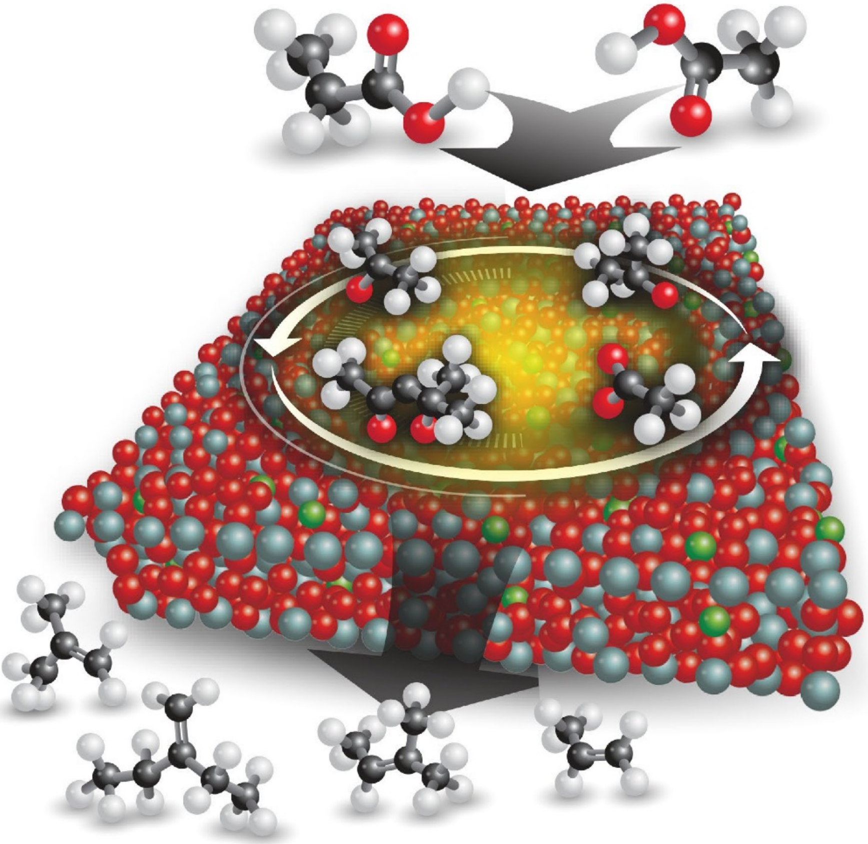
Pacific Northwest
NATIONAL LABORATORY

Institute for Integrated Catalysis

2019

PROGRAM BRIEFING



U.S. DEPARTMENT OF ENERGY
Office of Science

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ABBREVIATIONS

AIMD	ab initio molecular dynamic
AIChE	American Institute of Chemical Engineers
ATP	adenosine triphosphate
BES	Basic Energy Sciences
CME	Center for Molecular Electrocatalysis
DFT	density functional theory
DOE	U.S. Department of Energy
DRIFTS	diffuse reflectance infrared Fourier transform spectroscopy
EPR	electron paramagnetic resonance
EXAFS	extended X-ray absorption fine structure
IIC	Institute for Integrated Catalysis
NMR	nuclear magnetic resonance
PI	Principal Investigator
PNNL	Pacific Northwest National Laboratory
SAC	single atom catalyst
SCR	selective catalytic reduction of NO_x
STM	scanning tunneling microscopy
TEM	transmission electron microscopy
TPD	temperature-programmed desorption
XAFS	X-ray absorption fine structure
XAS	X-ray absorption
XRD	X-ray diffraction

INTRODUCTION

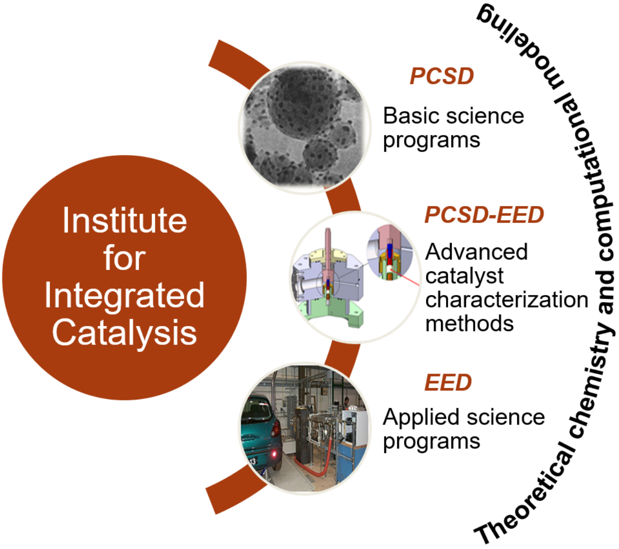
Economic wealth is directly correlated with the energy used to perform work, enable mobility, and provide the goods required to ensure our wellbeing. Today, more than 80% of chemicals and energy carriers are synthesized from fossil (hydro)carbon resources, which has led to an unprecedented increase in the levels of CO_2 in the atmosphere. Nearly all of these chemicals and energy 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.

The Institute for Integrated Catalysis explores and develops the chemistry and technology of catalyzed processes to reduce the environmental footprint.

Institute for Integrated Catalysis

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

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



The IIC integrates more than 100 scientists and engineers from different organizations at PNNL. These organizations include the Physical and Computational Sciences Directorate (PCSD) and the Energy and Environment Directorate (EED) and encompass a wide range of catalysis disciplines. The cross-disciplinary collaboration and mutual influence produce a unique creative environment, which is a prerequisite for transformative research. The key scientific challenges addressed within the IIC focus on adding hydrogen to oxo-functionalized carbon resources (such as biomass constituents or carbon dioxide), storing electric energy in hydrogen, oxygen, or nitrogen (key foci of the Center for Molecular Electrocatalysis (CME), an Energy Frontier Research Center), manipulating carbon–carbon and carbon–heteroatom bonds, and exhaust catalysis.

CORE BASIC ENERGY SCIENCES CATALYSIS PROGRAM: Transdisciplinary Approaches to Realize Novel Catalytic Pathways to Energy Carriers

Principal Investigator (PI): Johannes Lercher
Subtask PIs: Aaron Appel, Zdenek Dohnálek, Roger Rousseau, Janos Szanyi
Co-PIs and Key Personnel: S. Thomas Autrey, R. Morris Bullock, David A. Dixon (University of Alabama), John L. Fulton, Feng Gao, Bojana Ginovska, Vassiliki-Alexandra Glezakou, Oliver Y. Gutiérrez, Jian Zhi Hu, Enrique Iglesia (University of California, Berkeley), Andreas Jentys (Technical University of Munich), Abhijeet Karkamkar, Bruce D. Kay, Greg A. Kimmel, Libor Kovarik, John C. Linehan, Nikolay G. Petrik, Gregory K. Schenter, Wendy J. Shaw, Huamin Wang, Yong Wang (Washington State University), Eric S. Wiedner

The central goal of this BES Catalysis Sciences research program is to develop insight into novel approaches for designing catalytic centers and their environments. We aim to catalyze C-C and C-H bond formation and C-O bond cleavage on acid–base and hydrogenation sites with rates that exceed the current state of the art by at least an order of magnitude and with selectivities that match the best that are currently known. As schematically illustrated in Figure 1, we target the fundamental catalysis of these reactions because high reaction rates at mild conditions coupled with high selectivity is key for more flexible production of fuels and chemicals.

We are convinced that in order to enhance the rates and selectivity of acid–base catalyzed C-C coupling and metal-catalyzed hydrogen addition to C-O bonds, the nature of active sites has to be understood at a level of complexity that

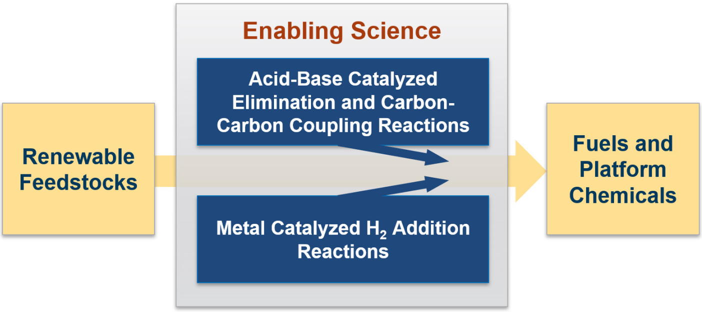


Figure 1. Our program provides the fundamental science base for processes, enabling the reductive conversion of renewable feedstocks to fuels and platform chemicals.

markedly exceeds the current state. We are acquiring and using new insights for the design of active sites (Figure 2) by placing specific emphasis on (1) the nature, nuclearity, and local environment of active centers; and (2) the extended chemical and structural environment around the active center to support suitable self-organization of reactants and solvents and to stabilize transition states. Our work is rooted in the knowledge that the nature of the active center (its electronic properties, spatial arrangement, and nuclearity) determines the chemical specificity and intrinsic reactivity. We are guided by the fundamental hypothesis of this program that activity along selected pathways for metal and acid–base catalyzed reactions can be markedly enhanced by (1) positioning of functional groups around the active center, (2) adjusting the available space around the active center to match that of the rate-limiting transition state, and (3) self-organization of solvent and reactant molecules around the active center. This environment can have the form of a void (maximizes van der Waals contacts with minimal distortions of the host and the guest in the transition state), a functional group aiding the stabilization of reactants along the reaction path, or an ensemble of solvent/reactant molecules engulfing the active center.

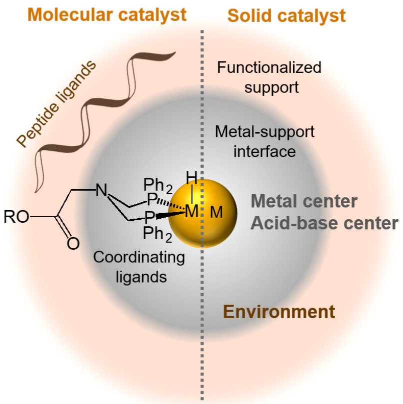
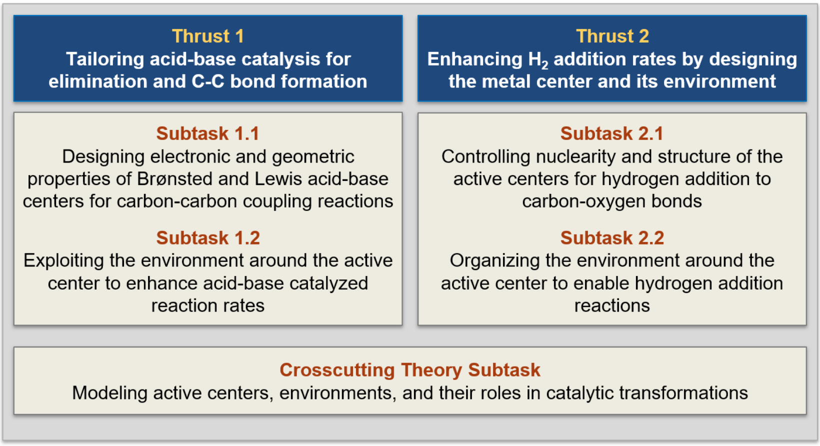


Figure 2. Schematic representation of an active site, consisting of an active center and its environment. The environment can be as local as the directly neighboring atoms of a support or the atoms in a ligand or a coordination compound.

To achieve our goal of enhancing rates and selectivities for our target reactions, the program is organized into two thrusts that focus on “tailoring acid–base sites for controlled C-C bond formation” and “enhancing H_2 addition rates by designing the metal center and its environment.” To gain a molecular-level insight into catalysis on both types of sites, computational catalysis is integrated in the cross-cutting subtask, “novel theoretical approaches to describe catalysts and catalysis,” and supports, enhances, and guides experimental efforts. The overall organization of the program is schematically shown in Figure 3. The first thrust explores the impact of the geometric and electronic properties of Lewis and Brønsted acid–base sites on C-C bond formation by combining precision synthesis of homotopic active sites of chosen nuclearity and the stabilization of such sites in homogeneous catalysts, inert substrates, faceted oxides, mesoporous solids, and zeolites. Spectroscopic characterization of these sites and the associated catalytic transformations allow for directed cross-coupling of the obtained insights. The second thrust addresses the fundamentals of hydrogen addition to CO groups in molecules such as CO_2, alcohols, aldehydes, ketones, and carboxylic acids. We exploit novel, highly active sites comprised of single metal atoms and small clusters of defined nuclearity supported by homogeneous scaffolds of increasing complexity and heterogeneous supports, such as graphene and faceted and microporous oxides. We designed our program structure to promote cross-disciplinary collaborations within and across thrusts and subtasks. The structure–activity relationships dominated by the acid–base or metal center are highlighted in the first subtasks in each thrust, while the second subtasks feature the impact of the environment (ligands, confinement, solvent, and reactant molecules).



Thrust 1
Tailoring acid-base catalysis for elimination and C-C bond formation

Thrust 2
Enhancing H_2 addition rates by designing the metal center and its environment

Subtask 1.1
Designing electronic and geometric properties of Brønsted and Lewis acid-base centers for carbon-carbon coupling reactions

Subtask 1.2
Exploiting the environment around the active center to enhance acid-base catalyzed reaction rates

Subtask 2.1
Controlling nuclearity and structure of the active centers for hydrogen addition to carbon-oxygen bonds

Subtask 2.2
Organizing the environment around the active center to enable hydrogen addition reactions

Crosscutting Theory Subtask
Modeling active centers, environments, and their roles in catalytic transformations

Figure 3. Structure of the BES Catalysis core program.

Thrust 1: Tailoring Acid–Base Catalysis for Elimination and C-C Bond Formation

The energy-efficient conversion of highly functionalized, distributed feedstocks into drop-in fuels requires precise control over many kinetically coupled steps. The key requirements of the catalytic chemistries utilized in such conversions include the efficient elimination of oxygen functionalities present in saturated (e.g., C–OH and C–O–C) and unsaturated (e.g., C=O) groups with simultaneous C-C bond formation and a minimized loss of carbon and hydrogen. In this

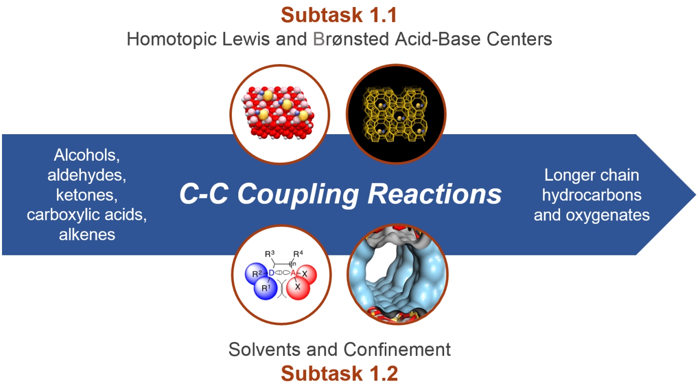


Figure 4. Thrust 1 aims to provide the fundamental understanding of carbon–carbon coupling reactions between simple oxygenates.

regard, well-defined catalytic sites with tailored Lewis and Brønsted acid/base properties are key for selectively guiding and enhancing the desired reaction pathways. In our prior research, we focused primarily on exploring the oxygen elimination of C–OH functionalities and hydrolysis and hydrogenolysis of C–O–C functionalities. While we continue using alcohol dehydration as a valuable probe reaction, our catalyst design efforts now primarily center on understanding C-C coupling reactions that include aldol condensation, ketonization, alkylation, and alkene oligomerization on complex but well-defined and supported oxide clusters and mixed oxide layers. The elementary steps of the elimination reactions of functional groups and the formation of C-C bonds should allow us to explore and exploit fundamental principles of acid–base catalysis at both gas–solid and liquid–solid interfaces.

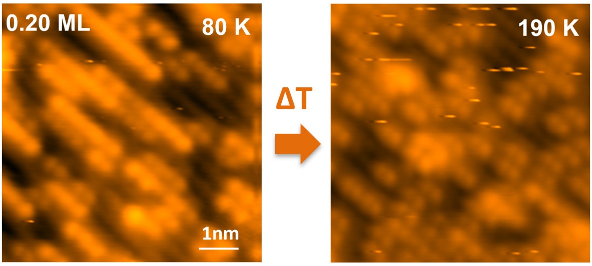
Subtask 1.1. Designing Electronic and Geometric Properties of Brønsted and Lewis Acid–Base Centers for Carbon–Carbon Coupling Reactions

Zdenek Dohnálek, David A. Dixon, Feng Gao, Oliver Y. Gutiérrez, Jian Zhi Hu, Greg Kimmel, Libor Kovarik, Johannes Lercher, Nikolay G. Petrik, Huamin Wang, Yong Wang

The principal goal of this subtask is to achieve a detailed fundamental understanding of how the geometric and electronic structure of complex Lewis and Brønsted acid–base centers on oxides control reaction mechanisms and energy landscapes of carbon–carbon bond formation and oxygen-elimination reactions. This insight provides the scientific basis for the design and synthesis of highly active and selective catalysts for the conversion of a broad range of oxygenates to platform molecules for fuel and chemical production. Homotopic planar surface science oxide models, high-surface-area faceted mixed oxides, and oxide clusters with well-defined nuclearity in zeolites are employed to provide insight into achieving higher activity and selectivity than currently possible with conventional oxides. Fine-tuning of the spatial and electronic structure of the acid–base pairs by changing the nature of the oxide and how it is anchored on or embedded in the host oxide lattice is utilized in gas phase reactivity studies to develop concepts that govern the design toward desired products of catalysts with optimized energy landscapes. To test and understand the oxide structure–function relationships, we employ simple alcohols, aldehydes, ketones, and carboxylic acids as reactants for elimination, aldol condensation, ketonization, and hydride transfer reactions. The experimental studies are closely coupled with theoretical investigations to provide a detailed, molecular-level understanding of the factors that control the function of the active centers. These studies are complemented by parallel acid–base chemistry studies in condensed media in Subtask 1.2, and the models developed here are further employed in Subtask 2.1.

