in the catalytic reaction (formation of H_2O vs. H_2O_2) was highly dependent on the adsorption method, indicating that medium effects are even more important than

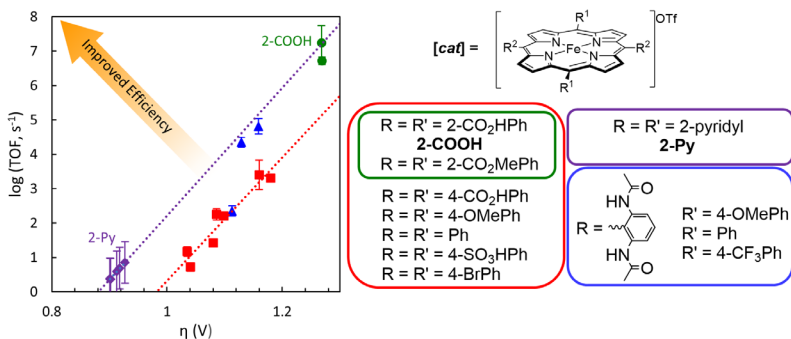


Figure 29. Rates vs. overpotential for ORR with $[\text{Fe}(\text{porphyrin})]\text{OTf}$ in non-aqueous solvents. Green: MeCN; Red, Purple, Blue: DMF.

electronic effects of the catalyst. An entirely new approach to the ORR was initiated using “electron-proton transfer mediators”. Using NO_x with TEMPO (tetramethylpiperidinyloxy) gives highly efficient reduction of O_2 at mild potentials, leading to an improvement of 200–500 mV in overpotential compared to metal macrocycles typically used as catalysts.

We determined the thermodynamic potential of the $\text{O}_2/\text{H}_2\text{O}$ couple in organic solvents using a new approach, thus enabling meaningful comparisons of catalysts in terms of the overpotentials and turnover frequencies. These efforts provide the basis for extending these concepts from H_2 and O_2 into the N_2 subtask.

The six-proton, six-electron reduction of N_2 to NH_3 in the N_2 subtask is a challenging reaction that provides an even more demanding test of our ability to design molecular electrocatalysts, and the efforts in this subtask benefit from principles developed in the CME for H_2 and O_2 reactions. It is the highest risk subtask, yet could provide a high reward. Controlling proton delivery is a key step in designing efficient molecular electrocatalysts. In this context, we evaluated the effects of varying the steric and electronic properties of pendant amine groups to control the protonation site of $\text{Mo}(\text{N}_2)$ complexes at the metal, the N_2 ligand, or the pendant amine group of the phosphine ligand (Figure 30). We have made notable advances in developing N_2 reduction chemistry with Cr. In a recent metal-based comparison examining the protonation of an isostructural series of Cr, Mo, and W– N_2 complexes, we showed that *only Cr* produces N_2 derived hydrazine and ammonia. In new efforts aimed at designing complexes for the oxidation of NH_3 , to extract energy stored in the N–H bonds, we

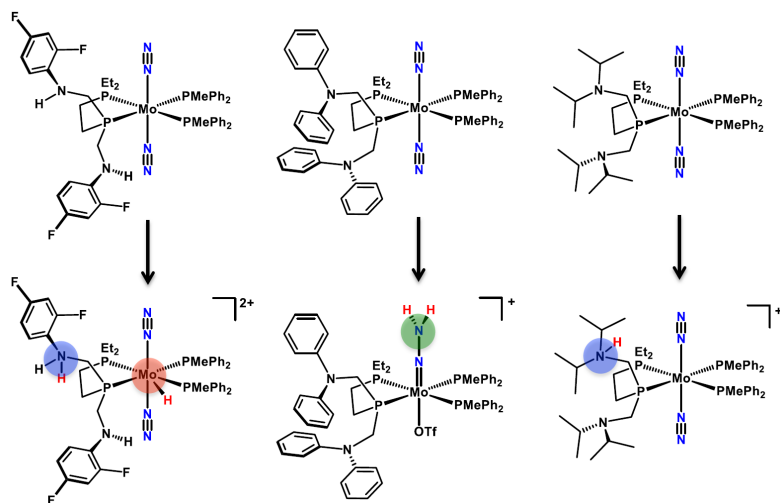


Figure 30. Controlling the site of protonation (at the metal, N₂, or pendant amine) in Mo-N₂ complexes was achieved by tuning the steric and electronic properties of the amine groups.

have initial evidence for proton transfer from NH₃ ligands following electrochemical oxidation. In addition, we have identified hydrogen bonding interactions of pendant amine groups with metal-bound NH₃ ligands and M-N_xH_y intermediates that form upon oxidation of the parent M-NH₃ complex.

Recognition by other research groups of the importance of controlling the delivery of protons for catalytic transformations exemplifies the broad impact of the CME in the catalysis community. Derivatives of catalysts from the CME have been used in the functionalization of surfaces, in combination with photosensitizers, for incorporation into Photosystem I, for studies of the outer coordination sphere, for oxidation of formate, and in mechanistic and spectroscopic studies of H₂ production catalysts. Research from the CME, as well as the efforts it has inspired, is driving electrocatalysis forward to enable the incorporation of new catalysts into devices for the production and use of solar fuels.

Physical Biosciences Program: Enzymatic Energy Conversion

PIs – Lance Seefeldt, Simone Raugei

Co-PIs – James Evans and Wendy Shaw

The Physical Biosciences program at PNNL aims at defining core principles used by enzymes that catalyze energy-relevant reactions, such as H₂ production and oxidation, CO₂ reduction, and N₂ reduction. The suite of enzymes that catalyze these reactions operate with high efficiency at ambient conditions. The activity 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 N₂ 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. The reduction of N₂ to NH₃ is a reaction fundamental to all life and is one of the most energy-consuming reactions. Bacteria catalyze this reaction using the 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 H₂, whose production from fossil fuels represents a majority of the feedstock costs and energy demands.

In addition to reducing N₂ and protons, nitrogenase can reduce a number of small, multiply bonded compounds. In particular, CO₂ can be catalytically reduced by 2 or 8 electrons/protons to CO or CH₄ at low rates. A better understanding of the mechanism by which nitrogenase catalyzes CO₂ reduction would provide insight into the challenging and environmentally important reduction of CO₂.

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 N₂ reduction. Electron accumulation at the catalytic center (the seven iron [7Fe-9S-Mo-homocitrate] FeMo cofactor, FeMo-Jco) is key for the efficient N₂ activation. A major effort is dedicated to elucidate

how protein structure and dynamics control the delivery of electrons in the nitrogenase system. Mutagenesis studies of the MoFe protein revealed that substitution of a few residues nearby the catalytic core of the MoFe protein results in a protein that can reduce N_2H_4 , a nitrogenase substrate and N_2 reduction intermediate, in the absence of the Fe protein. This reduction only occurs when a powerful electron donor, such as ligated Eu(II), is used as a substitute of the Fe protein. Our investigations support the proposal that these substitutions induce conformational changes

within the MoFe protein, usually achieved only transiently during docking with the Fe protein via a dynamical coupling between protein elements connecting the elements of electron transfer chain to the catalytic center. Our studies indicate that the binding of the Fe protein and subsequent structural changes associated with ATP hydrolysis couple to the MoFe protein to coordinate electron transfer, substrate binding, and N_2 reduction.