Formation of Metastable Water Chains on Anatase $TiO_2(101)$

Zdenek Dohnálek



Metastable Water Chains **Isolated Water Monomers**

Figure 5. STM images of water on anatase $TiO_2(101)$ that illustrate the initial formation of metastable water chains and their thermally induced conversion to isolated monomers.

In this initial surface science study of anatase $TiO_2(101)$, we employed scanning tunneling microscopy (STM) and focused on adsorption of water as a function of coverage and temperature. We demonstrated that at very low temperatures (80 K), water has transient mobility that allows it to move on the surface and form extended chains (Figure 5, left). In contrast to many other oxides, these water chains are metastable in nature. Adsorption at higher temperatures where sustained diffusion is observed (190 K) leads to isolated water monomers (Figure 5, right), which is in accordance with prior studies. The observed low-temperature mobility was interpreted as a result of adsorption in a long-lived precursor state with a low diffusion barrier.

Adsorption and Dissociation of Methanol on Anatase TiO_2(101) Single Crystals and Faceted Nanoparticles

Zdenek Dohnálek, Feng Gao, Gregory Kimmel, Nikolay Petrik, Yong Wang

We employ a cross-disciplinary approach to study the adsorption and dissociation of methanol on the anatase TiO_2(101) surfaces of single crystals (SCs) and faceted nanoparticles (FNPs). While STM is used to follow the spatial distribution of adsorbed methanol molecules and methoxy and hydroxy species on SCs, temperature-programmed desorption (TPD) and infrared reflection spectroscopy (IRAS) results are compared on both SC and FNP surfaces. We find that molecular methanol adsorbed at 80 K on SC TiO_2(101) clusters along the titania rows. These clusters are metastable and fall apart upon annealing due to the repulsion of neighboring molecules. We also find that on SC TiO_2(101), methanol deprotonates to produce neighboring methoxy and hydroxyl groups at high coverages following annealing to 290 K (Figure 6). The coverage of methoxy and hydroxyl groups can be increased with repeated adsorption and annealing cycles, and annealing above 290 K leads to the recombinative desorption of methanol. At higher pressures on FNP TiO_2(101), methanol adsorbs both molecularly and dissociatively at 290 K. With increasing temperature, molecularly adsorbed methanol gradually converts to methoxy. Therefore, close correlations and complementary information are found in adsorption and surface reactions on single crystal and nanoparticle surfaces.

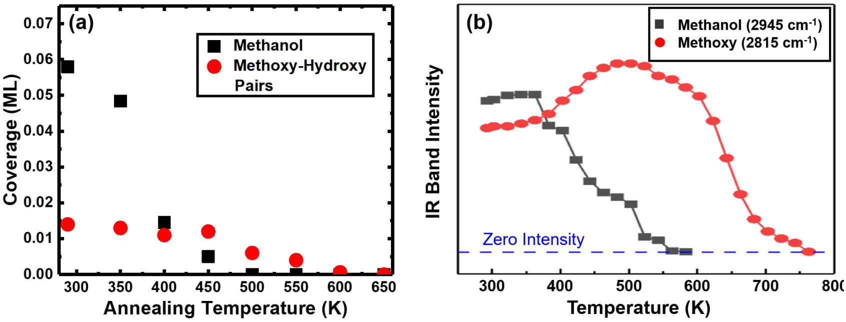


Figure 6. Similar trends for the evolution of molecularly adsorbed methanol and methoxy species on anatase TiO_2(101) SC (a) and FNPs (b). (a) Temperature-dependent coverage of methanol molecules and methoxy–hydroxy pairs from STM images. (b) Relative coverages of methanol and methoxy species obtained from IR spectroscopy.

Elucidation of the Active Sites for Alkanol Dehydration on Single-Facet Dominant Anatase TiO_2(101) and (001) Model Catalysts

Feng Gao, Libor Kovarik, Donghai Mei, Huamin Wang, Yong Wang

To elucidate the detailed mechanisms of alkanol dehydration on anatase TiO_2, two anatase titania model catalysts with preferential exposure of (101) and (001) facets were synthesized and studied for 2-propanol dehydration. A series of microscopic and spectroscopic techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), ammonia TPD, diffuse reflectance for infrared Fourier transform spectroscopy (DRIFTS), and chemical titration were employed to correlate the structure properties of the model catalysts to their catalytic performances. Based on selective site poisoning titration using 2,6-di-tert-butyl pyridine, surface Lewis acid sites were found to be active for 2-propanol dehydration. The higher activity of the TiO_2(101) catalyst was ascribed to the greater strength of its acid sites compared to those of the TiO_2(001) facets. Surface species present during steady-state reactions were probed using temperature-dependent DRIFTS and used to construct model surface structures to describe the elementary steps of 2-propanol dehydration using DFT. On both anatase surfaces, 2-propanol dehydrated via concerted E2 elimination pathways but with different initial states and different intrinsic activation barriers (Figure 7). Molecular 2-propanol dehydration dominates on TiO_2(101), while on TiO_2(001), 2-propanol simultaneously converts to the more stable 2-propoxide before dehydration, which requires higher activation energies for E2 elimination.

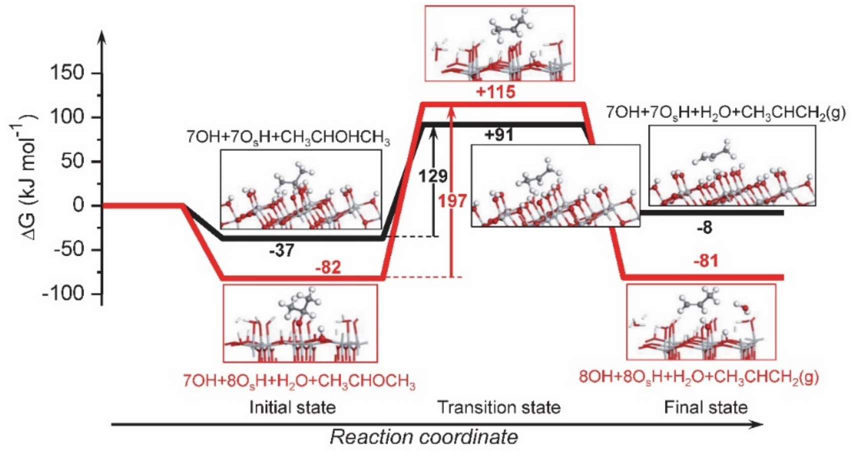


Figure 7. 2-propanol dehydration on the hydroxylated anatase TiO_2(101) and (001) surface via an E2 mechanism.

Formic Acid Adsorption and Binding on Anatase TiO_2(101)

Zdenek Dohnálek, Gregory Kimmel, Nikolay Petrik

Although formic acid is the simplest carboxylic acid, the molecular-scale understanding of adsorption configurations and the complexity of reaction selectivity on anatase TiO_2(101) have not been fully resolved. Here we focus on understanding the makeup of surface species at 80 and 150 K by a combination of STM and IRAS. At low coverages (< 0.2 monolayer), molecularly and dissociatively adsorbed formic acid coexist at 80 K, and the molecular form deprotonates at 150 K. At high coverages (> 0.2 monolayer), molecular formic acid is found to be stable at temperatures up to 150 K due to the site constraints. Short linear chains are observed along the [010] direction for the molecular form and along the [010], $[11\bar{1}]$, and $[\bar{1}11]$ directions for the dissociated form. At full monolayer, local (1 × 3) domains composed of alternatively arranged molecular and dissociated formic acid are revealed after annealing to 150 K. Using STM manipulation, we are able to cleave the O-H bond in molecularly adsorbed formic acid; the proton that is produced can be removed from the surface, leaving behind an isolated formate. The adsorbate configurations and their conversions are corroborated by following their vibrational signatures using IRAS (Figure 8). These studies provide the first experimental account of formic acid on a model anatase TiO_2(101) surface and complement prior extensive investigations on rutile TiO_2(110).

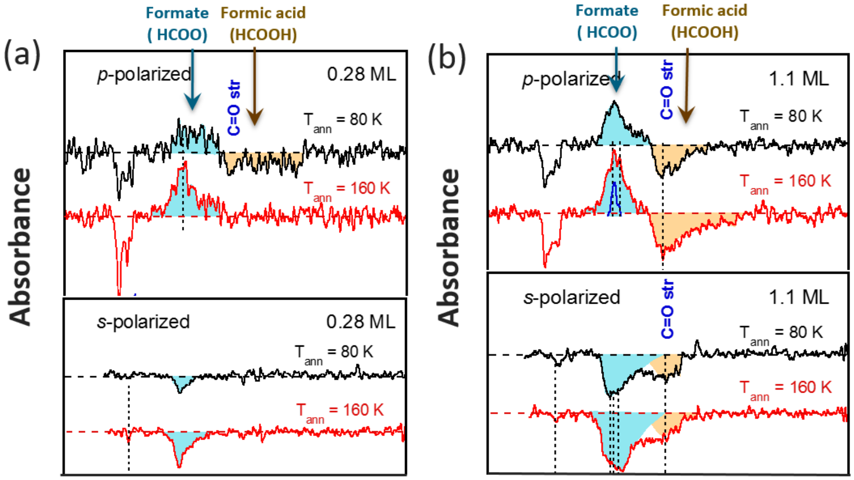


Figure 8. IRAS spectra of formic acid on anatase TiO_2(101) illustrates the higher stability of molecular formic acid at higher coverages at 160 K.

Identification of VO_x Structures at the Molecular-Level Using High Field Nuclear Magnetic Resonance

David Dixon, Jianzhi Hu, Yong Wang

The nature of the surface vanadia active sites on TiO_2 supports has received much attention to facilitate an improved understanding of the relationship between the molecular structures of the catalytic active sites and reactivity. By combing through detailed in situ spectroscopic measurements (NMR, Raman, and electron paramagnetic resonance (EPR)), quantum chemistry electronic structure calculations, and catalytic kinetic studies, we clarify the long-standing uncertainties in the molecular structures of surface vanadia. We further elucidate that incorporation of tungsten oxide alters the molecular structure of the surface vanadia sites by promoting the formation of oligomeric vanadia (Figure 9) into configurations that are favorable to reactions involving the two-site mechanism. This research strategy has provided direct evidence for the first time of the molecular structural changes that occur on the surface vanadium oxide active centers in the presence of the surface tungsten oxide promoter, demonstrating that the promotion mechanism of tungsten oxide proceeds via a structural effect and not as an electronic effect as widely proposed in the literature.

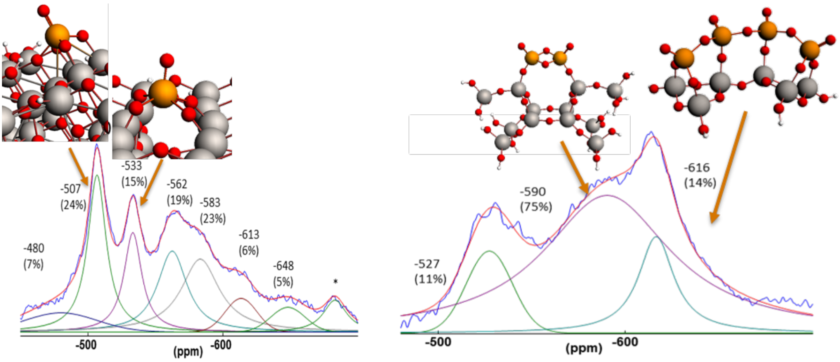


Figure 9. Solid-state ^{51}V MAS NMR spectra of dehydrated, impregnated 1% V_2O_5/TiO_2 (a) and 1% V_2O_5-5% WO_3/TiO_2 (b) catalysts with corresponding structural VO_x motifs determined by DFT. The spectral deconvolution summation is presented by the red line and compared to the collected data (blue). All spectra were externally referenced to V_2O_5 at 614 ppm.

Mechanistic Understanding of Ketone C-C Bond Coupling on $Zn_1Zr_{10}O_2$ Mixed Metal Oxides

Donghai Mei, Junming Sun, Yong Wang

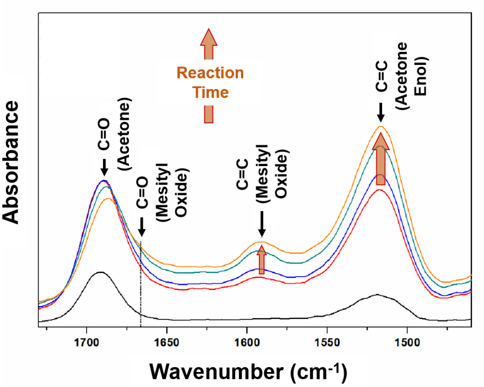


Figure 10. Time evolution of infrared spectra of adsorbed acetone on $Zn_1Zr_{10}O_z$ demonstrates the formation of the enolate intermediate.

Aldol condensation (or aldolization) is an extremely important reaction for C-C bond formation in both organic chemistry and heterogeneous catalysis. Aldol condensation of acetone has been practiced in both industry and academia to produce a wide range of valuable chemicals. The catalysts studied include zeolite with Brønsted acidity and (mixed) metal oxides with Lewis acid–base pairs. Even though it is still debated whether Brønsted acid sites or Lewis acid–base pairs are active sites, it is generally accepted that acetone enolate acts as the key intermediate in the C-C formation reaction. We identified acetone enolate and their subsequent surface aldolization reactions (C-C bond formation) using *in situ* DRIFTS. The real-time evolvement of surface species monitored by in situ DRIFTS of surface acetone (-d6) reactions and the heat flow from a micro-calorimetry measurement show unambiguous experimental evidence for the formation of acetone enolate (Figure 10) and subsequent aldolization via the Eley-Rideal mechanism on the $Zn_1Zr_{10}O_z$ mixed metal oxide.

Subtask 1.2. Understand and Control the Organization of the Environment Around the Active Site to Enhance Rates for C-C Bond Formation

S. Thomas Autrey, John Fulton, Oliver Y. Gutiérrez, Jian Zhi Hu, Enrique Iglesia, Andreas Jentys, Libor Kovarik, Johannes Lercher

Solvent and reactant molecules in the voids that host the active sites strongly influence the state of the active site and the free energy of ground and transition states. This subtask aims to use such self-organization of molecules around the active site to control catalysis. We hypothesize that having a better understanding of the physicochemical properties of catalyst environments, their ability to interact with hosted molecules, and, in particular, how they stabilize the transition state of desired reaction pathways will allow us to enhance both the rates of acid–base catalyzed reactions as well as the selectivity of those reactions' for a particular product. We use the dehydration of alcohols as a probe reaction to characterize the impact on the thermodynamic activity of reacting molecules and the activation energy and entropy to characterize the stabilization of the transition states. We use alkylation and alkene oligomerization as the most straightforward of bimolecular reactions in a constrained environment but strive to include the C-C bond formation in reactions between aldehydes and ketones as well as alkenes.

In investigating the impact of the density and polarity of the molecules around the active center, we shift the reaction environment from gas–solid to liquid–solid interfaces of increasing polarity and protic and aprotic properties of solvents and reactants. The transition to condensed media significantly increases the complexity because in the confines of the catalyst, the proximity of charge with protic solvents and the spatial self-organization as witnessed in the case of water induce a unique reaction environment that mimics quasi-solid electrolytes. This insight allows us to not only predict the impact of steric constraints on the targeted reactions, but also to use this specific environment to tailor the thermodynamic activity of the reactive substrates. This subtask complements and extends the effort in Subtask 1.2 to design the active site for acid–base catalyzed reactions.

Genesis and Stability of Hydronium Ions in Zeolite Channels

Donald M. Camaioni, Vassilliki Alexandra Glezakou, Oliver Y. Gutierrez, Jian Zhi Hu, Donghai Mei, Roger Rousseau, Yong Wang, and Johannes Lercher

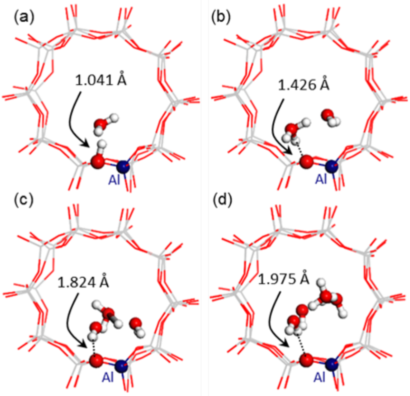


Figure 11. Structures illustrating the hydrating process in the H-ZSM5 zeolite channel with increasing numbers of water molecules optimized by DFT cluster calculations. From (a) to (d), the number of water molecules increases from 1–4, with the shortest O-H distance labeled in each instance.