Substrate access/product egress. There is ample evidence that the nitrogenase protein controls the size and type of substrates that can access the active site FeMo-co. Less is known about how the protein environment around FeMo-co must change to allow a substrate access and to accommodate substrate binding. Our hypothesis is that protein conformational dynamics opens up protein channels that allow substrate access to the active site. As proof-of-concept for this hypothesis, molecular dynamic free energy simulations carried out by us reveal a never-before-seen putative channel that extends from the protein surface to the FeMo-co core. In contrast to other proposed channels, this channel approaches one edge of the face of FeMo-co known to be implicated in

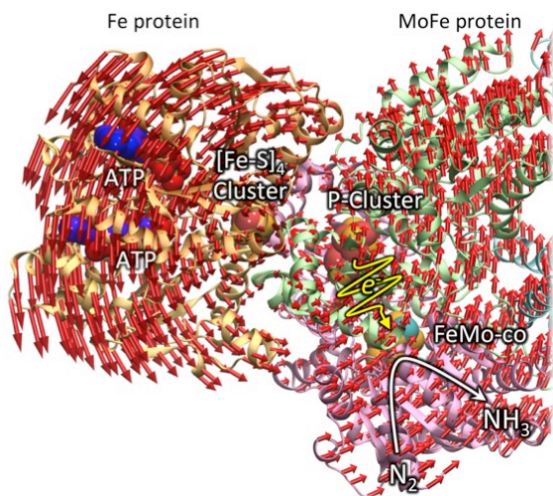


Figure 31. Computational analysis and mutagenesis experiments suggested a coupling between the Fe protein dynamics and the electron transfer between the two MoFe protein redox centers (the iron/sulfur clusters P-cluster and FeMo-co). The figure shows a collective motion corresponding to the rolling of the Fe protein on the MoFe protein surface as obtained from a coarse-grained normal mode analysis. The length of the arrows is proportional to the displacement of the amino acid residues.

N₂ binding, going past the critical functional side chains of α -70^{Val} and α -195^{His}. Other computational investigations and structural data indicate that perhaps more than one channel is operative for different substrates, and it is possible that one of these channels functions as a path for egress of products, away from the active site.

Substrate binding and activation. Early kinetic studies indicated that FeMo-co must accumulate 4 electrons and protons (the E₄ state in the Lowe and Thorneley kinetic model) before the first step of N₂ reduction, with the electrons delivered one at a time by the nitrogenase Fe protein, before N₂ can be reduced, and that N₂ binding coincides with the evolution of one equivalent of H₂.

Despite extensive research efforts, it is only recently that our team isolated and characterized three reduction intermediates. In particular two intermediates containing reduced forms of N₂. One intermediate was found in an $S = \frac{1}{2}$ spin state and attributed to the final catalytic state with the NH₃ product bound to FeMo-co. The other intermediate contains the [-NH₂] fragment bound to FeMo-co in an integer spin state and corresponds to the intermediate. We experimentally proposed that the four reducing equivalents in E₄ are stored as two [Fe-H-Fe] bridging hydrides bound to FeMo-co. Our current computational modeling support this proposal and it further indicates that two protons are stored on two under-coordinated inorganic sulfur atoms in the FeMo-co. Our calculations also suggest that the elimination of H₂ is the key thermodynamics driving force promoting N₂ binding and activation.

Very recently we found that nitrogenase reduces CO₂ by two electrons/protons to make formate (HCOO⁻) at rates up to 10-times faster than the rates of CO and CH₄ formation reported earlier. A quantum chemical exploration of the possible pathways for CO₂ reduction on FeMo-co revealed that the hydricity of the reduced FeMo-co well-match the requirement for a facile H⁻ transfer to CO₂ and yield energies that are consistent with the observed product distribution for CO₂ reduction. In addition, we showed that amino acid substitutions near FeMo-co in the MoFe protein can significantly alter the product distribution between formate and CO/CH₄.

Early Career Program: Combined Capture and Conversion of CO₂

PIs – David J. Heldebrant

Collaborators – Vassiliki-Alexandra Glezakou, Tom Heading (ISIS, UK), Martin Owen Jones, (ISIS, UK), Abhijeet Karkamkar, John Linehan, Roger Rousseau, Xiao-Ying Yu, Steven Saunders (Washington State University)

The goals of this project are to use a combined experimental/theoretical approach to explore in depth a potentially new heterogeneous, micro-domain solvent structure found in SWILs and determine how this structure impacts separation, concentration, and conversion of CO₂ into energy carriers. We aim to determine the correlation between the mesoscopic SWIL structure, *i.e.* defining the catalyst's location and structure inside the ionic domains and thorough evaluations of the alkylcarbonate hydride affinity (electrophilicity). This program was conceived from Subtask 2.2, and is synergistic with other CO₂-centric subtasks.

Simulations of heterogeneous solvent structure using molecular dynamics. Molecular-level simulations of a conventional DBU/1-hexanol (separate cation/anion) ion pair solvent system (Figure 32a) and a switchable zwitterionic IPADM-2-BOL (cation/anion reside on the same molecule) solvent system (Figure 32b) were performed at various CO₂ loadings to analyze their extended liquid structure. Analysis of the structures reveal that both conventional and zwitterionic systems form clusters of charged amidinium or guanidinium alkylcarbonates that result in a highly heterogeneous structure (Figure 33). The cluster size increases for both zwitterionic and conventional ion pairs as the number of charged species increases. On average, the cluster sizes are ~1-3 nm for 25% loading and ~2-6 nm for 50% loading, implying catalysts may reside inside.

Calculations of the autocorrelation function of the solvent box dipole using MD simulations provided estimates of the dielectric constant. Interestingly, for 1-IPADM-2-BOL the dielectric constant *decreases* as more polar molecules are present. This counter-intuitive finding is due to the extended solvent structure in which neighboring zwitterions arrange themselves in such a way

that the net dipole decreases. This effect is only possible because they are single molecule systems. This is not the case with DBU/1-hexanol, where the

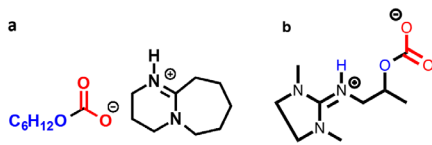


Figure 32. Molecular structure of a) DBU/1-hexanol + CO₂, b) IPADM-2-BOL + CO₂.

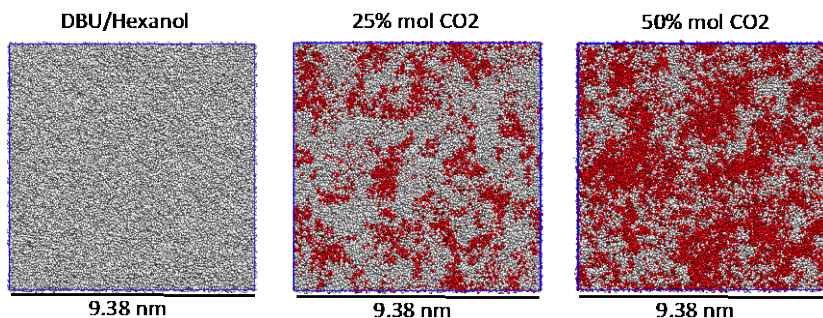


Figure 33. Extended solvent structure of DBU/1-hexanol with and without CO₂. DBU/1-hexanol in grey, [DBUH]⁺C₆H₁₂OCO₂⁻ ion pairs in red.

dielectric constant *increases* as more charged molecules are present. These differences offer insights why hydrogenations occur in DBU/1-hexanol but not 1-IPADM-2-BOL.

Catalytic conversions of alkylcarbonates in solution. As knowledge of the SWIL solvent structure is becoming clearer, we began to focus on determining if catalysts could reduce the alkylcarbonates in the ionic clusters and whether the alkylcarbonate is reduced via an inner sphere reduction or outer sphere reduction as is neutral CO₂ using homogenous *cis*-Ru(PNP)₂H₂ complex (Figure 34). CO₂ and [DBUH]⁺C₆H₁₂OCO₂⁻ showed distinctive reduction mechanisms; [DBUH]⁺C₆H₁₂OCO₂⁻ consumed only the *cis*-Ru(PNP)₂H₂ indicating an inner-sphere reduction, while free CO₂ with DBU consumed both *cis*-Ru(PNP)₂(H)(X) and *trans*-Ru(PNP)₂H₂ complexes indicating an outer-sphere reduction. CO₂ in the presence of DBU and 1-hexanol (prior to formation of [DBUH]⁺C₆H₁₂OCO₂⁻) showed a mixture of the two rates, indicating the reduction of CO₂ is faster than the rate of CO₂ fixation. The rate of reduction of carbonate appears to be faster than the reduction of CO₂. This inner-sphere mechanism is the first observed direct insertion of a negatively charged alkylcarbonate into metal hydride complex, indicating catalysts can be designed around this new reactivity.