Studies addressing the properties of Brønsted acid sites and zeolite frameworks in the presence of water in zeolite channels have shown that a number of species may co-exist, i.e., Brønsted and Lewis acid sites can exist alongside hydrogen-bonded water, hydrated hydronium ions, and physically adsorbed water, depending on the chemical potential of water. Identification of the conditions under which these different species exist has not been quantitative because of the lack of experimental access to information about the state of the adsorbed water under reaction conditions. To address this gap, we directly monitored the interaction between hydrogen species and silicon at the T site by ^{1}H-^{29}Si CP MAS NMR and theory. Quantitative spectral analysis showed the boundary conditions for the genesis, evolution, and stability of hydronium ions in HZSM5 pores.

Bridging hydroxyl groups are stable at water loadings of one H_2O/BAS or below. At these conditions, the O-H bond is elongated due to hydrogen bonding with the water molecule, but the proton remains bound to the Al T-site in the framework (Figure 11). The hydronium ion is formed upon proton transfer when two water molecules interact with the bridging hydroxyl group. We have unambiguously correlated this event with the appearance of a signal at 9 ppm in the ^{1}H NMR spectra (Figure 12). The hydronium ion has a longer spin–spin relaxation time than the strongly adsorbed water present at lower water loadings. DFT-based ab initio molecular dynamics studies support this conclusion and show the gradual formation of hydrated hydronium ions that are increasingly detached from the zeolite lattice (Figure 11).

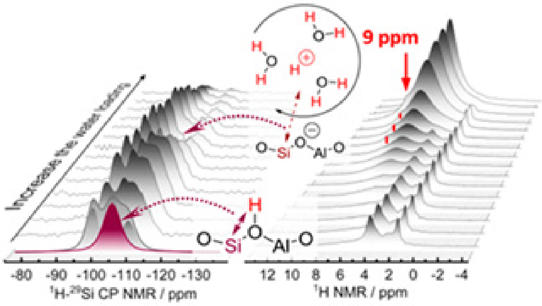


Figure 12. ^{1}H^{29}Si CP and ^{1}H NMR spectra as the concentration of water in the zeolite pores increases. The transition from a framework Brønsted site to a hydronium ion is indicated by the signal at 9 ppm.

Theory suggests that the confined cluster in the zeolite is more compressed than in the gas phase. In the confined cluster, 90–75% of the density is within 4 Å of the center of mass at 27–227 °C. In contrast, the gas phase cluster at 27 °C forms two shells around the central H_3O^+. In addition to the compression in the zeolite pores, the confinement enhances the proton mobility in the system but slightly increases the barriers for proton hopping. At loadings greater than ~ 8 H_2O/BAS, the excess water interacts with these Si-OH groups, causing them to disappear due to the fast exchange of water protons with the Si-OH proton of defects or outer crystal termination. The variation in the intensity of ^{1}H - ^{29}Si cross-polarization signal indicates that hydrogen bonds between water molecules and the tetrahedrally coordinated aluminum in the zeolite lattice weaken with the formation of hydronium ion–water clusters and increase the mobility of protons. Above 140 °C, however, fast proton exchange between bridging hydroxyl groups and water occurs even in the presence of only one water molecule per acid site.

Organization and Impact of Water in Pores of Brønsted Acidic MFI Zeolites

Johannes Lercher

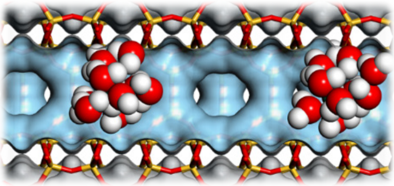


Figure 13. Schematic representation of hydrated hydronium ions separated by empty parts of zeolite channels, here depicted in a mordenite framework.

In the presence of sufficient concentrations of water, stable, hydrated hydronium ions are formed in the pores and at the surface of solid acids such as zeolites. For a particular pore size, such as that of zeolite MFI, the hydrated hydronium ions consist of eight water molecules and have an effective volume of 0.24 nm^3. The environment interacts with the sorbed molecules, either via directed bonds that include hydrogen bonding and electron–pair donor–acceptor interactions or via non-directed dispersion forces.

The relative dominance of the two types of interactions in an aqueous environment makes specific regions of the materials hydrophilic or hydrophobic characteristics that are manifested in colligative properties such as the specific surface tension, wetting, and the enrichment of polar or nonpolar components in complex mixtures.

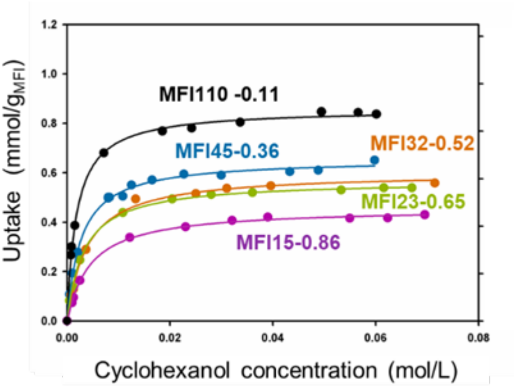


Figure 14. Adsorption isotherms of cyclohexanol at 300 K in the presence of water; the numbers right of the MFI notation correspond to the Si/Al ratio and concentration of hydronium ions in mmol/g.

For a series of MFI zeolites containing increasing concentrations of Brønsted acid sites, an increasing density of hydrated hydronium ions forms but is limited to about 7–8 water molecules per hydronium ion. This limitation is caused by the decreasing enthalpic stabilization with the increasing size of the hydration shell and is also influenced by the limiting repulsive interactions induced by the pore walls. Once the heat of adsorption approximates the heat of condensation, the much lower entropy hinders further adsorption of water molecules in the pores, and water condenses outside the zeolite. This leads to a situation in which discrete hydrated hydronium ions are separated by empty zeolite channels (Figure 13).

Organic molecules such as cyclohexanol are only able to adsorb in this void space. This is demonstrated in Figure 14, which shows decreasing cyclohexanol uptake with increasing concentrations of hydronium ions. These isotherms not only show a decrease in the maximum uptake of cyclohexanol, but also a gradual decrease of the adsorption constant with increasing hydronium ions.

This decrease in the adsorption constant is caused by the increase in the standard chemical potential of the adsorbate caused by an increase in the local ionic strength of the zeolite. The higher standard chemical potential leads to a lower interaction strength with the zeolite compared to a molecular sieve that is free of hydronium ions.

The results and their analysis provide new atomistic and molecular-level quantification of hydrophilic and hydrophobic properties of materials. The central parameters in the model presented, i.e., the size of $H_3O^+_{hydr.}$ in a confined space and the ionic strength in a “quasi-solid electrolyte” environment, are readily measurable and quantifiable for a large variety of microporous materials.

Organization and Impact of Water in Pores of Brønsted Acidic MFI Zeolites

Johannes Lercher

The presence of ion pairs, as induced by the formation of hydrated hydronium ions, decreases the strength of interactions between microporous sorbents and the organic sorbate. This weakening of the interactions is caused by an increase in the chemical potential of the sorbed reactant. The question arises whether this higher chemical potential translates to higher reactivity of the substrate.

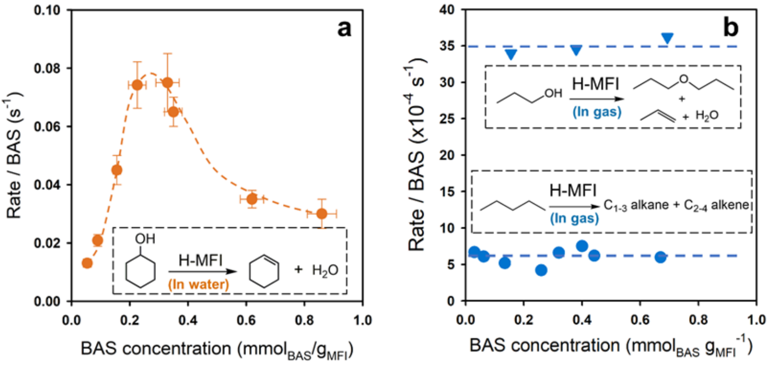


Figure 15. Brønsted acid site (BAS) normalized reaction rate in H-MFI catalyzed reactions in water and gas phases. (a) Dehydration of cyclohexanol at 423 K on H-MFI with different BAS concentrations in the aqueous phase. (b) Cracking of n-pentane at 763 K (●) and dehydration of 1-propanol at 433 K (▼) on H-MFI with different BAS concentrations in the gas phase.

Using a series of MFI zeolites with varying concentrations of Brønsted acid sites, we show that for gas-phase catalysis (using the elimination of water from 1-propanol and cracking of n-pentane), all Brønsted acid sites have the same catalytic activity. In the presence of water, which leads to the formation of hydrated hydronium ions, the catalytic activity for cyclohexanol dehydration increased first almost linearly with increasing concentration of hydronium ions. Beyond the ratio of one cyclohexanol molecule per hydronium ion, the turnover frequency markedly dropped (Figure 15).

The increase is similar to the higher thermodynamic activity observed with a Brønsted acidic aqueous phase for which the ionic strength is increased by the addition of NaCl. Detailed analysis shows that maximum activity is related to a constant increase in the chemical potential in the ground state as well as for lowering the chemical potential in the transition state. The experiments show for the first time that the thermodynamic standard chemical potential can be adjusted to enhance catalytic activity.

Alkene Dimerization Catalysis on Grafted Ni Cations at Sub-ambient Temperatures: Mechanism, Site Requirements, and Solvation Effects by Intrapore Liquids

Isabel Agirrezabal-Telleria, Shuai Wang, Enrique Iglesia

Recent studies have uncovered the strong effects of a non-polar liquid phase on the dimerization rates, selectivities, and stabilities of Ni-based solid catalysts. These catalysts deactivate rapidly and have previously shown lower reactivity and selectivity than their organometallic counterparts. This study has uncovered that oligomerization of small alkenes (ethene, propene, and butenes) occurs at high rates and with >98% initial selectivity to primary dimers at sub-ambient temperatures (240–260 K) on Ni(II) cations grafted within Al-MCM-41 mesopores and without detectable deactivation when reaction conditions lead to the formation of an intrapore liquid phase (Figure 16). The active sites consist of isolated $(\text{Ni-OH})^+$ species that replace protons in the aluminosilicate structures; these sites do not require the aluminoxane activators and co-catalysts that must be present in large excess for dimerization turnovers in organometallic catalysts and metal–organic framework catalysts. These active sites, however, deactivate very rapidly in the absence of an intrapore liquid phase but become stable for all alkenes (half-lives > 500 h) when the pressure of the alkene reactants (or of added inert alkanes), the temperature, and the diameter of the mesopores combine to cause the abrupt condensation of these molecules within the mesoporous network that contains the active Ni species. Such stabilization appears to reflect the preferential stabilization of the late transition states that mediate the desorption of bound oligomers, thus preventing their subsequent growth during the initial surface sojourn that forms them. These effects appear

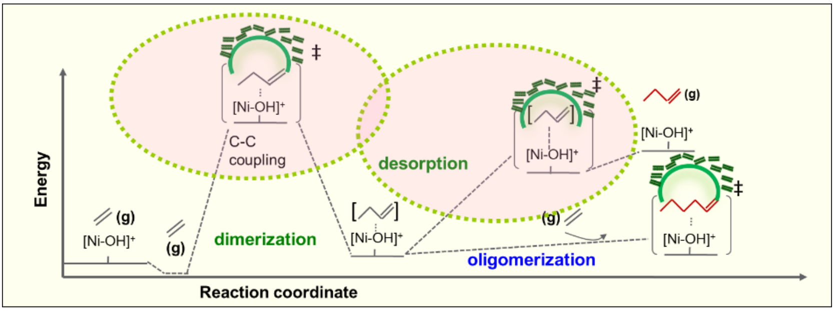


Figure 16. Reaction pathway of ethene dimerization on liquid-stabilized $(\text{Ni-OH})^+$ sites in silica-based mesoporous materials.

to be general to C-C bond formation reactions, in which subsequent chain growth of primary dimers leads to losses of selectivity and the formation of strongly bound, larger oligomers. Our studies have recently found similar effects for acetone–aldol condensation reactions on mesoporous TiO_2 solids. As in the case of Ni-catalyzed alkene dimerization, the formation of an intrapore liquid phase of non-polar molecules (in this case added inert n-heptane) within mesopores leads to an increase in the selectivity to the primary condensation products and to the stabilization of active Ti-O acid–base pairs against blockage by larger oligomers and fast deactivation.

Density functional theory calculations indicate that the grafted $(Ni\text{-}OH)^+$ active structures act as acid–base site pairs to stabilize the transition state for the formation of the C-C bond in dimerization events; this previously unrecognized mechanism exploits concerted interactions of the two alkene reactants with the acid and base centers in $(Ni\text{-}OH)^+$ at the bimolecular C-C bond formation transition states. The entropy losses associated with the formation of such organized structures very weakly influences activation free energies at these low temperatures, while enthalpic gains lead to a significant decrease in such activation barriers. Such transition states and binding modes account for the uniquely high reactivity of these materials and for the observed differences in dimerization turnover rates among alkenes of different chain lengths. These sites catalyze dimerization turnovers in the as-synthesized state, without requiring thermal treatments, activators, or co-catalysts for their function. The elementary steps and site requirements differ from those involved in the Cossee-Arlman and metallacycle routes prevalent in homogeneous catalysts and metal–organic framework materials. The stabilization effects and selectivity improvements conferred by the liquid phase contained within mesopores allow these materials to approach the performance metrics required for practical use. They have made possible the deliberate and systematic study of the mechanism of C-C bond formation reactions from alkenes and oxygenates using approaches previously precluded by the ubiquitous, rapid deactivation of Ni-based solids.

Thrust 2: Enhancing H_2 Addition Rates by Designing the Active Site and Its Environment

Catalytic hydrogenations of carbon–oxygen and carbon–carbon bonds are important reactions in the upgrading of highly dispersed renewable carbon resources. In Thrust 2, these reductions are focused on the carbon–oxygen bonds in CO_2, aldehydes, ketones, carboxylic acids, or esters, as well as the carbon–carbon bonds in aromatic alcohols or ethers, as schematically illustrated in Figure 17. To enable low-temperature pathways for efficient hydrogen addition reactions, higher activities of catalytic sites are needed. Catalysts for hydrogenation and hydrogenolysis have two essential functions: activation of H_2 and transfer of the reducing equivalents to an additional reactant. The activation and transfer of H_2 can occur through homolytic (H•) or heterolytic (H^+/H^-) pathways, depending on the nature of the catalyst and the environment. Therefore, we probe the interaction of H_2 with the catalytic sites, the nature of activated hydrogen, and the impact of the substrate structure on the hydrogenation. This thrust integrates a multidisciplinary team that encompasses all subdisciplines (homogeneous and heterogeneous catalysis, surface science, and theory) represented within the overall program and takes advantage of the state-of-the-art capabilities available at PNNL and other DOE user facilities for synchrotron X-ray spectroscopies and high-performance computing.

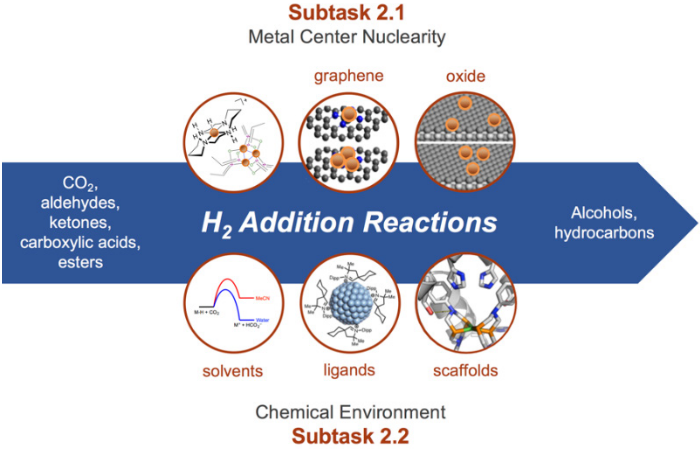


Figure 17. Thrust 2 is focused on the hydrogenation of carbon–oxygen and carbon–carbon bonds, with two complementary subtasks focused on the design of the active metal center (Subtask 2.1) and the design of the environment (Subtask 2.2).

Subtask 2.1: Controlling Nuclearity and Structure of the Active Centers for Hydrogen Addition to Carbon–Oxygen Bonds

Aaron Appel, Zdenek Dohnálek, Oliver Y. Gutiérrez, Abhijeet Karkamkar, Bruce Kay, Libor Kovarik, John Linehan, János Szanyi, Eric Wiedner

Catalytic hydrogenation of C=O bonds and the reductive cleavage of C-O bonds are important reactions in the upgrading of highly dispersed renewable carbon resources. Enabling low-temperature pathways for efficient hydrogen addition reactions requires a higher activity of catalytic sites than that found in industrial practice. To develop systems with higher reaction rates, homogeneous and heterogeneous catalysts are developed and tested in parallel. Identifying specific and common elements in the reaction paths of homogeneous and heterogeneous reactions aids the development of joint strategies for enhancing reaction rates. Single atoms, clusters of a few metal atoms, and sub-nm particles as catalytic centers supported on solid surfaces and stabilized in coordination compounds or decorated by their ligands will provide the platform for the joint activities. In this subtask, we investigate the activity of such systems for catalyzing the elementary steps of hydrogen addition to C=O functionalities and the associated reaction mechanisms. These reactions require activation of both molecular hydrogen and the reacting substrates. Therefore, we probe the interaction of H_2 with the catalytic sites, the nature of activated hydrogen, and the impact of the support structure on the hydrogenation of CO_2.