In previous work (Subtask 2.2), we attempted a direct hydrogenation of [DBUH]⁺CH₃OCO₂⁻ to methanol but the process stopped at methylformate (¾ of the way to methanol).

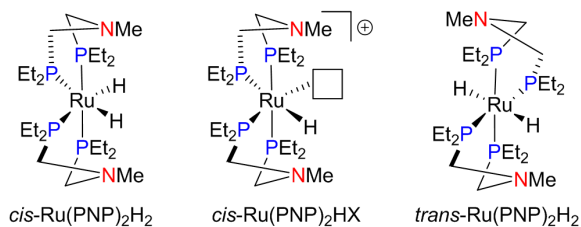


Figure 34. *cis*-Ru(PNP)₂H₂, *cis*-Ru(PNP)₂(H)(X), and *trans*-Ru(PNP)₂H₂ complexes.

To assess why, we calculated free-energy estimates for the reduction of CO₂ and a representative alkylformate in an acetonitrile solvent by summation of free energies for each reaction step. Free energies for CO₂ and alkylformate reduction differ only by the free energy for the equilibrium of CO₂ capture by an alcohol and base. These thermodynamic estimates indicate a tradeoff; more favorable CO₂ capture results in a less favorable reduction of formate. With DBU as a representative base, the reduction of CO₂ is thermoneutral (in acetonitrile) and the formation of [DBUH]⁺C₆H₁₂OCO₂⁻ is favored, thus we predict a positive free energy for alkylformate reduction. Future work will reduce the CO₂ capture strength by adjusting basicity to promote a more favorable alkylformate reduction.

CONNECTIONS TO APPLIED PROGRAMS

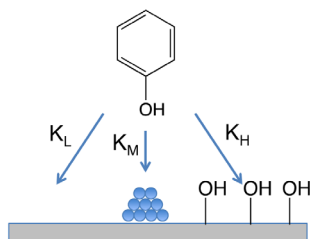
Important linkages to applied catalysis programs administered in other PNNL directorates are promoted by the IIC, all combining to attack “the Grand Challenge for catalysis science in the 21st century ... to understand how to design catalyst structures to control activity and selectivity,” and to put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

Catalyst Development for Efficient Biomass Conversion to Fuels

John Holladay, Roger Rousseau, Vassiliki-Alexandra Glezakou, Donghai Mei, Robert Weber

Overview. In the past several years, researchers in PNNL’s fundamental sciences catalysis group (responding to the DOE BES program in catalysis science) have interacted with researchers in PNNL’s applied programs (responding to the DOE Energy Efficiency and Renewable Energy (EERE) Bioenergy Technologies Office (BETO)) to develop new concepts for capturing the subtleties of catalyzed reactions involving condensed reaction media. In addition, advanced characterization techniques (performed at the Environmental Molecular Sciences Laboratory (EMSL)) and computational studies have played a noticeable role in the development of the kinetics of biomass conversions into fuels.

Research highlights. Once they condense to a liquid, the initial precursors to renewable fuels derived from biomass are not easily revaporized because the constituents readily oligomerize into coke and “gunk.” Therefore the upgrading reactions that hydrogenate and stabilize the polymerization sites must be run at temperatures where the reaction medium remains condensed. We have shown that both energy and entropy contribute to the structuring of the liquid adjacent to the solid catalyst, a region we have termed the “cybotactic region” after its counterpart in solution chemistry, and explained how it bears on the activity of



$$\frac{K_M}{K_L} = 8 \times 10^{11} \ll \frac{K_M}{K_H} = 6 \times 10^{18}$$

Figure 35. A lipophilic support will decrease the concentration of substrate near a supported metal site while a hydrophilic support will funnel phenol towards the hydrogenation sites. The numbers result from a recent molecular dynamic study of the interaction of phenol with Pd catalysts supported on hydrophilic and lipophilic surfaces.

catalysts active for the hydrogenation of model compounds. The cybotactic region is a thermodynamic phase, not merely a consequence of finite rates of mass transport. Therefore its composition, structure and, likely, its dynamics can be manipulated by varying the solvophilicity of the catalyst. In fact, because the surface of a supported catalysts predominately consists of the support (the metal surface area may be <1% of the exposed area) and because the cybotactic structures extend over nanometers, changes in the cybotactic region arising from changing the support is a new type of support effect. We are in the process of determining how this new support effect can be exploited to enhance the activity, selectivity, longevity, and productivity of processes for the upgrading of bio-oil. The new support effect is evidently related to the theme of catalysis in confined environments that is part of the new portfolio of the IIC.

Future directions. We are working under the auspices of EERE/BETO-funded projects to expand our tangency with the Catalyst Working Group to equip it with robust simulations of pragmatic catalysis of realistically complex reaction networks. In addition, we have proposed projects to two of DOE's large facility laboratories (SSRL, APS, and EMSL) to devise *in operando* characterizations of the cybotactic region.

Electrochemical Upgrading of Pyrolysis Oil

Vassiliki-Alexandra Glezakou, Roger Rousseau, Michael A. Lilga

We are working on a combined theoretical /experimental study (funded by DOE-EERE-BETO) to perform room temperature electrochemical hydrogenation of pyrolysis oil.

The intention is to replace the first stage in the upgrading process where the bio-oil is stabilized by thermal hydrogenation of aldehydes and ketones prior to further processing at elevated temperatures. These functional groups are the cause of polymerization reactions, and they ultimately lead to reactor plugging.

Capabilities for modeling electrochemical reactions in explicit condensed phase models were first developed on BES-funded projects, and subsequently were adapted for modeling of the heterogeneous electro-catalytic processes, Figure 36. Our mechanistic studies indicate that electrocatalytic hydrogenation of

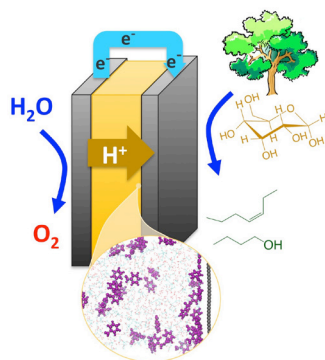


Figure 36. Schematic representation of electrocatalytic conversion, combining theory and experiment.

aldehydes/ketones to alcohols proceeds by a coupled proton transfer mechanism and that speciation within the electrode double layer is critical for controlling reaction selectivity.

Chemical Transformations Initiative

John Holladay, Johannes Lercher, Roger Rousseau

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 are typically “uphill.” Moreover, they will be effected at 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 like 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. Therefore, we seek new catalysts that are very 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 towards kinetically coupling them to reduce oxygen atoms from carbonyls to alcohols, to cleave oxygen carbon bonds through dehydrations, and to control carbon-carbon 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 (i) affords economical scaling to the required small sizes, (ii) reduces the inefficiencies (overpotential) associated with producing high pressure H₂, (iii) achieves efficiency and durability at low temperatures, (iv) provides a means for oxidative cleanup of produced water, and (v) utilizes renewable electrons by storing the electrical energy in chemical bonds. While electrocatalytic reduction allows effective use of the in situ available protons and electrons to create a product stream that is richer in hydrogen, the product will still be undesirable as

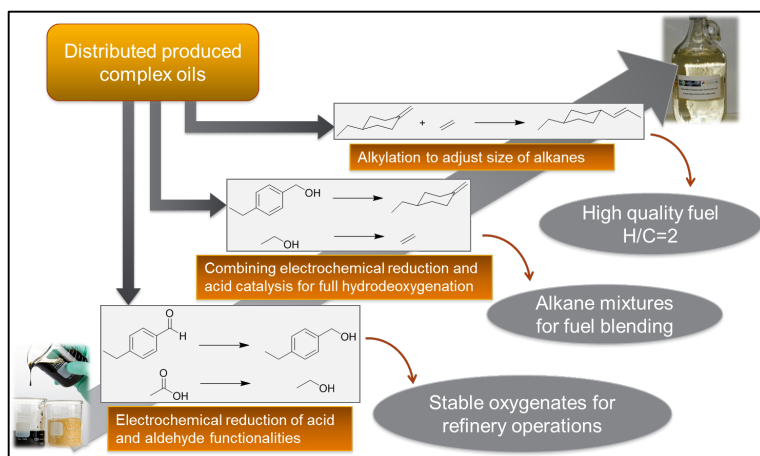


Figure 37. CTI's staged roadmap that combines electrochemical reductions with dehydration reactions, alkylation reactions, and other critical reactions for low-temperature catalysis that produce carbon energy carriers.

a fuel since it will contain a high content of oxygen. Kinetically coupled acid-base functionalities are required for further dehydration and carbon bond manipulation 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, on-going work.