Homogeneous Catalysts for Hydrogenation of CO_2

Aaron Appel, John Linehan, Eric Wiedner

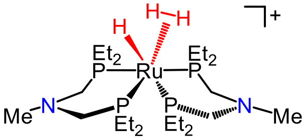


Figure 18. For the first time, a key intermediate for hydrogenation of CO_2 by ruthenium phosphine complexes was detected by operando NMR spectroscopy.

Ruthenium bis(diphosphine) dihydride complexes with the general formula cis-RuP_4H_2 were among the first molecular catalysts shown to catalyze the reaction between CO_2 and H_2 to produce formate. A metal–dihydrogen complex has long been postulated to be a catalytic intermediate during catalysis, although this has not yet been observed. We have used our unique high-pressure polyether ether ketone (PEEK) cells to carry out multinuclear operando NMR measurements to directly observe cis-$[Ru(P^{Et}N^{Me}P^{Et})_2(H_2)H]^+$ as a major species during catalysis (Figure 18), supporting its assignment as a key catalytic intermediate.

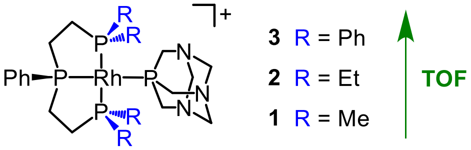


Figure 19. The ligand electronics control the TOF for hydrogenation of CO_2 to formate by structurally similar Rh catalysts.

One of the difficulties in understanding how molecular catalysts work is determining whether differences in catalytic activity are the result of structural or electronic effects. We studied a series of rhodium triphosphine compounds that allowed us to investigate the catalytic properties of CO_2 hydrogenation without changing the structural core at the metal center (Figure 19). Extremely small structural changes were observed when the R groups on the triphosphine ligand were changed from electron-donating methyl groups (**1**), to moderately electron-donating ethyl groups (**2**), to even less electron-donating phenyl groups (**3**). Even though the structural changes were minimal, the catalytic turnover frequency at 20 °C increased from 24 h^{-1} to 45 h^{-1} to 320 h^{-1} for complexes **1**, **2**, and **3**, respectively. The electronic differences of these catalysts suggest that H_2 activation limits the rate of catalysis instead of hydride transfer.

We have studied a ruthenium complex that catalyzes the hydrogenation of CO_2 to formate at room temperature without phosphine ligands. $[CpRu(CH_3CN)_3]^+$ can hydrogenate CO_2 to formate at room temperature in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). No other base, either weaker or stronger, resulted in catalysis. We have determined through careful thermodynamic and kinetic studies that two DBUs must bind to the ruthenium center before an active catalyst is produced (Figure 20). The activation parameters for hydrogenation of CO_2 to formate were measured as $\Delta H^‡ = 6.8$ kcal mol^{-1} and $\Delta S^‡ = -41.3$ cal K^{-1} mol^{-1}, corresponding to a turnover frequency (TOF) of 300 h^{-1} at 20 °C ($\Delta G^‡ = 19.1$ kcal/mol). These results demonstrate that the binding of DBU to a ruthenium center is critical to the activity of the catalyst, even though most researchers consider DBU a very poor ligand.

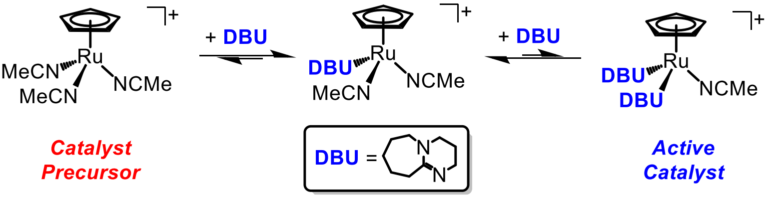


Figure 20. A ruthenium precatalyst must bind two equivalents of the DBU base to form the active catalyst.

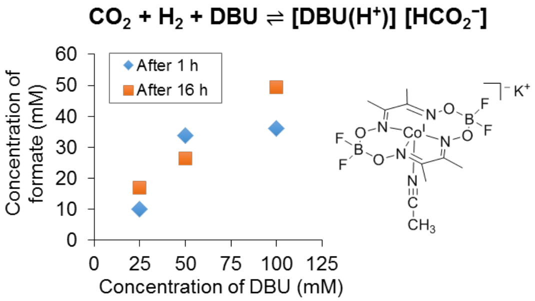


Figure 21. A cobaloxime can hydrogenate CO_2 to formate without the need for phosphine ligands.

A continuing challenge in molecular catalysis is to design catalysts based on earth-abundant metals without using phosphine ligands. We found that a cobaloxime complex, $[Co(dmgBF_2)_2(MeCN)]^-$, can hydrogenate CO_2 to formate using DBU (1,8-diazabicyclo(5.4.0)undec-7-ene) as the base and acetonitrile as the solvent (Figure 21). In batch reactor studies, catalysis was consistently observed to consume ~60% of the DBU base. These results suggest that the hydricity of the Co^IH intermediate is closely matched to formate, resulting in an equilibrium between CO_2 and formate under catalytic conditions. These studies provide a rare example of an earth-abundant molecular catalyst for hydrogenation of CO_2 that does not rely on phosphine ligands.

Understanding Heterolytic H_2 Cleavage and Water-Assisted Hydrogen Spillover on $Fe_3O_4(001)$-Supported Single Palladium Atoms

Zdenek Dohnalek, Vassiliki-Alexandra Glezakou, Bruce D. Kay, Roger Rousseau

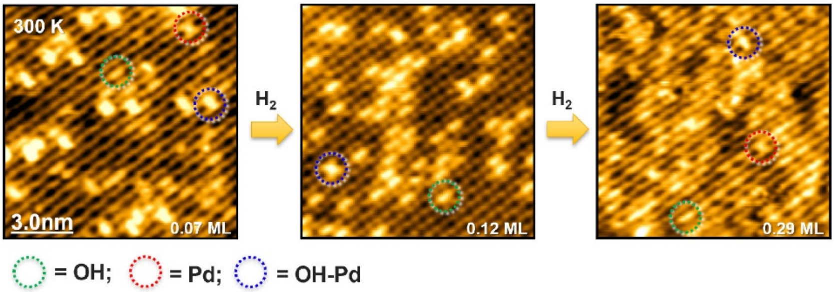


Figure 22. High-resolution STM images illustrating the increasing level of hydrogenation of model catalytic surfaces comprised of single Pd atoms on $Fe_3O_4(001)$.

The high specific activity, unique properties, and cost-effectiveness of single atom catalysts (SACs) provide great promise for the development of novel catalytic chemistries. In hydrogenation reactions, the mechanisms of critical steps such as hydrogen activation and spillover are far from understood. Here, we employ a combination of STM and DFT and demonstrate that on a model SAC comprised of single Pd atoms on $Fe_3O_4(001)$, H_2 dissociates heterolytically between Pd and surface oxygen. The efficient hydrogen spillover allows for continuous hydrogenation (Figure 22) to high coverages, which ultimately leads to the lifting of Fe_3O_4 reconstruction and Pd reduction and destabilization. The reducibility of Fe_3O_4 is critical for continuous H_2 activation. We find that water plays an important role in reducing the hydrogen diffusion barrier, thereby facilitating the redistribution of hydroxyls away from Pd. We further establish how the oxidation state and stability of Pd change with the increasing level of hydrogenation. Annealing of the hydrogenated surfaces leads to water formation and one-layer-deep pits on the terraces due to lattice oxygen extraction. Our study demonstrates a distinct H_2 activation mechanism on single Pd atoms and corroborates the importance of charge transport on a reducible support away from the active site.

From Single Atoms to Clusters: Manipulating CO_2 Reduction Pathways on Rh Catalysts

Oliver Y. Gutiérrez, John Fulton, Libor Kovarik, Johannes A. Lercher, János Szanyi

Understanding the factors that determine the hydrogenation activity of catalysts will provide valuable tools for engineering active catalytic sites. We hypothesize that tuning the environment and nuclearity of the metal allows the rates of C-O cleavage and hydrogenation to be controlled. We are testing this hypothesis using Rh catalysts for CO_2 hydrogenation. We investigated the catalytic pathways for this reaction on a series of catalysts ranging from SACs to nanoparticles. We prepared catalysts with varying Rh loadings on Fe_3O_4 and SiO_2, following strategies based on electrostatic interactions and on cationic replacement. According to the

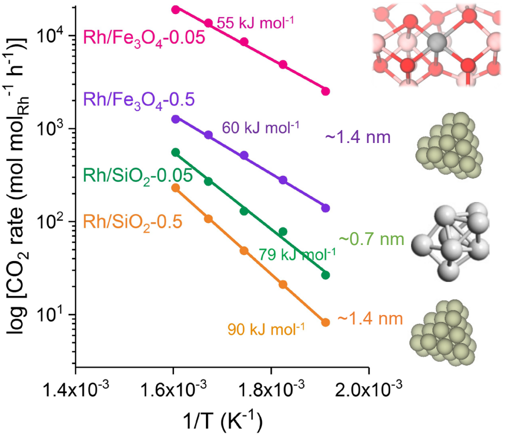


Figure 23. Rates of CO_2 hydrogenation on Rh catalysts (from bottom to top): Rh particles supported on SiO_2, Rh clusters supported on SiO_2, Rh particles supported on Fe_2O_3, Rh single atoms on Fe_3O_4. The activation energies decrease in the same order from 90 kJ mol^{-1} to 55 kJ mol^{-1}.

time of flight secondary ion mass spectrometry (TOF-SIMS) and high-angle annular dark-field scanning TEM (HAAD-STEM) characterization performed at PNNL together with extended X-ray absorption fine structure (EXAFS) (performed in collaboration with APS at Argonne National Laboratory), single Rh atoms are stabilized at the surface of Fe_3O_4. These single atoms occupy octahedral sites and bind to the magnetite surface lattice via covalent Rh-O-Fe linkages. By simply increasing the Rh loading (in the 0.05–0.5 wt. % Rh range), we also prepared Rh_8 and Rh_{18} clusters on Fe_3O_4 and SiO_2 in a controlled way.

Single Rh atoms on Fe_3O_4 have an intrinsic activity one- to two-orders of magnitude higher than Rh particles/clusters on Fe_3O_4 and SiO_2 for the reverse water–gas shift reaction (Figure 23). This high activity originates from the ionic environment of the Rh-O-Fe sites, which has a strong affinity toward CO_2 and a low affinity for CO. Thus, the presence of Rh-O-Fe sites is mandatory to achieve such an extraordinary increase in rates. In turn, sites at the perimeter of Fe_3O_4-supported Rh particles have the same functionality as single atom sites. Recent results show that the adsorptive properties and catalytic performance of Rh-O-Fe sites are common for a series of SACs with different Pt-group metals in the active site. Quantification of this fundamental understanding will enable precise predictions of catalytic performance and rational catalyst design.

The Role of In Situ-Formed, Metastable Active Sites in CO_2 Hydrogenation Over Pd/Al_2O_3 Catalysts

Vassiliki-Alexandra Glezakou, Manh-Thuong Nguyen, Roger Rousseau, János Szanyi

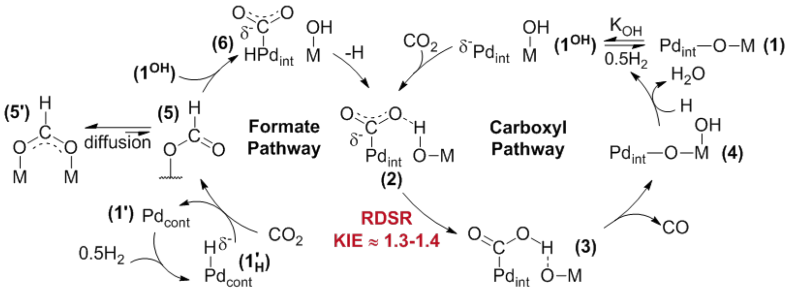


Figure 24. Proposed water–gas shift mechanism derived from experimental observations.

The focus of this project is to understand the activation of C-O bonds using molecular hydrogen. Carbon dioxide, CO_2, is an ideal substrate owing to its ubiquitous derivatives (e.g., carboxylic acids, esters, acetal, etc.), which implies that the trends for CO_2 activation can be extended to these other substrates.

Additionally, carbon monoxide (CO) is a common product from CO_2 hydrogenation that can undergo further hydrogenation. This suggests we could learn something about activating the C-O bonds in ketones, aldehydes, alcohols, etc.

Our work using palladium (Pd) particles supported on transition metal oxides has shown that the formal heterolytic dissociation of hydrogen is the preferred or lowest-energy pathway to convert CO_2 to CO. The hydrogen heterolysis step results in hydroxylation of the metal–support interface. This creates a metastable active site characterized by its regio- and chemoselective hydrogen addition to CO_2 to yield the carboxyl (COOH) intermediate (Figure 24). The metastable active site derived from heterolytically dissociated hydrogen, (1^{OH}), does not yield formate (HCOO) nor does it react with CO to form methane (CH_4). Formation of the formate intermediate and the CO methanation reaction requires the homolytic activation of hydrogen, which occurs on the extended Pd surface, (1'). The results demonstrate the divergent chemical behavior between homo- and heterolytically activated hydrogen toward CO_2 and CO. Future work will focus on extending the substrate scope and using catalysts that are only able to activate hydrogen heterolytically. This will allow us to determine the relationship between the mode of hydrogen activation and its functional group reactivity.

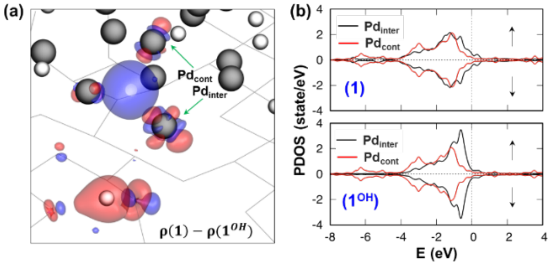


Figure 25. Electron density difference map between (1) and (1^{OH}) at iso surface value of 0.01 au. (b) Projected density of states onto the 4d orbitals of interfacial Pd (Pd_{inter}) and contiguous Pd (Pd_{cont}). Two spin channels are shown.

The formation of the metastable active site, (1^{OH}), causes the electronic restructuring of Pd via reduced coordination. The reduced coordination causes a localized increase in electron density on the interfacial Pd atom, as evidenced by both experiment and theory (Figure 25). The in situ creation of a transition metal active site via ligand decoordination is common in molecular catalysis but has rarely been evidenced or even considered in heterogeneous systems. The observation provides a bridge between homo- and heterogeneous catalysis that could form the basis to unify the seemingly disparate disciplines. Our work addresses a fundamental question in catalysis: Is catalysis the result of the interaction between active sites and reactants or does the interaction between the reactants and the catalytic material result in the formation of the active site?

Subtask 2.2: Enhancing H_2 Addition Rates by Designing the Active Site and Its Environment

Aaron Appel, S. Thomas Autrey, R. Morris Bullock, David Dixon, John Fulton, Bojana Ginovska, Oliver Y. Gutiérrez, Abhijeet Karkamkar, Johannes Lercher, John C. Linehan, Greg Schenter, Wendy J. Shaw, Eric S. Wiedner

The environment around a catalyst has a critical impact on both homogeneous and heterogeneous catalysis, leading to remarkable changes in catalytic activity and selectivity. This subtask focuses on understanding and controlling the environment for hydrogenation of carbon–oxygen and carbon–carbon bonds, emphasizing the role of solvents, confining supports, organic ligands, or a bioinspired scaffold. Studies of the solvent's role include developing and using solvent-dependent free energies for hydride (H^-) transfer as a design parameter of new catalysts for the reduction of carboxylic acids and CO_2. Studies of the activity of nanoparticle catalysts for hydrogenations of aromatic alcohols and ethers focus on the effects of confinement using periodic structures to stabilize and position hydronium ions, as well as the impact of organic ligands to control particle formation and function. Bioinspired scaffolds provide precise control of the environment and will be used to position charged and hydrogen-bonded functional groups to enhance catalytic hydrogenation of CO_2.

The Impact of Solvent on the Design of Catalysts

Eric S. Wiedner, John C. Linehan, Aaron Appel

The solvent can have a huge impact on the favorability of individual steps in catalytic hydrogenation of CO_2. In a Minireview, we described recent and emerging studies on the impact of the solvent on the mechanisms for hydrogenation of CO_2 by molecular catalysts. The solvent can affect the thermodynamics and kinetics for hydride transfer from the catalyst to CO_2 and, in some cases, switching between solvents can reverse the direction of hydride

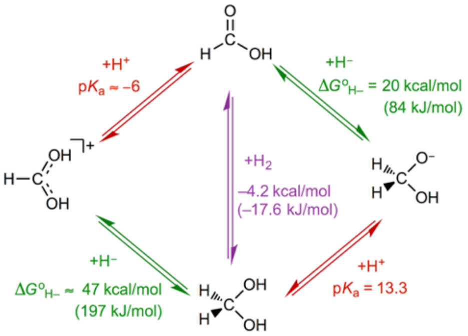


Figure 26. Reduction of challenging intermediates will be greatly benefited by thermodynamic insight into the free energies for H^+ and H^- transfer reactions, as illustrated with the net hydrogenation of formic acid.

transfer. The speciation of CO_2 into carbonate species, both inorganic and organic, is also affected by the solvent and allows the possibility of multiple hydride transfer pathways. Additionally, the solvent can be used to lower the thermodynamic barrier for hydrogenation of CO_2 to formic acid, as well as enable the subsequent formation of methanol by activating formic acid to accept more hydride equivalents from the catalyst. In particular, we established a thermodynamic cycle to describe the hydride acceptor ability of formic acid as a function of its protonation state (Figure 26). These solvent effects provide a basis for using the solvent as a key parameter to rationally control catalyst performance.

Operando X-Ray Absorption Fine Structure Studies on Rh(Cyclic Alkyl Amino Carbene)-Catalyzed Arene Hydrogenation

R. Morris Bullock, John Fulton, John Linehan, Johannes Lercher

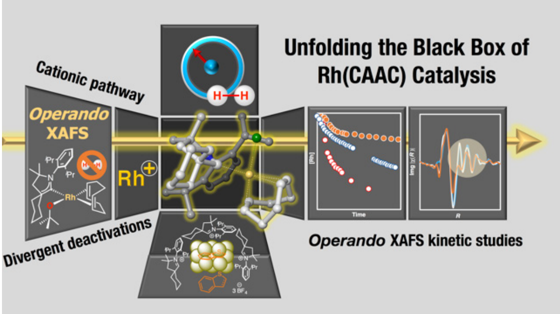


Figure 27. XAFS spectroscopy studies provided a detailed understanding of the evolution of a molecular Rh complex into catalytically active Rh nanoparticles.

Catalytic hydrogenation of arenes has a key role in large-scale industrial processes. Traditional heterogeneous catalysis systems generally require high pressures and elevated temperatures, which can lead to low selectivity and poor functional group tolerance. Increasing interest has focused on molecular complexes that can lead to high reactivity and good selectivity. We found that catalysis starting from a molecular Rh complex that bears a cyclic alkyl amino carbene (CAAC) ligand gives excellent reactivity at room temperatures and mild pressures of H_2 (6.8 atm). Our initial experiments included filtration, fractional poisoning, infrared spectroscopy, and microscopic measurements that implicated a heterogeneous catalyst. Recent operando studies using Rh K-edge X-ray absorption fine structure (XAFS) experiments provided a direct examination of the Rh species before the addition of H_2 and during hydrogenation of Ph_2O (Figure 27). Experiments carried out at the Advanced Photon Source (APS) at Argonne National Laboratory, illuminate the role of the silver cation on pre-catalyst reactivity, the effect of increasing H_2 pressure on increasing catalytic efficiency, the stabilizing influence of Ph_2O on the relative rate of formation of active Rh nanoparticles, and the absence of soluble single-site Rh species that might leach from bulk heterogeneous Rh nanoparticles. Increasing the pressure of H_2 leads to faster formation of Rh nanoparticles and, in turn, to higher concentrations of Rh nanoparticles giving enhanced rates of arene hydrogenation. Our detailed studies determined that Rh nanoparticles decorated with protonated CAAC ligands are the active catalysts for arene hydrogenation from a well-defined molecular complex.

Palladium-Catalyzed Reductive Insertion of Alcohols into Aryl Ether Bonds

Oliver Y. Gutiérrez, Donald M. Camaioni, and Johannes A. Lercher

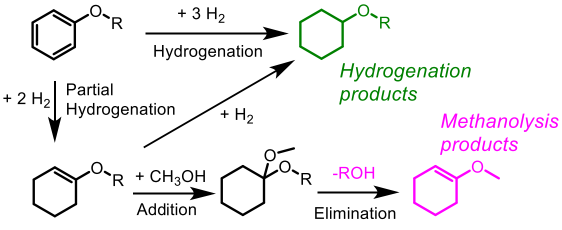


Figure 28. General mechanism of the reductive solvolysis of aryl ether on palladium. This figure illustrates the reaction pathways in methanol (i.e., methanolysis competes with hydrogenation).

We recently reported the mechanism of the selective hydrolytic cleavage of the arene–oxygen bond in aromatic ethers. The aromatic C-O bond is cleaved by insertion of water upon the partial hydrogenation of the arene ring to an enol ether. Water rapidly adds to the enol ether to form a hemi-ketal, which undergoes elimination to cyclohexanone and phenol/alkanol. The question arose, Can alcohols also cleave such ether bonds and be used for transetherification? In our most recent study, we found that Pd/C does catalyze C-O bond cleavage of aryl ethers (diphenyl ether and cyclohexyl phenyl ether) by alcohol in H_2. Figure 28 illustrates the competing hydrogenation and solvolysis occurring in methanol. The aromatic C-O bond is cleaved by reductive methanolysis, which is initiated by Pd-catalyzed partial hydrogenation of one phenyl ring to form an enol ether. The enol ether reacts rapidly with methanol to form a ketal, which generates methoxycyclohexene by eliminating phenol or an alkanol. Subsequent hydrogenation leads to methoxycyclohexane. We also demonstrated that this solvolysis mechanism applies to a variety of alcohols in the presence of H_2. The attack of alcohol, however, is slower than the attack by water; thus, the selectivity for alcoholysis is lower than for hydrolysis under comparable conditions. The selectivity toward reductive alcoholysis is inversely proportional to the carbon number of the alcohol. The selectivity of the different metals to catalyze hydrogenation of the enol ether is a feature that remains to be explored in greater detail.

Impact of a Biological Scaffold

Wendy J. Shaw, Bojana Ginovska, Greg Schenter, John Linehan

In developing a mechanistic understanding of the outer coordination sphere on molecular catalysts for CO_2 hydrogenation, we evaluated two series of complexes, $Rh(P^{Ph2}N^{amino\ acid}P^{Ph2})_2^+$ and $Rh(P^{Et2}N^{amino\ acid}P^{Et2})_2^+$ (Figure 29). Six to eight different amino acids were evaluated for each species, and three complexes were compared that had the same amino acid and differed only in their P substituent. We would expect similar relative effects on each set of complexes if the only impact on catalytic performance were the first coordination sphere, i.e., the substituent on P. However, in one case, we see that the Ph-complex is two times faster, in another case it is 10 times slower, and in the case with no pendant amine or amino acid, the rates are the same; all of this points to a clear effect of the outer coordination sphere. We are now using computational studies to understand the nature of the difference, and we are also using a structured scaffold to facilitate increased control and thereby evaluation of the impact of the outer coordination sphere.

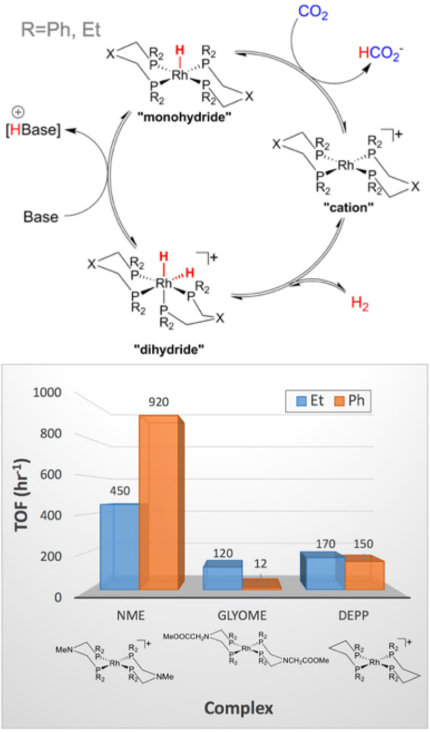


Figure 29. Using a series of Rh bis(diphosphine) complexes, the impact of bio-inspired second and outer coordination spheres are being evaluated in the context of catalyst design principles.

Cross-Cutting Thrust

Subtask CC: Modeling Active Centers, Environments, and Their Role in Catalytic Transformation

David A. Dixon, Bojana Ginvoska, Vassiliki-Alexandra Glezakou, Roger Rousseau, Gregory K. Schenter

The cross-cutting theory and simulation thrust serves the critical function of formulating general principles and cross-fertilizing research across the entire program by building synergies between disciplines. Using the capabilities outlined in this thrust, the PIs in theory and computation strengthen the overall activities of the program by: (1) providing, developing, and refining mechanistic hypotheses; (2) formulating structure–activity relationships; and (3) interpreting experimental data. This task takes advantage of state-of-the-art methodologies in modern simulation capabilities and DOE's computational infrastructure, which allows us to formulate and address hypotheses at a level far beyond what is routinely practiced in catalysis science.

We specifically advance new capabilities in areas where current approaches are not satisfactory in terms of capturing the essential physics and chemistry and which are critical to the overall scientific objectives of this program. We are currently pursuing two scientific objectives: (1) Quantitative Energy Landscapes of Complex Catalyst Systems, and (2) Rigorous Description of Dynamics and Collective Motions of Catalytic Sites and Their Environment (Figure 30). Through these objectives, we are able to understand reactivity at the complex interfaces prevalent in Thrusts 1 and 2 of the current program.

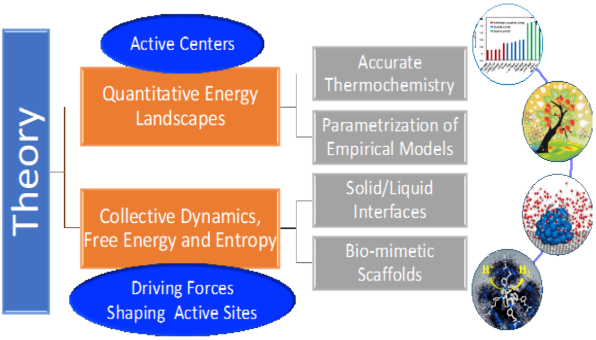


Figure 30. Scientific objectives for the cross-cutting theory task.

Benchmarking Transition Metal Oxide Cluster Reactivity with High-Level Quantum Chemistry

David A. Dixon

Our program relies on the cornerstone of measuring and computing reliable thermodynamics and reaction energy landscapes on model systems. Through advanced computing methods, we continue our benchmarking of transition metal oxide reactivity relevant to biomass conversion catalyzed by small RuO_2 clusters (Figure 31). Group 8 $(RuO_2)_n$ (n= 1 to 4) nanoclusters, their anions, and the hydrolysis reactions of the neutral clusters have been studied with the DFT and coupled cluster CCSD(T) theory. The ground state is predicted to be a singlet and a doublet for the neutral RuO_2 clusters and anionic clusters, respectively. The CCSD(T) method is required to predict the correct ground state. These nanoclusters are characterized by small singlet–triplet gaps (< 15 kcal/mol) and fluoride affinities (< 95 kcal/mol) that are smaller than those of the Group 4 $(MO_2)_n$ and Group 6 $(MO_3)_n$ metal oxide clusters. The electron affinities range from 2.2 to 3.4 eV, showing that the RuO_2 clusters are quite reducible. Clustering energies and heats of formation were also calculated. The water physisorption energies are predicted to be −10 to −20 kcal/mol. The hydrolysis reactions are exothermic for the monomer and dimer clusters and are slightly endothermic or neutral for the trimer and tetramer clusters. H_2O is readily dissociated on the monomer and dimer but not on the trimer and tetramer.

Hydrogen adsorption on small Group 4 metal oxide clusters (Figure 32) for both the singlet and the first excited triplet states was also investigated using density

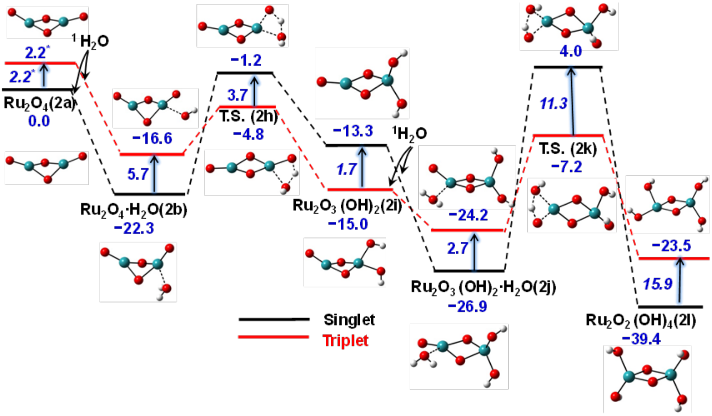


Figure 31. Potential energy surfaces for the hydrolysis of the singlet and triplet Ru_2O_4 clusters at the CCSD(T)/aD// B3LYP/aD level in kcal/mol. Proton transfer to a bridge –O atom.

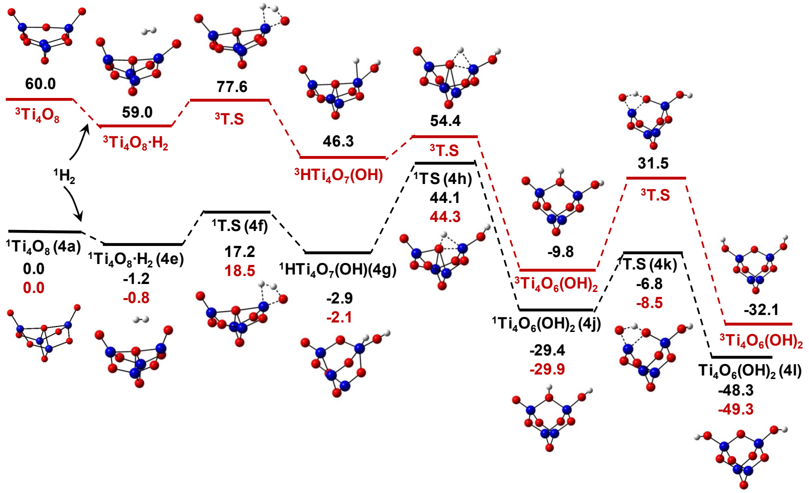


Figure 32. Potential energy surfaces for $H_2 + Ti_4O_8 \rightarrow HTi_4O_7(OH)$ for the ground state singlet and the first excited triplet Ti_4O_8 clusters at 0 K. Relative energies at the CCSD(T)/aD (black) and /aT (red) level for the singlet and the R/UCCSD(T)/aD (black) level for the triplet in kcal/mol.

functional theory and correlated molecular orbital theory at the coupled-cluster CCSD(T) level.

The reaction starts with hydrogen physisorption on a metal center followed by the formation of metal hydride/hydroxides due to H_2 splitting into H^- and H^+. The hydrogen physisorption energies are predicted to be -1 to -8 kcal/mol for the singlet and -1 to -26 kcal/mol for the triplet. The formation of metal hydrides/hydroxides does not involve redox processes. Chemisorption leading to the formation of metal hydrides/hydroxides is exothermic by -10 to -50 kcal/mol for the singlet and exothermic by up to -60 kcal/mol for the triplet. The predicted energy barriers are less than 20 kcal/mol. Formation of metal dihydroxides from the metal hydride/hydroxides is generally endothermic for the monomer and dimer and is exothermic for the trimer and tetramer. Formation of the dihydroxide is a proton-coupled electron transfer (PCET) process. The singlet energy barriers for the $H^- \rightarrow H^+$ transfer process are predicted to be 35 to 60 kcal/mol, in comparison to triplet energy barriers of less than 15 kcal/mol for the $H\cdot \rightarrow H^+$ transfer process. For trimers and tetramers, there exist two different pathways: the first is a direct pathway with PCET to a terminal oxygen, and the second is a two-step pathway with the initial formation of a bridge OH group followed by a proton transfer to generate a terminal OH group.

Understanding Heterolytic H_2 Cleavage and Water-Assisted Hydrogen Spillover on $Fe_3O_4(001)$-Supported Single Atom Model Catalysts

Zdenek Dohnalek, Vassiliki-Alexandra Glezakou, Bruce D. Kay, Manh-Thuong Nguyen, Roger Rousseau

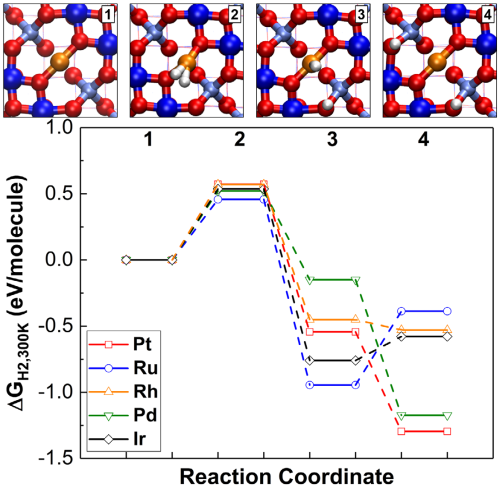


Figure 33. DFT-predicted Gibbs free energy (300 K, 10^{-6} Torr H_2) pathway of H_2 dissociation on single Pd, Pt, Rh, Ir, and Ru atoms on $Fe_3O_4(001)$, demonstrating different stabilities of metal hydride species relative to hydroxyl species.