Using Theory to Accelerate the Development of CO₂ Capture Solvent Systems

Charles Freeman, Vassiliki-Alexandra Glezakou, David Heldebrant, Roger Rousseau

The regeneration costs of aqueous amine systems are too high to allow their use for CO₂ capture from flue gas, and prohibits their deployment in numerous applications. An alternate family of single component solvents, known as CO₂-binding organic liquids (CO₂BOLs), show significant lower regeneration costs, but the ionic liquids formed after CO₂ binding and their high viscosities also limit their use. This first paper tackles some of these challenges relying on the advanced computational techniques, algorithms, and computer architectures (all supported, tested and developed by concurrent BES funded efforts) that allow us

to use realistic models and extended simulations to describe physical properties of complex systems.

The outcome of this work offers two new major accomplishments: (1) the description of a well-defined computational protocol that can provide fast and reliable estimates of viscosities of various solvents, and (2) the quantification of CO₂ free energetics and fundamental understanding of how to implement molecular modifications that lead to a neutral CO₂ capture.

The simulations show that the experimentally observed fast uptakes are the result of the spatial proximity of the alcohol and amine groups and a concerted mechanism of CO₂ binding and proton transfer. Ultimately, the proton transfer and the relative populations of the zwitterion and the neutral species is what determines the viscosity. We show for the first time that this equilibrium can be chemically tuned, Figure 38, and controlled to shift towards a CO₂-loaded neutral solvent with viscosities that can be half of that for a Zwitterion, in particular for higher loadings.

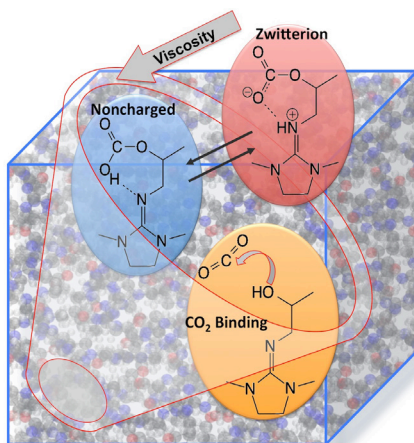


Figure 38. The molecular structure of CO₂ capture solvents can be tuned to favor an equilibrium towards a neutral (acid form) that could reduce the viscosity by 50% at higher loadings.

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 at PNNL supports DOE's Vehicle Technologies mission of advanced combustion engine research and development through its work on emissions controls technologies that enable improved engine designs. Expertise and capabilities for this work have been developed in large part by programs funded by DOE's Office of Science. For example, our work in efficient particulate controls, hydrocarbons/carbon monoxide oxidation, and NO_x reduction catalysts involves the use of sophisticated surface science techniques, advanced computational chemistry, modeling and simulation, and systems optimization. We also employ state-of-the-art characterization tools at the Environmental Molecular Sciences Laboratory, a DOE Office of Biological and

Environmental Research user facility, as well as BES-funded facilities within the IIC. Our work focuses on reducing efficiency losses in emissions controls devices with improved catalyst materials and processes, by minimizing regeneration penalties, systems optimization, and enabling new combustion strategies.

We conduct this work with collaborators at several universities: Bill Schneider (Notre Dame University), Raul F. Lobo (University of Delaware); Fabio Ribeiro, Raj Gounder, and Nick Delgass (Purdue University); and Jean-Sabin McEwen (Washington State University). We also collaborate with people at several companies: Alex Yezerets and Neal Currier (Cummins, Inc.), Christine Lambert and Bob McCabe (Ford Motor Company), Hai-Ying Chen (Johnson Matthey), Craig DiMagio (FCA), 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 CO₂ 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 IIC have been developing new catalysts for the selective catalytic reduction (SCR) of NO_x, coupled with either upstream urea injection or passive ammonia (NH₃) generation, which is a promising innovation for controlling NO_x.

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. However, researchers at IIC have developed a class of novel SCR catalysts that may satisfy these pre-requisites. An SCR technology, based on Cu/SSZ-13 but with additional co-cations, provides increased NO_x conversion efficiency at lower exhaust temperatures more typically encountered with higher efficiency engines. In particular, using adapted ion-exchange methods, sodium (Na) or other alkali/alkaline earth ions have been incorporated into the catalyst in order to promote the NO_x reduction activity of the copper (Cu) species, while further enhancing the hydrothermal stability of the catalysts by neutralizing vulnerable acidic sites.

An appropriate measure of low-temperature activity is the so-called T-90, measured as part of a performance “light-off” curve. Such curves are measures of the conversion of a reactant as a function of temperature. For SCR with NH₃, this is typically NO conversion, and the T-90 measures the temperature at which conversion is 90%. As shown in Figure 39, while the T-90 for the industry standard catalyst, Cu/SSZ-13, is ~205 °C, a newly discovered formulation has a

significantly low T-90 of ~185 °C. This new material is being further tested and improved in order to meet industry needs for conversion efficiencies of 90% at 150 °C while also maintaining sufficient durability to meet regulatory requirements.

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_x 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.

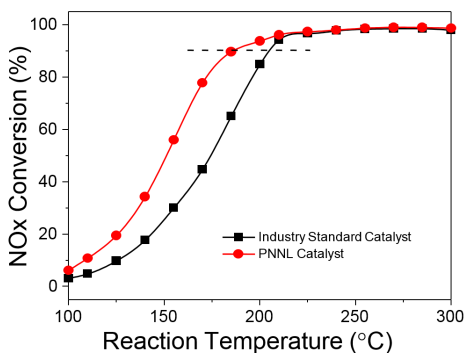


Figure 39. NO_x conversion efficiency for a novel SCR formulation developed and tested at PNNL. Both catalysts were hydrothermally aged to simulate base in-use vehicle durability. Test conditions include surrogate vehicle exhaust components.

STAFF BIOS

- ▶ Aaron Appel
- ▶ Tom Autrey
- ▶ Nigel Browning
- ▶ R. Morris Bullock
- ▶ Donald M. Camaioni
- ▶ Herman Cho
- ▶ Mirosław Derewinski
- ▶ Zdeněk Dohnálek
- ▶ John L. Fulton
- ▶ Feng Gao
- ▶ Bojana Ginovska
- ▶ Vassiliki-Alexandra Glezakou
- ▶ David J. Heldebrant
- ▶ Michael A. Henderson
- ▶ John Holladay
- ▶ Jian Zhi Hu
- ▶ Abhi Karkamkar
- ▶ Bruce D. Kay
- ▶ Gregory A. Kimmel
- ▶ Libor Kovarik
- ▶ Johannes Lercher
- ▶ Mike Lilga
- ▶ John Linehan
- ▶ Jun Liu
- ▶ Igor Lyubinetzky
- ▶ Donghai Mei
- ▶ Michael T. Mock
- ▶ Molly O'Hagan
- ▶ Mariefel V. Olarte
- ▶ Nikolay Petrik
- ▶ Simone Raugei
- ▶ Roger Rousseau
- ▶ Gregory K. Schenter
- ▶ Wendy Shaw
- ▶ Janos Szanyi
- ▶ Huamin Wang
- ▶ Yong Wang
- ▶ Robert Weber
- ▶ Eric Wiedner



Aaron Appel

Catalysis Science
Physical Sciences Division

Principal Investigator:

Subtask 2.1: Designing Catalysts Using an Energy-Based Approach: Molecular Catalysis for CO₂ Reduction

Phone: (509) 375-2157

E-mail: aaron.appel@pnnl.gov

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 work with electrochemical and thermochemical studies to understand the limiting factors in catalytic systems (identification of high-energy steps). I have incorporated bifunctionality into catalysts to avoid high-energy species and to increase catalyst performance through improved rates and energy efficiency.

I am leading the subtask entitled Designing Catalysts Using an Energy-Based Approach: Molecular Catalysis for CO₂ 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 those for the production and utilization of hydrogen.



Tom Autrey

Catalysis Science
Physical Sciences Division

Principal Investigator:

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

Phone: (509) 375-3792

E-mail: tom.autrey@pnnl.gov

My research interest is focused on understanding the chemical and physical properties of bifunctional catalytic sites 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 like 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

Materials Science
Physical Sciences Division

Phone: (509) 375-7569

E-mail: nigel.browning@pnnl.gov

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, we can understand how

changes in the support and cluster chemistry change the location and type of interactions with porous materials such as Zeolites and MOFs. In more recent work on MoVTaNb oxide catalysts used for alkane oxidative dehydrogenation, we were able to evaluate the different activity associated with the different facets of the material, and by using ab-initio simulations identify unique atomic interactions that could potentially be responsible for the activity of the system.



R. Morris Bullock

Catalysis Science
Physical Sciences Division
Director of the Center for Molecular
Electrocatalysis

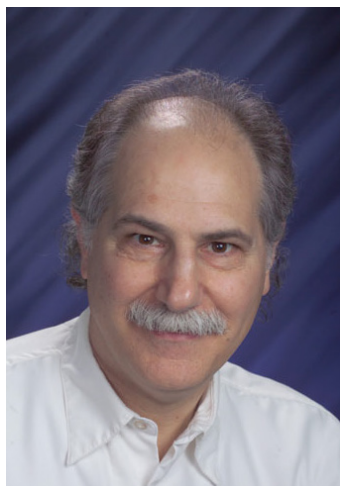
Phone: (509) 372-6589

E-mail: morris.bullock@pnnl.gov

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

I serve as Director of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center. The Center includes collaborators at Yale University, the University of Illinois, and the

University of Wisconsin. 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, and reduction of nitrogen, by studying how proton relays regulate the movement of protons and electrons within and between molecules to enhance rates of electrocatalysis. This research involves synthesis, mechanistic studies, electrochemistry, determination of thermochemical properties, and evaluation of catalysis performance.



Don Camaioni

Catalysis Science
Physical Sciences Division

Phone: (509) 375-2739

E-mail: donald.camaioni@pnnl.gov

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

Catalysis Science
Physical Sciences Division

Phone: (509) 372-6046

E-mail: hm.cho@pnnl.gov

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.



Miroslaw Derewinski

Catalysis Science
Physical Sciences Division

Phone: (509) 375-3856

E-mail: miroslaw.derewinski@pnnl.gov

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.



Zdenek Dohnálek

Catalysis Science
Physical Sciences Division
Deputy Director
Institute for Integrated Catalysis

Principal Investigator:

Subtask 1.2: Fundamentals of Acid/base and Redox Reactions on Metal Oxide Catalysts

Phone: (509) 371-6150

E-mail: zdenek.dohnalek@pnnl.gov

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, photocatalytic water splitting, and CO₂ 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 monodis-

persed 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 oxide catalysts with tailored chemical properties. Studies are complemented by collaborative theoretical investigations to achieve detailed generalizable structure-reactivity relationships. Systems recently investigated include rutile TiO₂(110) and RuO₂(110) surfaces and supported WO₃, MoO₃ and CeO₂ clusters.



John L. Fulton

Chemical Physics & Analysis
Physical Sciences Division

Phone: (509) 375-2091

E-mail: john.fulton@pnnl.gov

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

Catalysis Science
Physical Sciences Division

Phone: (509) 371-7164

E-mail: feng.gao@pnnl.gov

My research interest is in heterogeneous catalysis; in particular the understanding of structure-function relationships on well-defined catalytic systems using (in situ) spectroscopies and reaction kinetics. In Thrust 1, Subtask 2 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 CeO_2 , TiO_2 , and ZrO_2 as catalysts or catalyst supports for oxygen removal, C-C coupling, and oxidative dehydrogenation (ODH) reactions.

My research team also conducts research associated with diesel engine exhaust cleaning, supported by DOE

EERE, Vehicle Technologies Office. We work on developing novel zeolite-based catalysts for use in selective catalytic reduction (SCR) and passive NO_x adsorber (PNA) 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., FCA, and PACCAR, to provide solutions to their practical problems.



Vassiliki-Alexandra Glezakou

Chemical Physics and Analysis
Physical Sciences Division

Phone: (509) 375-6961

E-mail: vanda.glezakou@pnnl.gov

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/CO₂ 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.



Bojana Ginovska

Catalysis Science

Physical Sciences Division

Phone: (509) 375-5979

E-mail: bojana.ginovska @pnnl.gov

My research interests focus on theory-based investigation and modeling of metal- and non-metal-based catalysts for energy applications using a variety of methodologies, including quantum mechanical calculations, classical and quantum mechanics/molecular mechanics simulations, and enhanced sampling techniques. Specifically, my work focuses on understanding the role of the outer coordination sphere on catalysis in natural enzymes and biomimetic metal-based molecular catalysts. I am exploring the effects of structural flexibility and mutations on the thermodynamic 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, probing the structure-function relationships. My research on the non-metal molecular catalysts (frustrated Lewis pairs) focuses on fundamentally understanding the mechanism of small molecule activation and subsequent catalytic reduction of unsaturated substrates, as well as the effects of the solvent environment on catalysis.



David J. Heldebrant

Applied Synthetic Chemistry
Energy and Environment Division

Phone: (509) 372-6359

E-mail: david.heldebrant@pnnl.gov

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 CO_2 , COS , SO_2 , and H_2S 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 (CO_2 surrogates) into chemicals such as fuels (CH_3OH). 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 CO_2 -activating/concentrating solvents to develop catalytic systems to provide renewable energy storage or value added products from CO_2 .



Michael A. Henderson

Catalysis Science
Physical Sciences Division

Principal Investigator:

Subtask 3.1: Fundamental Studies of
Water Splitting on Model Multifunctional
Photocatalysts

Phone: (509) 371-6527

E-mail: ma.henderson@pnnl.gov

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

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

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

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



John Holladay

Energy and Environment Sector
Energy & Environment Directorate

Phone: (509) 375-2025

E-mail: john.holladay@pnnl.gov

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 EERE'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 gasses, 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

Biological Sciences Division
Earth and Biological Science Directorate
Phone: (509) 371-6544
E-mail: jjianzhi.hu@pnnl.gov

My research experience includes 32 years in solid state and liquid state nuclear magnetic resonance (NMR), magnetic resonance spectroscopy, and imaging. 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 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 and high-pressure magic angle spinning NMR capabilities.
- ▶ Ultra-high field (850 MHz) NMR and computational modeling of NMR parameters.
- ▶ Development of unique high-resolution slow magic angle spinning NMR metabolomics tools for biosignature discovery in biological tissues with sample volume from less than about 0.2 μl to more than 1 cm^3 using a single probe



Abhi Karkamkar

Catalysis Science
Physical Sciences Division

Phone: (509) 372-4973

E-mail: abhi.karkamkar@pnnl.gov

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

ambiphilic 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 nanoalloy materials.



Bruce D. Kay

Chemical Physics and Analysis
Physical Sciences Division

Phone: (509) 371-6143

E-mail: bruce.kay@pnnl.gov

My catalysis-related research focuses on exploring the dynamics, kinetics, and reactivity of adsorbates on model oxide surfaces with an emphasis on understanding heterogeneous catalytic 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 A. Kimmel

Chemical Physics and Analysis
Physical Sciences Division

Phone: (509) 371-6134

E-mail: gregory.kimmel@pnnl.gov

My catalysis-related research focuses on exploring the dynamics, kinetics, and reactivity of adsorbates on model oxide surfaces. This experimental work is performed in collaboration with Nikolay Petrik and other scientists involved in Michael Henderson's Subtask 3.1. We use 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 hydroxylated $\text{TiO}_2(110)$. Currently, we are investigating the photooxidation of acetone on $\text{TiO}_2(110)$. The goal of these investigations is to provide a fundamental understanding of the physical and chemical properties of oxide surfaces that are relevant for their use in catalysis and photocatalysis.