Using DFT, we focused on predicting and understanding the dissociation pathway of H_2 and the stability of resulting surface species on Pd, Pt, Rh, Ir, and Ru SACs on $Fe_3O_4(001)$ (Figure 33). This study directly expands on our surface science studies of Pd single atoms on $Fe_3O_4(001)$ that are highlighted in Thrust 2 (shown in Figure 22). While molecular adsorption of H_2 under ultrahigh vacuum conditions is unfavorable on all metals, as shown by state 2, the heterolytic cleavage to hydride and hydroxy species (state 3) is thermodynamically strongly preferred. In a subsequent step (step 4) leading to two hydroxyl species, significant differences can be seen in Gibbs free energies for different metals. While the formation of two hydroxyls is strongly favored for Pd and Pt, for Rh and Ir, the hydride–hydroxyl and hydroxyl–hydroxyl states are fairly close in energy, suggesting a possible equilibrium between hydride and hydroxyl species. For Ru, the hydride–hydroxyl pair becomes strongly preferred. These results imply that Ir and Rh are good at potentially preventing hydrogen spillover onto Fe_3O_4 but also provide additional access to the hydride, which can be utilized for subsequent catalytic reductions. Overall, we demonstrate that the catalytic activity of SACs can be tuned by the careful selection of the metal. Future studies will focus on understanding the detailed hydrogenation mechanisms and catalytic nature of such SACs on $Fe_3O_4(001)$.

Targeted Theory Development for Modeling Catalysis In Complex Environments

Vassiliki-Alexandra Glezakou, Mal-Soon Lee, Roger Rousseau

In collaboration with the group of Prof. Chris K. Skylaris (U. Southampton, United Kingdom), we are using state-of-the-art explicit solvent *ab initio* molecular dynamics (AIMD) simulations and kinetic measurements of reactivity and adsorption at solid–liquid interfaces to help guide the construction of implicit solvent models (Figure 34). We have recently developed a model based on Fisicaro's soft sphere solvation cavities that can faithfully capture the electronic structure changes of metal surfaces in contact with liquids as well as quantitative changes in solvation free energetics.

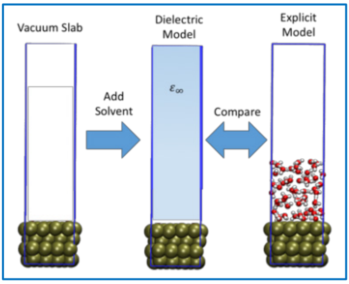


Figure 34. Development of continuum solvation models are based on combined experimental measurements and AIMD simulations of solid–liquid interface.

Through a long-standing collaboration with Prof. Michele Parrinello (ETH Zurich, Switzerland), we are investigating the development and use of advanced collective variables (CVs) that capture the appreciable effects on the reaction free energy emanating from complex chemical environments such as flexible extended coordination spheres and confined spaces (Figure 35).

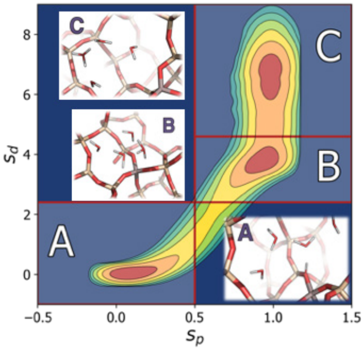


Figure 35. Relative free energy of three protonation states in water-filled zeolites: (A) undissociated state; (B) contact ion pair; and (C) solvated proton state.

Recently, we developed a set of CVs able to access the acid–base properties of complex catalysts independent of the number of acid–base species simultaneously present, nature of reactants, and kind of solvent. This has allowed us to understand the evolution of acid/base properties inside of zeolite pores as a function of the pore size/shape and number of water molecules present. We find that it is a delicate balance between enthalpic and entropic drivers that determine the protonation state in zeolites, with the preferred state being a protonated water cluster whose size is dependent on that of the zeolite pore in which the water is confined.

Effects of the Protein Scaffold on the Activity of the Rh-Based Molecular Catalyst in LmrR

Bojana Ginovska, Wendy J. Shaw, Gregory K. Schenter

From enzymatic catalysis, we know that the outer coordination sphere, i.e., the amino acid residues around the catalytic center, can have a great impact on catalysis. We hypothesized that *positioning diverse functionality around the active site creates an anisotropic environment to control the free energy landscape for H_2 addition and CO_2 substrate activation.* To test this, a model molecular catalyst was embedded in the LmrR protein scaffold, and molecular dynamics was employed to evaluate the changes in the environment near the metal center, as a function of point-site mutations (Figure 36). In addition to the wild-type scaffold, we studied two mutants (W99R and D103R) in which residues near the active sites were replaced with arginine (Arg, R), a positively charged residue. By replacing aspartic acid residues (Asp, D) with Arg in each of the monomers of the LmrR homodimer, we change the overall charge by 4e, and by replacing the neutral tryptophan residues (Trp, W) with Arg, we change the charge by 2e.

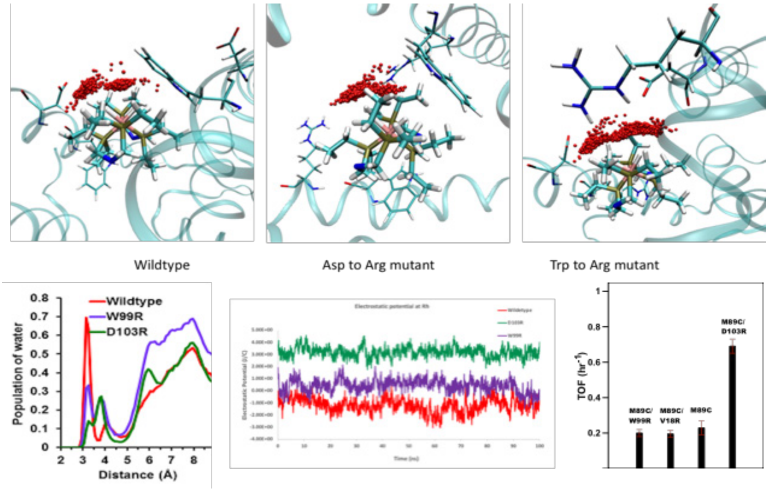


Figure 36. Water distribution in the WT, D103, and W99R mutants of LmrR (top panel). Radial distribution function for the water–Rh distance (bottom left corner). Electrostatic potential caused by the protein charges experienced at the metal center (bottom middle). Experimentally measured catalytic activity (bottom right).

These substitutions were selected to mimic the active site of formate dehydrogenase, where Arg residues are believed to assist in positioning CO_2 at the active site. We find that the changes in the scaffold imposed by the point-site mutations affect both the electrostatic potential that the metal center experiences, as well as the organization of water near the active site. More importantly, we find that these changes correlate with the experimentally measured catalytic activity of the different variants. The mutation of D103R shows more than 3-fold increase in catalytic activity. This mutation also results in appreciably more positive values of the electrostatic potential experienced by the metal center as well as a shift in the water distribution, as reflected in changes of the radial distribution about the metal center.

Recognitions and Honors

Aaron Appel

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

R. Morris Bullock

- Panel lead, Basic Research Needs: Catalysis Science to Transform Energy Technologies workshop, 2017
- Member, Washington State Academy of Sciences, 2018

Zdenek Dohnálek

- Fellow, American Vacuum Society, 2017
- Advisory Editorial Board, *Surface Science,* 2018
- Exceptional Scientific Achievement Award, PNNL, 2018

David Dixon

- Blackmon-Moody Award, The University of Alabama, 2018
- President's Faculty Research Award, Senior Level, The University of Alabama, 2019

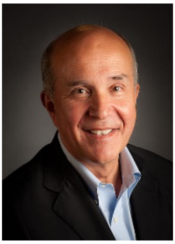
Enrique Iglesia

- Panel co-chair, Basic Research Needs: Catalysis Science to Transform Energy Technologies workshop, 2017
- William H. Walker Institute Award for Excellence in Contributions to Chemical Engineering Literature, American Institute of Chemical Engineers (AIChE), 2018
- Doctor Honoris Causa, Technical University of Munich, 2018
- Michel Boudart Award for the Advancement of Catalysis, North American Catalysis Society, 2019
- Chair, 17th International Congress in Catalysis, 2020

Bruce Kay

- Division Chair, American Vacuum Society Surface Science Division, 2017
- Member, Washington State Academy of Sciences, 2017

Johannes Lercher



- Co-chair, Basic Research Needs: Catalysis Science to Transform Energy Technologies workshop, 2017
- Foreign member, National Academy of Engineering, 2017
- Fellow, National Academy of Inventors, 2019

Roger Rousseau

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

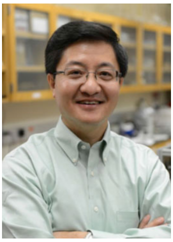
Wendy Shaw

- Invited panelist, Basic Research Needs: Catalysis Science to Transform Energy Technologies workshop, 2017
- Editorial Board Member for Biophysical Journal, 2017

Huamin Wang

- Organization committee member, 17th International Congress on Catalysis, 2020

Yong Wang



- Invited panelist, Basic Research Needs: Catalysis Science to Transform Energy Technologies workshop, 2017
- Fellow, American Chemical Society, Industrial & Engineering Chemistry Division, 2017
- Practice Award, AIChE, Catalysis and Reaction Engineering Division, 2019

Publications

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

- Total of 179 peer-reviewed publications (January 2016–June 2019)
  - *Science* (2), *Nature Catalysis* (1), *Nature Materials* (1), *Nature Reviews Chemistry* (1), *Nature Communications* (4), *Proceedings of the National Academy of* Sciences (PNAS) (1), *Journal of the American Chemical Society* (JACS) (13), *Angewandte Chemie International Edition* (9).
  - 7 review articles (*Chemical Reviews, Accounts of Chemical Research, Chemical Society Reviews*, and others).
  - 3 book chapters.

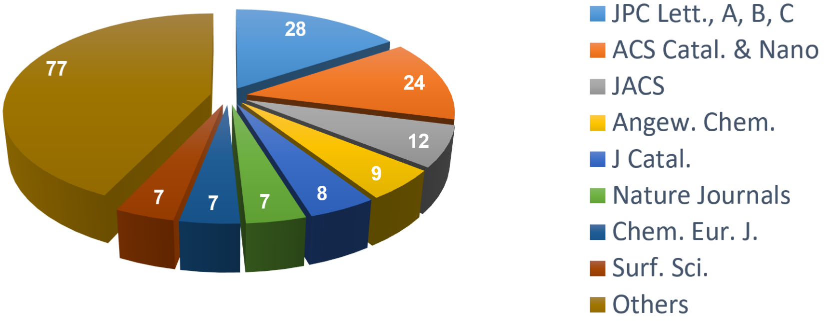


Figure 37. 132 publications (out of 179) in the journals with the highest occurrence (January 2016–June 2019).

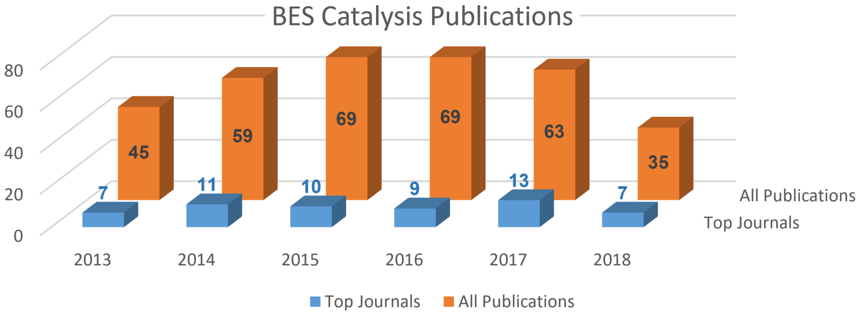


Figure 38. The total number of publications (orange) and publications in top journals (blue, includes Science, Nature journals, PNAS, Angewandte Chemie International Edition, and JACS) per the calendar year.

Journal Covers (January 2016–June 2019)

ASSOCIATED BASIC ENERGY SCIENCES PROGRAMS

Energy Frontier Research Center: Center for Molecular Electrocatalysis

Director: R. Morris Bullock
Deputy Director: Sharon Hammes-Schiffer
Co-PIs at PNNL: Aaron Appel, Simone Raugei, Eric Wiedner
University Collaborators: James Mayer (Yale University), Sharon Hammes-Schiffer (Yale University), Shannon Stahl (University of Wisconsin–Madison), Yogi Surendranath (Massachusetts Institute of Technology), Thatcher Root (University of Wisconsin–Madison), Brandi Cossairt (University of Washington), Jeffrey Miller (Purdue University)

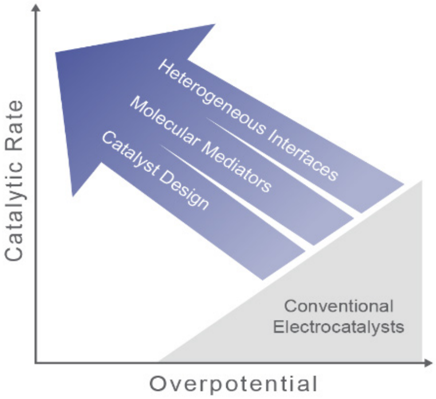


Figure 39. A major goal of CME is to dramatically increase catalyst performance by transcending conventional rate–overpotential relationships through a system-level approach.

The scientific mission of the CME is to establish the fundamental principles needed for efficient interconversion of electrical energy and chemical bonds through precise control of electron and proton transfers. Understanding these principles will provide a level of control that will allow the design of electrocatalysis processes that achieve unprecedented performance by smoothing the energy landscape and lowering the barriers, both for molecular and heterogeneous catalysts (Figure 39). We are pioneering a system-level approach to improve catalyst performance by targeting three integrated goals: (1) Transcending Scaling Relationships, (2) Enhancing Catalysis Using Mediators, and (3) Achieving Molecular Control of Interfaces. Three complementary research thrusts are aligned to meet these goals: *Catalyst Design*, *Molecular Mediators*, and *Heterogeneous Interfaces*. Our experimental efforts are closely coupled to novel theoretical and computational studies, grounded in thermochemical studies that have been a hallmark of the CME progress since its inception. We seek to bypass the linear scaling relationships associated with conventional catalyst systems (Figure 39).

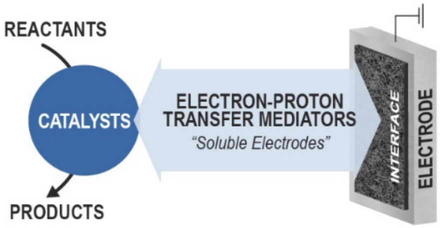


Figure 40. Mediated catalyst design improves system performance by delivering H^+/e^- away from the electrode.

In our *Catalyst Design* research thrust, we are demonstrating how the mechanistic characterization of catalytic reactions reveals not one, but multiple scaling relationships. An improved understanding of these relationships will contribute to the strategic design of new catalyst systems with markedly improved performance. The *Molecular Mediators* research thrust is demonstrating that electron–proton transfer mediators (EPTMs) provide an effective means to achieve "redox communication" between an electrode and a molecular or heterogeneous catalyst in bulk solution. The use of EPTMs as "soluble electrodes" (Figure 40) greatly expands the scope of electrode-driven redox processes and provides the basis for dramatic improvements in the rates and/or overpotentials of these reactions. In the *Heterogeneous Interfaces* research thrust, we address the challenge of controlling e^-/H^+ transfer steps at heterogeneous interfaces. Proton-coupled electron transfer at the surface of electrodes and heterogeneous catalysts is a crucial basic science frontier underlying diverse electrochemical energy transduction reactions.

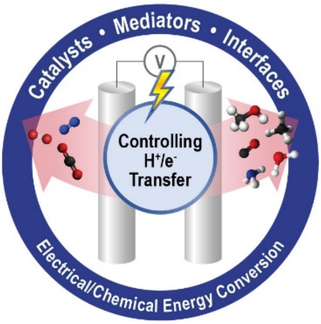


Figure 41. The CME seeks a fundamental understanding of the principles needed to design electrocatalysts for fast, efficient interconversion between electrical and chemical energy.

Electrocatalysis is the cornerstone of efficient interconversion of chemical and electrical energy, and recent research progress from the CME has contributed to a deeper understanding of the fundamental problems that must be addressed. CME's integrated four-year research goals align with our three research thrusts, guiding our work on interdisciplinary areas of substantial scientific importance throughout the field of electrocatalysis and beyond. (Figure 41). The progress toward these goals was enabled by strong collaborations among the different research groups of the CME.

Progress toward our **goal of transcending the limitations of conventional linear free-energy correlations between rate and overpotential** was achieved by changing the thermodynamics of O_2 reduction through variation of the acid. Selectivity is controlled, with stronger acids favoring the production of H_2O_2 vs. the formation of H_2O that is prevalent when using weak acids. Experimental work from the Stahl group, combined with theoretical studies by Hammes-Schiffer, provided a new understanding of the mechanism of electrocatalysts for reduction of O_2 to H_2O_2, with overpotentials as low as 90 mV. This new understanding differs from the commonly accepted mechanism, specifically in regards to our evidence that supports a Co^{III}-OOH resting state with a rate-limiting proton transfer to the hydroperoxide ligand. These results provide an understanding of the low overpotential and a basis for further improvements in electrocatalysis.

Novel cooperative reactivity was discovered in a system involving Cr and Fe to oxidize H_2, even though neither metal complex alone is capable of heterolytically cleaving H_2. This reaction is enabled by a rarely observed metal-to-metal hydrogen atom transfer. The new reactivity discovered involves molecular mediators, as the Cr complexes react with H_2 and transfer hydrogen atoms to the Fe complex, which undergoes electrochemical oxidation and deprotonation steps.

Recent efforts in the CME have established principles of the fundamental steps required for molecular electrocatalysts for oxidation of NH_3. A synergistic, computationally led approach evaluated the homolytic N-H bond dissociation energies of a series of M-NH_3 complexes. For a series of polypyridyl complexes, the N-H bond of Mo complexes is decreased by more than 20 kcal/mol compared to similar Fe complexes. These computations were complemented by experimental studies that established that NH_3 is oxidized and N_2 results, as verified through isotopic labeling.