Libor Kovarik

Microscopy Group
Environmental Molecular Sciences
Laboratory

Phone: (509) 375-4377

E-mail: libor.kovarik@pnnl.gov

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 environmental 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 δ - Al_2O_3 and θ - Al_2O_3 .



Johannes Lercher

Catalysis Science
Physical Sciences Division
Director of the Institute for Integrated
Catalysis

Principal Investigator:

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

Phone: (509) 375-2725

E-mail: johannes.lercher@pnnl.gov

My research interests focus broadly on elucidating common principles in catalytic reactions facilitated by molecular, surface model, and complex multi-functional 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 methane; and the hydrogenation and hydrodefunctionalization of biogenic and fossil feedstocks (such as lignin and aromatic molecules containing oxygen, nitrogen, and sulfur). The elementary steps and selective control of sorption and diffusion in molecular sieves is another significant focus of my work outside the catalysis area.



Mike Lilga

Chemical and Biological Process
Development Group
Energy and Environment Directorate
Phone: (509) 375-4354
E-mail: mike.lilga@pnnl.gov

My research focuses on the catalytic and electrocatalytic conversion of biomass-derived materials to renewable transportation fuels and chemicals. Processes that use catalysts to enable high carbon efficiencies, low temperature and/or pressure conditions, and control of product selectivities are of particular interest. A goal for fuel production is to develop methods for the production of open-chain hydrocarbon blend stocks for jet and diesel fuels. Routes to both drop-in and new chemical products are being developed. Methods range from catalyst screening using combinatorial methods, to 1-5 cc flow reactors, to 30-70 cc flow reactors, 50-300 mL batch reactors for dehydrations, oxidations, reductions, polyol

cracking, olefin oligomerization, and olefin metathesis. The electrochemical stabilization and upgrading of bio oil is being studied in experimental and theoretical investigations. Our work has been conducted both for DOE and for numerous industrial collaborators.

- ▶ Development of catalysts and catalytic processes for the production of biorenewable transportation fuels,
- ▶ Development of catalysts and processes for value-added chemical products from biomass,
- ▶ Distinguished inventor with 15 issued patents in the area of catalysis and renewable fuels and chemical production.



John Linehan

Catalysis Science
Physical Sciences Division

Phone: (509) 375-3983

E-mail: john.linehan@pnnl.gov

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 CO₂ 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 CO₂ 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.



Jun Liu

Energy Processes & Material Division
Energy & Environmental Directorate

Phone: (509) 375-4443

E-mail: jun.lui@pnnl.gov

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

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



Igor Lyubinetsky

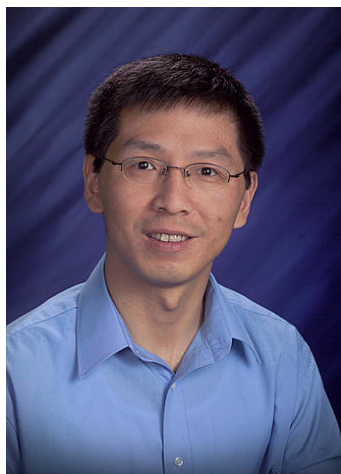
Materials Science
Physical Sciences Division

Phone: (509) 371-6267

E-mail: igor.lyubinetsky@pnnl.gov

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

scanning probe techniques, variety of molecular-level spectroscopies together with theoretical studies (in collaboration) is used. In the past year, my team has continued our work on identifying reaction pathways and mechanisms related to surface reactivity and photocatalytic processes on reduced $\text{TiO}_2(110)$. In particular, we have examined the origin of reactant coverage dependence in photo-reactivity on $\text{TiO}_2(110)$.



Donghai Mei

Catalysis Science
Physical Sciences Division

Phone: (509) 375-6303

E-mail: donghai.mei@pnnl.gov

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 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 lignin-derived phenolic compounds to long-chain hydrocarbons via hydrodeoxygenation and carbon-carbon coupling processes using bifunctional zeolite-based transition metal catalysts. In particular, the aqueous-phase effects on the catalytic activity and selectivity have been investigated with the explicit description of aqueous phase using *ab initio* molecular dynamics simulations.



Michael T. Mock

Catalysis Science
Physical Sciences Division
Center for Molecular Electrocatalysis
Phone: (509) 375-2975
E-mail: michael.mock@pnnl.gov

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

This research combines experiment and theory and uses earth-abundant transition metals such as tungsten, molybdenum, chromium, and iron to study dinitrogen and ammonia complexes with diphosphine ligands containing non-coordinating pendant amine groups. These studies seek to answer fundamental questions regarding the role of pendant bases in the second coordination sphere and aim to utilize their ability to modulate the reduction and oxidation potentials of a metal complex, promote proton-coupled electron transfer reactions, and facilitate proton transfer processes relevant to energy storage in N-H bonds, and for the multi-proton, multi-electron electrocatalytic reduction pathway of dinitrogen to ammonia.



Molly O'Hagan

Catalysis Science
Physical Sciences Division
Center for Molecular Electrocatalysis
Phone: (509) 371-6741
E-mail: molly.ohagan@pnnl.gov

My research is focused on mechanistic studies of structure/function relationships in molecular catalysts. In the Center for Molecular Electrocatalysis (an Energy Frontier Research Center), we use nuclear magnetic resonance spectroscopy to identify catalytic intermediates, understand structural dynamics, and study the mechanism of proton movement in earth-abundant bioinspired catalysts for H₂ oxidation and production. We also investigate the role of the medium in these

processes to develop an understanding of how the medium composition can be used to modulate catalytic efficiencies. My efforts have been closely coupled with theoretical efforts to provide mechanistic details to develop design principles for improved catalysts.

I am also interested in using biologically derived and inspired catalysts to develop a fundamental understanding of the function of metalloenzymes and how this can be applied to designing improved molecular catalysts.



Mariefel V. Olarte

Chemical & Biological Process
Development Group
Energy and Environment Directorate

Phone: (509) 375-2200

E-mail: mariefel.olarte@pnnl.gov

My research is focused on catalytic upgrading of bio-oils to produce hydrocarbons and the analysis of the reactant and product streams. This involves working with teams at PNNL and external collaborators to develop catalyst, process and analytical methods. The stability of the catalyst, both in activity and mechanical integrity, as well as its regeneration in the presence of thermally unstable oxygenated compounds, condensed water, steam, inorganic impurities and heteroatoms (such as S) in the feed stream are of interest. Continuous flow reactors at different scales are used to test the catalyst activity and time-on-stream performance. Analyses of the spent catalyst are done through nitrogen physisorption, X-ray

diffraction, microscopic techniques, elemental analysis, and solid state nuclear magnetic resonance spectroscopy. Results of these experiments, coupled with techno-economic analysis, provide feedback to catalyst and process design.

Catalytically upgrading bio-oils to different levels and subsequent analyses of these streams enable identification of functional groups or impurities that can adversely affect catalyst activity, as well as possible co-processing points in the existing liquid fuel infrastructure. Nuclear magnetic resonance spectroscopy, gas and liquid chromatography, mass spectroscopy, titration techniques, and elemental analysis all contribute to this effort.



Nikolay Petrik

Chemical Physics & Analysis
Physical Sciences Division

Phone: (509) 371-6151

E-mail: nikolai.petrik@pnnl.gov

My research is focused on fundamental experimental studies of non-thermal processes at surfaces and interfaces, including heterogeneous photocatalysis, 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) and TiO₂(110)) and a wide spectrum of inorganic and organic adsorbates, from simple molecules (CO₂, CO, O₂, H₂O, 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 effects in photocatalysis, the role of surface dipoles in the charge transfer of photo-generated electrons and holes to the adsorbate, the correlation of the structure of the adsorption complex with photo-reactivity on TiO₂(110), the interaction of molecules with radiation-induced defects on the surfaces, the role of surface diffusion in surface reactions.



Simone Rauegi

Catalysis Science
Physical Sciences Division
Center for Molecular Electrocatalysis
Phone: (509) 372-6902
E-mail: simone.rauegi@pnnl.gov

My activity focuses on the development and application of computational methodologies to study the relationships between structure and function in biomolecules and metal complexes as well as chemical-physics processes in the liquid phase. I am the PI of the BES Biophysical Sciences Program at PNNL. The program's focus is to uniquely characterize key biochemical and biophysical features of enzymatic processes related to production of a suite of small sustainable energy carriers to drive the design of synthetic catalytic platforms with enhanced performances. Initial efforts are directed toward understanding hydrogenase and nitrogenase enzymes using a variety of computational and experimental approaches. I am also the PNNL PI for

the ARPA-e REMOTE program "Anaerobic methane conversion to methanol" (PI: Stephen Ragsdale, University of Michigan). Within this program, I seek an atomistic understanding of methane activation by the enzyme Methyl Coenzyme-M reductase, the key enzyme in the microbial methane conversion. Finally, I am the PI for the crosscutting theory tasks in of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center (Director: 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 hydrogen production/oxidation and oxygen reduction.



Roger Rousseau

Catalysis Science
Physical Sciences Division

Principal Investigator:

Subtask 2.2: Multifunctional Catalysts for
CO₂ Reduction to Energy Carriers

Phone: (509) 372-6092

E-mail: roger.rousseau@pnnl.gov

My research work has focused on the application of quantum mechanical methods in simulations of the properties and reactivity of molecules, solids, and surfaces. My current research interests involve the application and development of ab initio molecular dynamics methods to study hetero- and homogenous 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 C₂-oxygenate synthesis from syngas and

steam reforming of biomass-derived tars, thermal and electrochemical upgrading of bio-oils to fuel precursors; design of CO₂ capture solvent systems for flu-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 BES program. These methods are then adapted and deployed on projects relevant to DOE's technology offices where we have active programs in applied catalysis and materials.



Gregory K. Schenter

Chemical Physics and Analysis
Physical Sciences Division

Phone: (509) 375-4334

E-mail: greg.schenter@pnnl.gov

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 mater-



Wendy Shaw

Catalysis Science
Physical Sciences Division

Principal Investigator:

Subtask 3.3: Modulating Catalysts with an Enzyme-Like Outer Coordination Sphere

Phone: (509) 375-5922

E-mail: wendy.shaw@pnnl.gov

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 mimicked enzymatic function by controlling the reactivity of a complex for CO₂ hydrogenation with an attached azobenzene which alters the structure of the complex with the application of

a stimulus, in this case light. In the area of proton pathways, we have synthesized the first electrochemically reversible molecular complexes for hydrogen oxidation/production catalysts by including outer coordination sphere amino acids. Essential features include a three-membered proton pathway and having side chains that can interact to control the active site structure. In the absence of these features, reversibility is either lost or rates drop at least an order of magnitude. The cooperativity of the elements is reminiscent of enzymes and is resulting in design principles for the outer coordination sphere. In developing complexes with larger outer coordination spheres, we designed and tested a series of hydrogen production catalysts with appended β -hairpin peptides. The rates suggest important dynamic and steric interactions that influence reactivity.



Mark Stewart

Modeling and Analysis
Nuclear Science Division

Phone: (509) 375-2179

E-mail: mark.stewart@pnnl.gov

My job is to help industry make use of cutting edge chemical conversion processes and the latest insight into reaction rates and mechanisms. Our partners at vehicle OEMs and major component suppliers are knowledgeable in their fields of study and sophisticated users of current technology. Nevertheless, they are anxious to take advantage of the advanced analytical capabilities and expertise of leading researchers at national laboratories. Promising new catalysts developed at PNNL are being evaluated with teams

of industrial collaborators under the grueling conditions expected in the field. If successful, new exhaust treatment catalysts could help enable adoption of next-generation fuel efficient engines, while still meeting ever-tightening limits on criteria pollutants. Studies at PNNL are also helping industry optimize current catalyst technologies, improve exhaust aftertreatment system durability, and create better models to assist in overall vehicle design.



János Szanyi

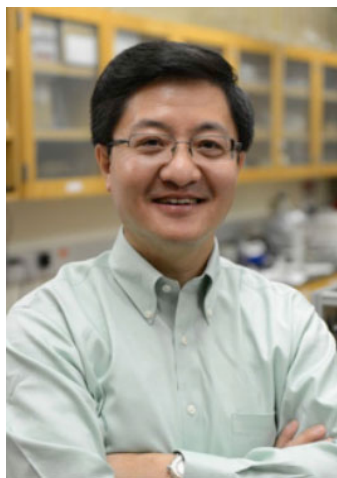
Catalysis Science
Physical Sciences Division

Phone: (509) 371-6524

E-mail: janos.szanyi@pnnl.gov

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 UHV conditions. Our results provide information on the energetics of the interactions between highly dispersed metals and selected probe molecules. Applying in situ RAIR spectroscopy, we study the binding configurations of adsorbates to metals and identify surface species present on the metal and support materials under elevated

reactant pressures. Simultaneously, we are conducting detailed kinetics and *operando* spectroscopy measurements on model high surface area supported metal catalysts using flow reactors and SSITKA/FTIR/MS 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 CO₂. 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_x on zeolite-based catalysts, low temperature NO and CO oxidation on metal oxides, and low temperatures NO_x and HC storage in zeolites.



Yong Wang

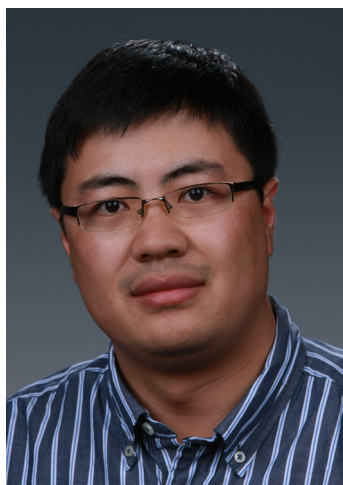
Hydrocarbon Processing
Energy Processes & Materials Division

Phone: (509) 371-6273

E-mail: yong.wang@pnnl.gov

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.



Huamin Wang

Chemical and Biological Process
Development
Energy Processes & Materials Division
Phone: (509) 371-6705
E-mail: huamin.wang@pnnl.gov

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 (fast pyrolysis and hydrothermal liquefaction) of biomass into fuels, catalytic fast pyrolysis of biomass, and converting biomass-derived alcohols 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 the conversion of biomass-derived oxygenates.



Robert Weber

Catalysis Science
Physical Sciences Division

Phone: (509) 372-4748

E-mail: robert.weber@pnnl.gov

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 kinetic modeling efforts and experimental activities focus on reactions 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 thermo-chemical processing of biomass into fuel precursors, and the electrochemical and photochemical transformations of organic molecules

into active pharmaceutical ingredients.

We have proposed to use solvatochromism of luminescent surface-supported chromophores to probe the cybotactic region at the interface of complex reaction media with the surfaces of supported metal catalysts. In recent work, we found catalysts that exhibit strong solvatochromic shifts and parallel, strong changes in the activation of hydrogen. We inferred from the data that the catalyzed transfer of hydrogen involves heterolytic bond breaking and formation. We have used models of the cybotactic region to motivate the definition of a new type of support effect: The Mr. Roger's Support Effect refers to catalyzed systems in which the support differentially attracts substrates to the neighborhood of the catalytic site.