Progress toward our **goal of enhancing electrocatalysis through molecular mediators** came from notable discoveries that followed collaborative work between Stahl and Hammes-Schiffer on cobalt complexes for O_2. Stahl and new CME partner Root devised a new flow cathode fuel cell design using an organic quinone mediator with an off-electrode heterogeneous catalyst based on earth-abundant cobalt for O_2 reduction. This mediated fuel cell concept introduces a new approach to achieve electrode-driven chemical redox transformations. It achieves a power density of > 240 mW/cm^2 that is sustainable for hours. The highly substituted quinones designed and synthesized in the CME exhibited more than two orders of magnitude greater stability compared to those used previously as mediators in aqueous flow batteries. The scientific progress achieved in these studies points to the remarkable benefits of molecular mediators in electrocatalysis, a major new focus of efforts in the CME.

In the CME's recently initiated thrust on heterogeneous interfaces, progress toward the **goal of achieving control of heterogeneous interfaces using insights from molecular chemistry** is highlighted by discoveries on the interfacial chemistry of electrocatalytic materials. Carboxylates and amines were added to cobalt phosphide nanocrystals, and the influence of the molecular ligands on the surface was determined for hydrogen evolution. Our new results suggest that the surface ligands impede catalysis of H_2 production through inhibition of substrate access to the active sites on the surface instead of poisoning of the active sites. Studies of ligand lability modulation are rare for heterogeneous catalysis. We intend to use the molecular approach emphasized in the CME to determine how ligand manipulation can enhance catalytic activity.

Physical Biosciences Program: Enzymatic Energy Conversion

PI: Simone Raugei

Co-PIs: Bojana Ginovska, Marcel Baer, and Lance C. Seefeldt

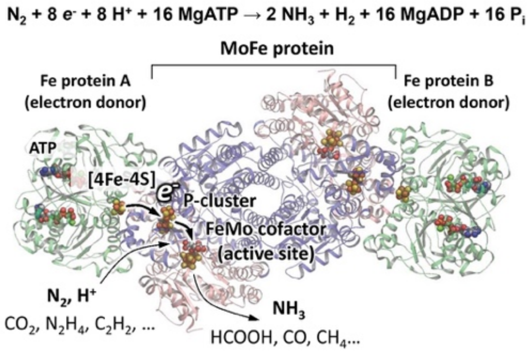


Figure 42. Nitrogenase proteins and cofactors. Shown are the Fe proteins (left and right) and an αβ unit of the MoFe protein (center) along with two ATP molecules, the [4Fe–4S] cluster of the Fe protein, the P-cluster, and the FeMo-co of the MoFe protein. Atom colors are: Fe in rust, S in yellow, C in gray, O in red, and Mo in purple.

The Physical Biosciences program at PNNL aims to provide a better understanding of the core principles employed by enzymes in order to control the flow of energy and matter to achieve remarkable specificities, efficiencies, and catalytic rates. Our program integrates state-of-the-art theory and computation with experimental efforts across the U.S. Department of Energy's (DOE's) Basic Energy Sciences (BES) Physical Biosciences community to fill critical knowledge gaps in knowledge about how enzymes orchestrate spatial and temporal events to direct electrons, protons, and substrates for selective conversions and allosteric regulation. These advances will contribute to the design of next-generation synthetic catalysts.

Our research is divided into three general themes to fill outstanding gaps in knowledge and explore transferability of concepts learned: understand how dynamic confinement imposed by the enzyme scaffold controls specificity and selectivity (Theme 1); understand how electrons and protons are delivered and accumulated at the active site (Theme 2); and understand how mechanical energy and electro- or thermochemical energy are interconverted in biomolecules (Theme 3).

Nitrogenase as a Paradigm

Our current focus is mostly dedicated to understanding production of bacterial $N_2$by the nitrogenase complex. This is a multi-subunit metalloenzyme (Figure 42) comprising two electron carrier Fe proteins and the MoFe protein core. It catalyzes the reduction of N_2 to NH_3 and H_2 with electrons provided by the Fe protein upon adenosine triphosphate (ATP) hydrolysis. The nitrogenase complex vividly exemplifies the hierarchical complexity of enzymes. One Fe protein with two bound ATP molecules binds to one half of the MoFe protein. This initiates a series of events that involve large-scale conformational motions that result in the transfer of an electron from the Fe protein ending on the [7Fe-9S-Mo-homocitrate] catalytic cofactor (FeMo-co) via the [8Fe-7S] P-cluster in the MoFe protein. Then, the hydrolysis of two ATP to adenosine diphosphate (ADP) induces the dissociation of the Fe protein. This cascade of events must be repeated eight times for every N_2 molecule and involves large-amplitude conformational changes, resulting in the unidirectional transfer of electrons and protons to the FeMo-co that leads to the reduction of N_2 molecule.

N_2 Activation by Nitrogenase

One of the most puzzling aspects of nitrogenase chemistry is the necessity to produce at least one H_2 molecule for every two molecules of NH_3, as illustrated by the limiting stoichiometry reported in Figure 42. Our combined experimental (with Brian Hoffman, Northwestern University) and computational activity largely contributed to give insight into the enzymatic coupling of N_2 binding and H_2 release that prevents the futile production of two H_2 molecules without reduction of N_2. In the 1980s, Lowe and Thorneley put forward a kinetic model for catalysis by the MoFe protein, including rate constants for the formation of each intermediate state designated as *En*, where *n* indicates the number of electrons and protons accumulated. Only in recent years has our team isolated and characterized a few intermediates and located them within the Lowe-Thorneley model. We recently carried out an extensive quantum chemical study of N_2 activation by nitrogenase. Binding and activation of N_2 take place at the E_4

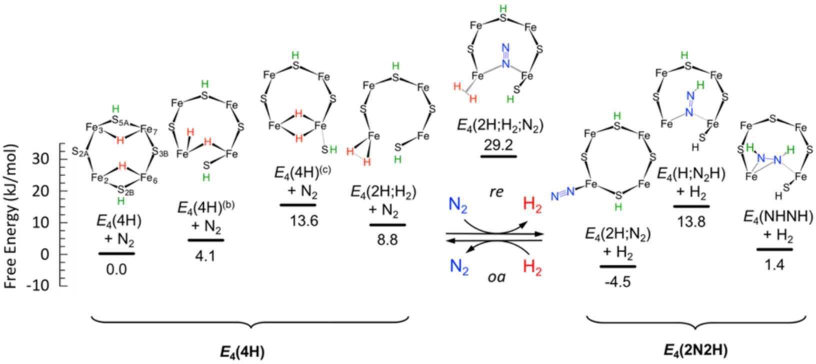


Figure 43. Relative free energy of various E_4 species (left) potentially involved in FeMo-co reductive activation (*re*) of H_2 and the breaking of the N_2 triple bond (right). Protic and hydridic hydrogens are indicated in green and red, respectively.

state, which is activated by the accumulation of $4e^-/H^+$ and is accompanied by the concomitant reductive elimination of H_2. Our results suggest that at ambient temperature, various low-lying E_4 isomers coexist (Figure 43, left). In particular, the lowest in energy, E_4(4H), has two [Fe-H-Fe] bridging hydrides consistent with low-temperature electron-nuclear double resonance measurements by Hoffman. A second relevant low-lying E_4 state is the dihydrogen species E_4(2H;H_2), which features a strongly activated di-hydrogen located on Fe_2 and illuminates our recent finding that an H_2 complex forms during reductive elimination of the hydrides of E_4(4H). Notably, we found a nearly isoergic equilibrium in which the loss of H_2 is coupled to N_2 binding and the possible formation of a diazene-level intermediate, which is in close agreement with the recent direct measurement of this equilibrium. In this process, E_4(4H) undergoes reductive formation of H_2 with the formation of the di-hydrogen adduct E_4(2H;H_2); this binds N_2 to form E_4(2H;N_2) with the concomitant elimination of H_2 and subsequently to the diazene E_4(NHNH) intermediate (Figure 43, right).

It is possible to achieve a profound understanding of the thermodynamic necessity of coupling H_2 formation via *re* to cleavage of the N≡N triple bond by looking at the overall process for the formation of any of the diazene-level intermediates from E_0. Focusing just on the formation of E_4(NHNH), which requires the consumption of four ATP, the overall process is exergonic by $\Delta G_{E4} = -103$ kJ/mol at pH = 7. What makes this process so favorable can be understood by decomposing it into the two parts: (1) the endergonic formation of E_4(NHNH) from E_0, N_2, $2H^+$, and $2e^-$ provided by the Fe protein and the hydrolysis of four ATP, with $\Delta G_{DZ} = +67$ kJ/mol, and (2) the exergonic formation of H_2 from $2H^+$ and $2e^-$, again provided by the Fe protein via ATP hydrolysis, with $\Delta G_{H2} = -170$ kJ/mol. *Thus, although the direct formation of E_4(NHNH) without generation of H_2 is thermodynamically unfavorable, nitrogenase couples this unfavorable reaction of N_2 with a highly favorable one, generation of H_2, resulting in an overall exergonic process to drive N_2 fixation.*

Electron Transfer in Nitrogenase

Recent studies support a “deficit-spending” mechanism for the net electron delivery to FeMo-co, where the interaction of the Fe protein and the MoFe protein triggers an initial electron transfer event that involves intramolecular delivery of one electron

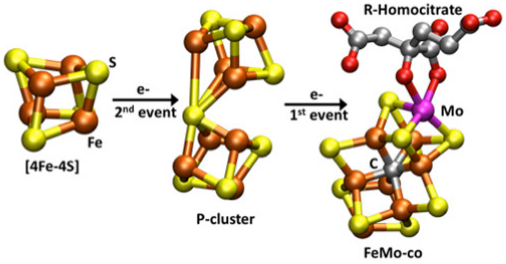


Figure 44. Electron transfer events in the deficit spending mechanism in nitrogenase.

from the P-cluster to FeMo-co (Figure 44). This situation results in the P cluster having a "deficit" of one electron, designated P^{1+}, relative to the all-ferrous P^N resting state. The deficit could then be erased in a second step involving the reduction of P^{1+} to yield P^N through intermolecular delivery of an electron from the Fe protein's $[4Fe–4S]^{1+}$ cluster. A tightly integrated quantum chemical and structural (X-ray) study carried out by Peters (Washington State University) and our team revealed that the nearby Ser residue favorably binds to the P^{1+} upon P^0 oxidation while a backbone amide binds after further oxidation to P^{2+}. These observations suggest a possible mechanism for how conformational changes around the P cluster could alter the $E^{o\prime}$ of the $P^{N/1+}$ couple. Creation of an activated P^{N*} state upon Fe protein binding pushes the OH from Ser and the N from the backbone closer to the P cluster, driving the redox potential, $E^{o\prime}$, of the $P^{N/1+}$ couple more negative. A more negative $E^{o\prime}$ for the P^{N*} state would result in prompt electron transfer from the P^N state to the FeMo-cofactor. The oxidized P^{ox*} state would then promptly bind the ligands and drop to the P^{ox} state. The P^{ox} state is rapidly reduced by the Fe protein, returning the P^{1+} cluster to the P^N state.

Early Career Program: Combined Capture and Conversion of CO_2

PI: David J. Heldebrant

Collaborators: Leo Bañuelos, (University of Texas at El Paso), Jotheeswari Kothandaraman, David Hoyt, Eric Walter, John C. Linehan, Vassiliki-Alexandra Glezakou, Roger Rousseau, Xiao-Ying Yu, Juan Yao

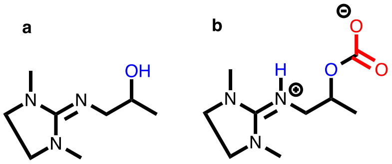


Figure 45. Structure of a) IPADM-2-BOL, b) IPADM-2-BOL + CO_2.

Nature has perfected "reactive separations," where the capture/concentration of reagents and activation/conversion are implemented in a synergistic step. With respect to power generation from fossil fuels, CO_2 capture and any subsequent conversion are performed as two distinctive energy-intensive steps. The aim of this project was to learn how to mimic nature and perform synergistic capture and conversion in the same solvent using the same chemicals. Switchable ionic liquids (SWILs) are promising solvents being studied for CO_2 capture and exhibit unique physical and thermodynamic property changes as they chemically fixate CO_2. SWILs are coincidentally comprised of amine bases and or alcohols which have been shown to promote the catalytic reduction of CO_2 to CH_3OH. This work encompasses a joint experimental and theoretical approach that aims to characterize the disparate (ionic/non-ionic) micro-domain structure and assess how this structure can be manipulated to control diffusion and chemical complexation of CO_2 in regard to capture while learning how changes in the solvent structure can be used to govern the reactivity of CO_2 captured in solution. The aim is to fully characterize the solvent structure and chemical speciation of the fluid to learn how the mesoscopic structure originates and how this dynamic structure governs the diffusion and reactivity of CO_2 in solution. We also focus on optimizing the thermodynamics of CO_2 conversion by matching the electrophilicity (hydride acceptor strength) of the CO_2 captured in solution to the hydride donation strength of catalysts used for subsequent catalytic conversions into value-added products.

Anomalous High CO_2 Diffusion in Switchable Ionic Liquids

The capture and conversion of CO_2 are both mass-transfer limited. As a consequence, understanding how CO_2 moves through the liquid is critical to learning how to control reactivity in SWILs. SWILs exhibit anomalous behavior in that they have been shown to exhibit higher mass transfer rates of CO_2 than aqueous solvents even at viscosities that are 1–2 orders of magnitude higher. Our hypothesis was that this anomalous behavior was linked to the mesoscopic structure of SWILs, though it was not clear *how* these viscous fluids could rapidly move CO_2 through them, as diffusion has a direct correlation to viscosity in nearly all other liquids. Thus, we set out to decipher how the solvent's mesoscopic structure enables CO_2 to move differently through SWILs compared to aqueous solvents or conventional ionic liquids by performing the classical molecular dynamics simulations of CO_2 diffusion through 1- isopropyl-alcohol-N,N dimethyl-2-binding organic liquid (1-IPADM-2-BOL) to ascertain which domain in the fluid CO_2 would solvate and diffuse.

The CO_2 molecules chemically fixated in the ionic regimes were expected to interact strongly with neighboring ions, which would limit the rate of molecular diffusion. Earlier molecular dynamics (MD) simulations had confirmed the slow molecular diffusion of zwitterions, following conventional Stokes-Einstein behavior. The challenge to deciphering diffusion is that ab initio-based MD simulations and experimental NMR data have shown that CO_2 physically absorbed in solution establishes an equilibrium with the zwitterions in a ratio of about 1:10 at an estimated temperature of absorption (40 °C). The energy barrier computed for this interconversion was ~16 kJ/mol, which indicates rapid transitions between the two species on the order of nanoseconds.

We hypothesized that molecular CO_2 dissolved in solution dominates the macroscopic mass transfer by diffusing through SWILs via pores or channels of low-polarity regions in which CO_2 could easily move. This proposed phenomenon is exemplified using 1-IPADM-2-BOL as an archetypical SWIL with CO_2 diffusion pathways illustrated by the yellow line (Figure 46). CO_2-free IPADM-2-BOL (grey) is relatively low polarity and non-viscous, providing a medium where CO_2 could readily diffuse. Even at higher CO_2 loadings, CO_2 would likely diffuse through pockets or channels of CO_2-free solvent rather than the polar and viscous CO_2-bound ionic regions. Experimental data has shown that SWILs are heterogeneous at any CO_2 loading above 0%, suggesting that pockets or channels within the fluid always exist, providing regions wherein non-polar gases such as CO_2 or N_2O could diffuse; this accounts for the higher-than-expected mass transfer.

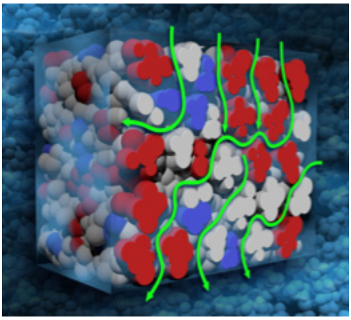


Figure 46. MD simulations of IPADM-2-BOL and IPADM-2-BOL-CO_2 with CO_2. Green arrows are CO_2 diffusion pathways.

In this work, we have shown that mesoscale heterogeneity is likely the root cause of the facilitated CO_2 transport in water-lean carbon capture solvents. If these disparate regions within the fluid could be controlled with defined shape and size, pockets or linear channels could be made within the fluid where gases such as CO_2 can more readily diffuse and react with the CO_2-free solvent, irrespective of the viscosity of the solvent. We hypothesize that all water-lean carbon capture solvents would exhibit a similar heterogeneous molecular structure, as many formulations have been measured to have anomalously high rates of mass transfer at high solution viscosities. Current efforts are underway to determine if these structures are more common than previously anticipated, noting that if the size, shape, and orientation of these mesoscopic domains can be manipulated in these solvents, CO_2/solvent superhighways could be designed, enabling even faster and more efficient materials for CO_2 capture.