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

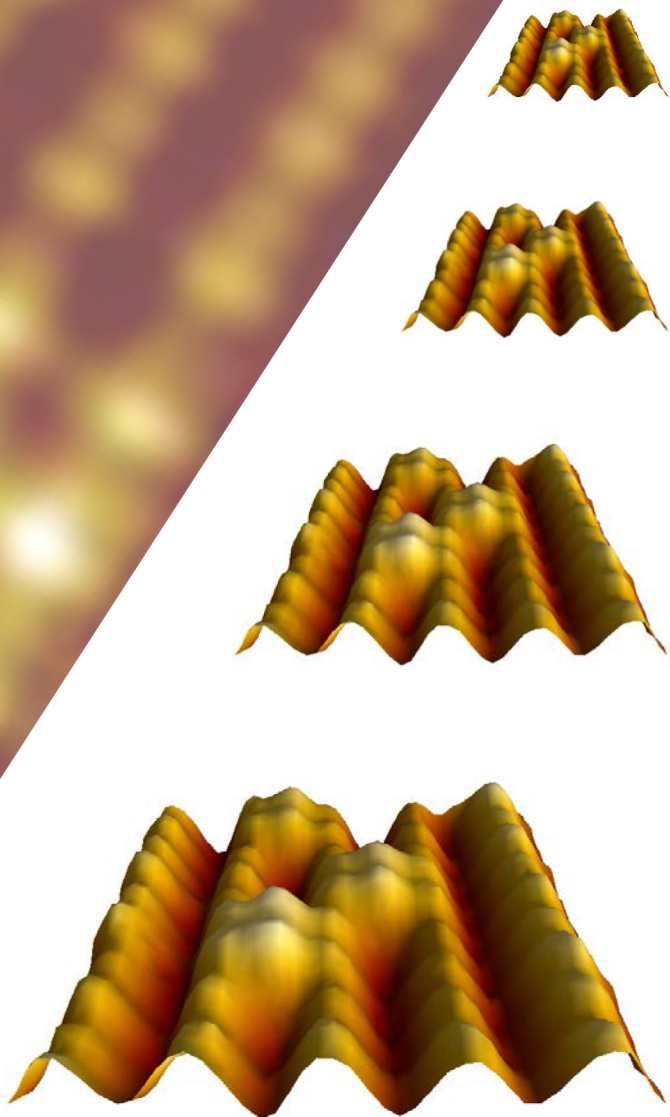


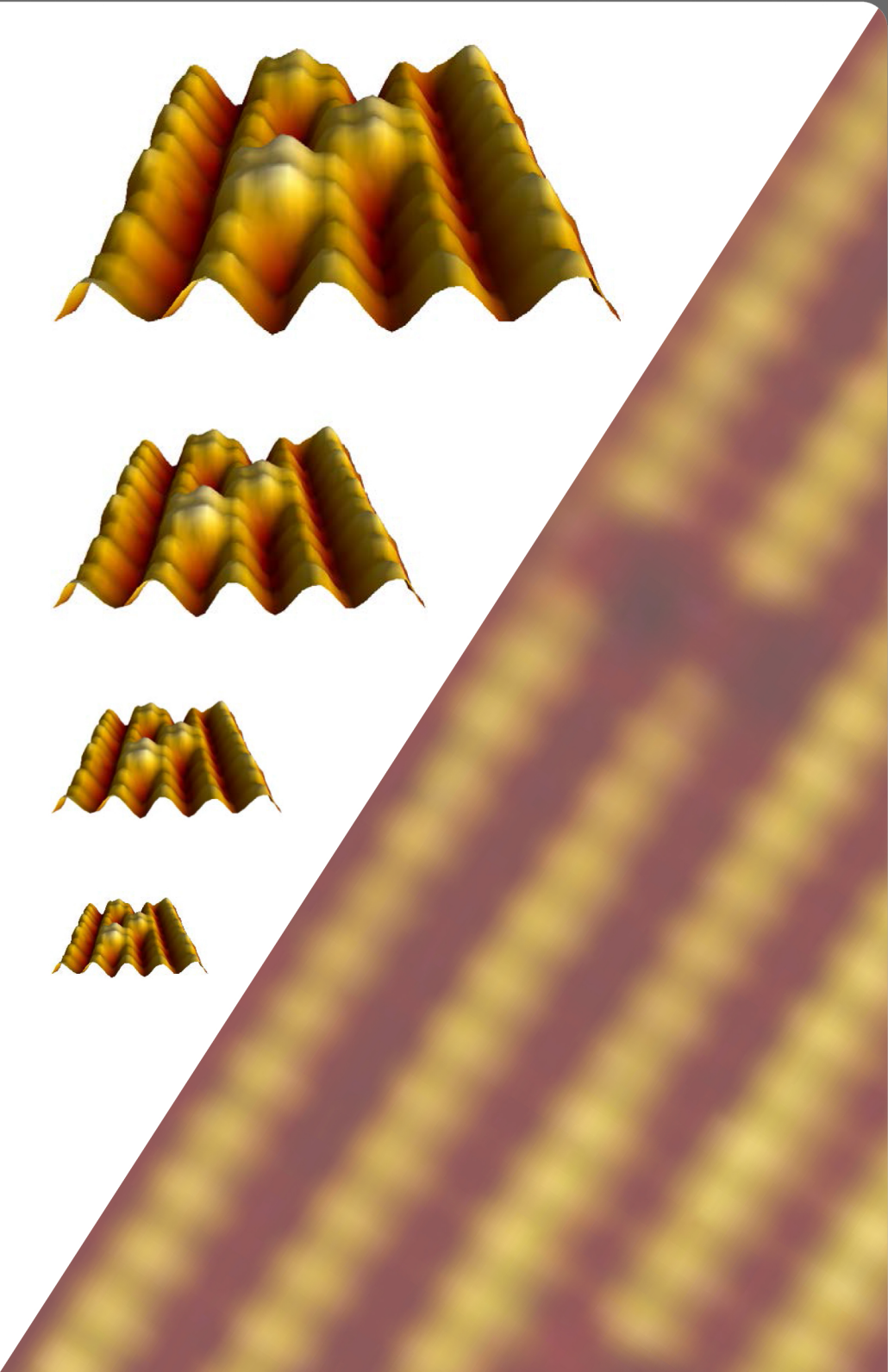
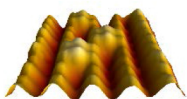
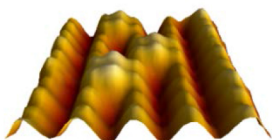
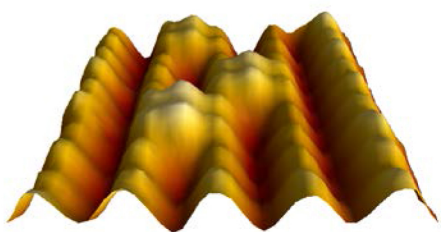
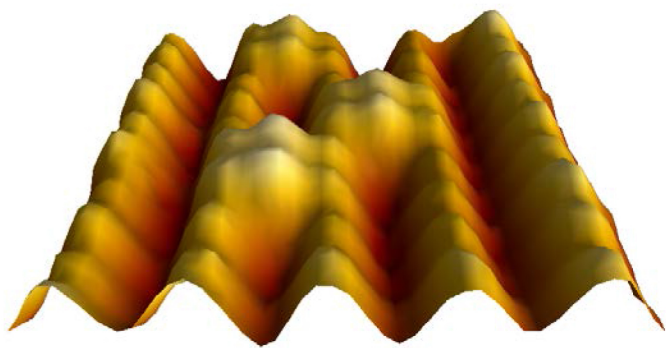
Eric Wiedner

Catalysis Science
Physical Sciences Division
Center for Molecular Electrocatalysis
Phone: (509) 372-4368
E-mail: eric.wiedner@pnnl.gov

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 electrocatalytic reduction of carbon monoxide as part of Subtask 2.1, Designing Catalysts Using an Energy-Based Approach: Molecular Catalysis for Carbon Dioxide Reduction, 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

CONTACTS

Johannes Lercher, Director
Institute for Integrated Catalysis
johannes.lercher@pnnl.gov
(509) 375-2725
iic.pnnl.gov

R. Morris Bullock, Director
Center for Molecular Electrocatalysis
morris.bullock@pnnl.gov
(509) 372-6589
efrc.pnnl.gov

PNNL-SA- 118502 | June 2016.



Pacific Northwest
NATIONAL LABORATORY

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

P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)
www.pnnl.gov

U.S. DEPARTMENT OF
ENERGY

Office of Science