Conversion of Captured CO_2

The second thrust of this program is to study the reactivity of 'captured' CO_2, i.e., carbonates and carbamates, toward catalytic conversions. To assess the reactivity of the carbonates or carbamates in solution, we set out to study condensed-phase catalytic hydrogenations using catalysts that typically are used under gas-phase conditions. Here, this would enable direct comparisons of reactivity of the carbonate or carbamate to gaseous CO_2 or CO. We chose a $Cu/ZnO/Al_2O_3$ catalyst, as it is commercially available and is known to perform

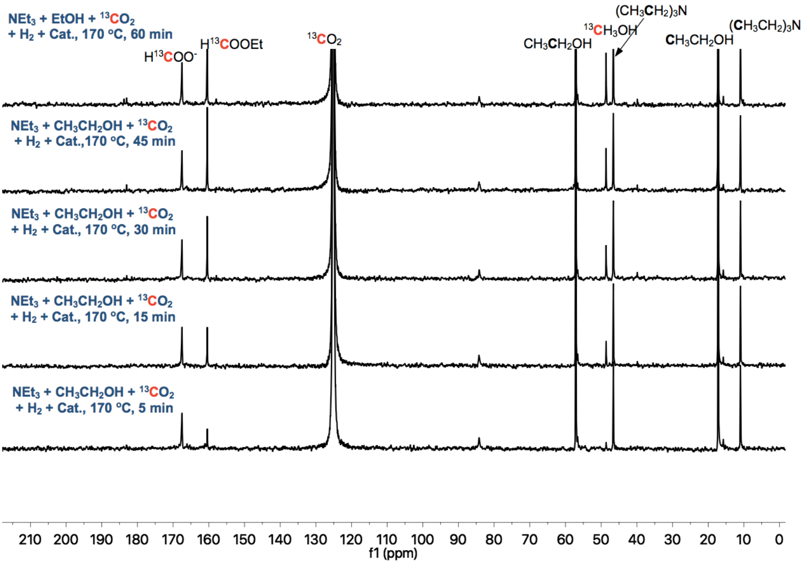


Figure 47. ^{13}C **MAS NMR of the reaction.**

gas-phase hydrogenations in which the reaction proceeds via CO_2 → CO → HCOOH → CH_3OH.[8] Hydrogenations were performed at 170 °C under 60 bar CO_2: H_2, conditions that have been previously shown to hydrogenate CO_2 to methanol. 1° and 2° amines (carbamates) were hydrogenated to their respective formamides but were incapable of continuing to CH_3OH, which we attribute to the low hydride acceptor strength (low electrophilicity) of formamides compared to that of formate esters. 3° amines such as triethylamine (NEt_3) exhibited no reactivity. Similarly, alcohols such as ethanol showed no conversion. The combination of the 3° amine and alcohol together were found to be reactive, producing CH_3OH in varied conversion ratios depending on the combination of amine and alcohol. The lack of reactivity of the base and alcohol separately suggests that neutral CO_2 cannot be the active species and that anionic alkylcarbonate could be the active species.

The combination of non-nucleophilic bases and alcohols appeared to validate our hypothesis that CH_3OH production proceeds via an alkylcarbonate → formate → formate ester route due to a lack of definitive spectroscopic evidence that the alkylcarbonate is the active species at 170 °C under 25 bar CO_2. Recent efforts have focused on performing operando ^{13}C magic angle spinning (MAS) NMR to determine reaction mechanisms and speciation under operating conditions (Figure 47). Recent results studying a 1:10 NEt_3 and reaction ethanol mixture at 20 bar of ^{13}C-enriched CO_2 at 120 °C showed ethylcarbonate (158.9 ppm) in solution at a concentration 2.2 times that calculated for the active sites on the catalyst. Additionally, we observed ethylcarbonate bound to the catalyst (165.7 ppm) at a concentration that is 22% of that calculated for the catalyst's active site, indicating ethylcarbonate exists in a significant enough concentration to participate in the reaction up to at least 120 °C. These measurements were the first spectroscopic evidence that alkylcarbonates do exist under catalytic conditions and are observed to directly coordinate to the catalyst surface. Operando ^{13}C MAS NMR of this reaction at 170 °C at 50 bar pressure was performed, showing the near-immediate formation of triethylammonium formate (168.5 ppm) rapidly growing concurrently with ethyl formate (161.2 ppm). The CH_3OH signal at 48.7 ppm started to grow quickly at less than 5 min of heating at 170 °C, confirming our proposed mechanism. We are currently studying the reactivity of captured CO_2 toward other chemicals and materials such as cyclic and polymeric carbonates.

CONNECTIONS TO APPLIED PROGRAMS

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

Chemical Transformations Initiative

Initiative Lead: Roger Rousseau

Co-Leads: Karis Alderson, Michael Elliott, Johannes A. Lercher

Chemical Transformations Initiative (CTI) is establishing the science for the efficient electrochemical conversion of underutilized carbon resources into value-added chemicals and fuels. By integrating fundamental and applied sciences, we are discovering novel phenomena at solid-liquid interfaces, new chemical reactions, and new catalysts to enable low-temperature and low-pressure conversion of these resources. We are increasing our understanding of how complex interfaces arise between solid electrocatalysts under an external electrochemical bias and how mixtures of liquid water and organics affect the activity and selectivity of the catalyzed reactions. We are incorporating this growing understanding of novel reactors and process designs. The CTI team is working toward understanding and controlling electrocatalytic hydrogenation of oxygenated organic compounds. We employ theory and computation—coupled with careful thermodynamic/kinetic measurements and in situ spectroscopy—to enable us to understand the mechanisms of electrocatalytic hydrogenation. This understanding ultimately enables us to control the activity, selectivity, and electrochemical efficiency of these conversions and allows us to design better reactors and processes, moving us closer to implementation.

Multiscale Modeling of Electrocatalytic Conversions Provides Insights into the Role of Electrical Double Layer in Controlling Conversion.

Vassiliki-Alexandra Glezakou, Mal-Soon Lee, Manh-Thuong Nguyen, Roger Rousseau

To predict electrocatalytic kinetics, we must understand how mass and charge move in and out of the electrochemical double layer and interact on the electrode surface. This requires simulations that are at the forefront of what can be achieved using state-of-the-art computing, involving processes occurring simultaneously on time scales ranging from picoseconds to seconds and length scales spanning nanometers to micrometers. The CTI Theory Team has developed a multiscale model that includes quantum mechanical calculations to understand chemical reactivity, molecular dynamics to understand electrical double layers, and electron transfer theory to predict rates. Working closely with the CTI experimentalists, we have begun to validate many of the discoveries from this model. These include the competition between hydrogen and organics for access to the surface of the electrocatalyst and the role of solvents and pH in controlling the catalysis.

We find that although simple thermodynamics models based on static calculations are good for predicting relative overpotentials of electrocatalytic reactions, we need to explicitly account for solvent and double layer effects to understand reaction rates. Transferring this knowledge toward the conversion of realistic feeds—such as hydrothermal liquefaction oils—requires that the models address an even higher level of complexity. The team is currently moving forward to understand how to contend with multicomponent solvent mixtures and competition between adsorbates.

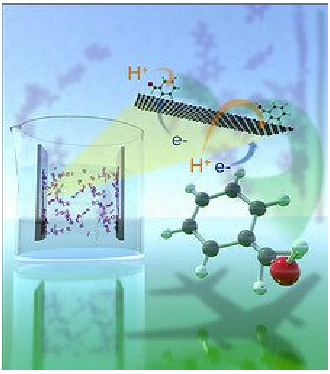


Figure 48. Theory and modeling shed light on how organics are transformed at electrode interfaces.

Mechanistic Insights into Electrocatalytic Hydrogenation are Allowing us to Optimize Rates.

John L. Fulton, Vassiliki-Alexandra Glezakou, Oliver Y. Gutiérrez, Jamie D. Holladay, John E. Holladay, Johannes A. Letcher, Juan Ruiz Lopez, Roger Rousseau

The fundamental and applied hydrogenation teams have taken on the challenge of determining kinetic parameters, which are often overlooked in traditional electrochemical synthesis. The teams are using them to draw guidelines for catalyst and process optimization. From the fundamental point of view, we have shown increases in conversion rates, by orders of magnitude, by minimizing the Ohmic drop between electrodes; have counteracted the rollover of hydrogenation rates due to excessive dehydrogenation of adsorbates; have studied the effects of hydronium ion concentration on hydrogenation; have optimized the particle size of metals to maximize rates; and have suppressed H_2 evolution during hydrogenation on Pd.

Aiming at understanding electrocatalysis in mixtures, we recently found that the rates of carbonyl hydrogenation (like in benzaldehyde) are enhanced by the co-adsorption of a second organic compound (e.g., phenol, and benzoic acid) that is able to form a hydrogen bond with the carbonyl group. This rate enhancement

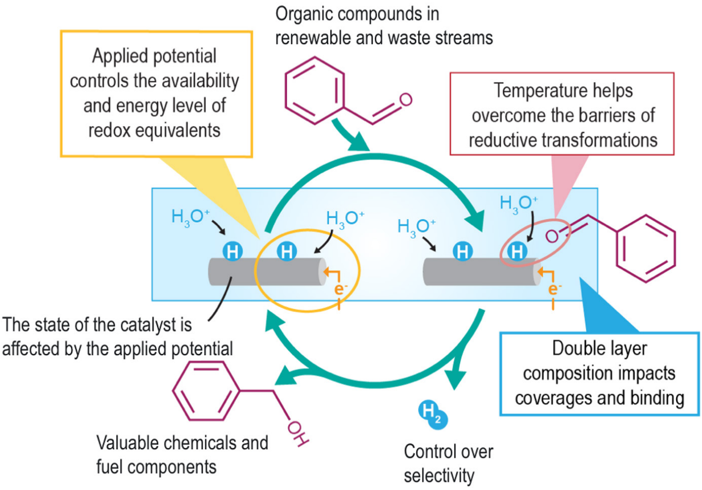


Figure 49. Mechanistic insights allow us to enhance rates of electrocatalytic hydrogenation.

does not occur if the hydrogenation occurs via thermal catalysis with molecular H_2.

We propose that in mixtures, there are intermolecular interactions that may offer alternative reaction pathways. These routes are activated when e^-/H^+ pairs drive the reduction rather than H_2. The team is currently testing this hypothesis following our trademark approach of combining kinetics, physicochemical and electrochemical characterizations, and theory.

Consortium for Computational Physics and Chemistry

Vassiliki-Alexandra Glezakou, Mal-Soon Lee, Asanga Padmaperuma, Roger Rousseau

This consortium combined capabilities from Oak Ridge National Laboratory, Argonne National Laboratory, National Renewable Energy Laboratory, National Energy Technology Laboratory, and PNNL for the study of biomass conversion to fuels and is funded out of DOE's Energy Efficiency and Renewable Energy, Bioenergy Technology Office. PNNL's role is to use the advanced theory and computation tools developed on our core BES catalysis program to support the development of catalysts and process for biomass conversions. Through our leadership role in this consortium, we are able and transfer capabilities and learnings from our BES program to impact catalysis research across many other DOE labs.

Collaboration on Indirect liquefaction via Metal-Doped Zeolite Catalysts

Vassiliki-Alexandra Glezakou, Mal-Soon Lee, Zhenglong Li (ORNL), Roger Rousseau

To explore the reaction mechanisms of ethanol conversion over Cu-Zn-Y-incorporated beta polymorph A (BEA) zeolite, multiple models of single Cu, Zn, and Y sites were first proposed based on the experimentally-measured coordination numbers (4, 4, and 6, respectively). The simulated EXAFS patterns of these metal-incorporated sites were also projected based on the ensemble collected from AIMD simulations performed at experimentally-relevant temperatures of 300 K. Cu, Zn, and Y were introduced into the largest micropore of BEA zeolite as extraframework, where the additional charge is compensated by the presence of another metal residing in the framework. Both Cu and Zn prefer to form the tetrahedral coordination with neighboring O atoms in the framework and H_2O molecule, as shown in Figure 50. More importantly, the simulated EXAFS patterns of Cu and Zn match well with the available experimental data. In contrast, Y forms the octahedral coordination environment with neighboring O atoms as well as 2 H_2O molecules. Further improvement on the Y site model is in progress to match the simulated EXAFS pattern against the experimental result, specifically below 1 Å region. The initial study of the reaction energy pathway of ethanol conversion over Cu and Zn-incorporated sites shows that different types of reaction intermediates are stabilized based on the type of metal introduced into BEA zeolite catalyst.

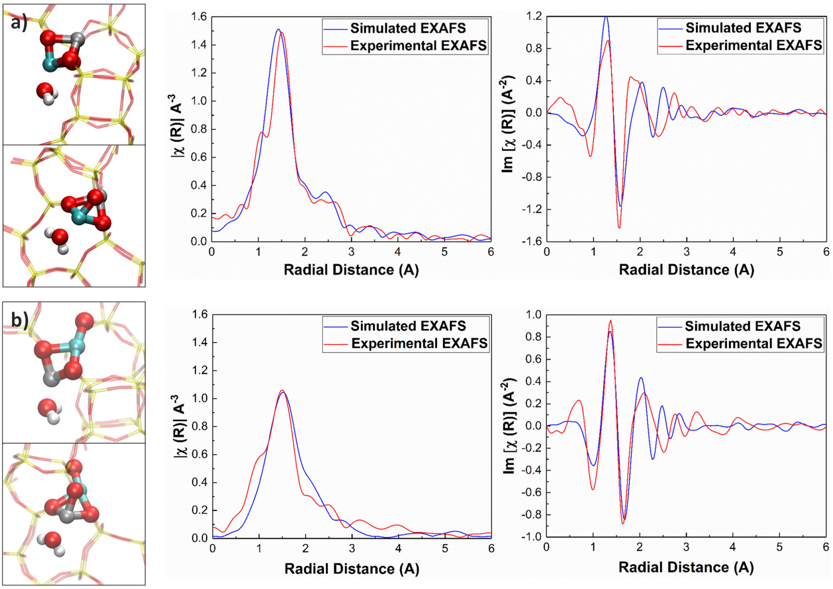


Figure 50. DFT-optimized geometry of a) Cu- and b) Zn-incorporated sites in BEA zeolite, along with the corresponding magnitude and imaginary part of simulated EXAFS. Grey, red, yellow, cyan, and white balls represent Zn, O, Si, Cu, and H, respectively. at the metal center (bottom middle). Experimentally measured catalytic activity (bottom right).

Controlling the Selectivity between Butene/Butadiene on Ag/ZrO$_2$/SIO$_2$ Catalysts through Metal Oxidation State and Dispersion

Robert Dagle, Vanessa Dagle, Vassiliki-Alexandra Glezakou, Yong Wang, Roger Rousseau

The reaction mechanisms of ethanol conversion were investigated Ag supported on amorphous SiO$_2$ in the presence of ZrO$_2$ as an oxide promoter. Here, two different models, in the form of dispersed Ag and Ag nanoparticle, were considered to represent the potential Ag structure on SiO$_2$ support shown in Figure 51a. Subsequently, the Gibbs free energy of adsorption was computed for a series of plausible reaction intermediates (Figure 51b) in order to understand the change in selectivity of Ag at two different metal concentrations. The dehydrogenation of ethanol into acetaldehyde is found to be a key rate-determining step on Ag/SiO$_2$/ZrO$_2$ catalyst, and high Ag dispersion energetically favors ethanol dehydrogenation. In contrast, the formation of ethylene is favorable on Ag nanoparticle relative to dispersed Ag, indicating that using dispersed Ag is better at controlling the undesirable production of ethylene. The charge state of dispersed Ag and Ag nanoparticle was also determined to be very

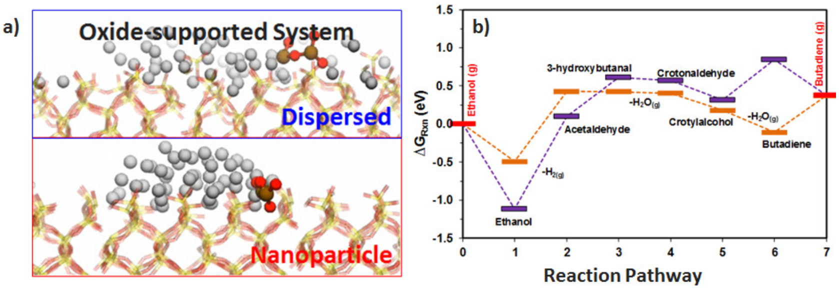


Figure 51. a) Schematic of DFT-optimized dispersed and nanoparticle model of Ag supported on amorphous SiO_2 in the presence of ZrO_2, along with b) Gibbs free energy diagram of ethanol conversion on dispersed (orange path) and nanoparticle (purpose path) model. More negative values indicate more favorable adsorption energy of reaction intermediates. Grey, red, yellow, and brown balls represent Ag, O, Si, and Zr, respectively.

different ($Ag^{\delta+}$ and Ag^0, respectively) and, most importantly, is closely related to the selectivity towards butadiene and ethylene. Overall, having dispersed Ag (possessing $Ag^{\delta+}$ charge state) predominantly leads to the desirable formation of butadiene, while having less-dispersed Ag nanoparticle (possessing Ag^0 charge state) enhances the production of undesirable ethylene for the $Ag/SiO_2/ZrO_2$ catalyst.

Catalyzed Organo-Metathetical (COMET) Process to Mg Production

Homogeneous Catalyst Development for the Regeneration of Alkyl-Li for Mg Exchange (Advanced Research Projects Agency–Energy Project)

Vassiliki-Alexandra Glezakou, B. Peter McGrail, Mal-Soon Lee, Roger Rousseau

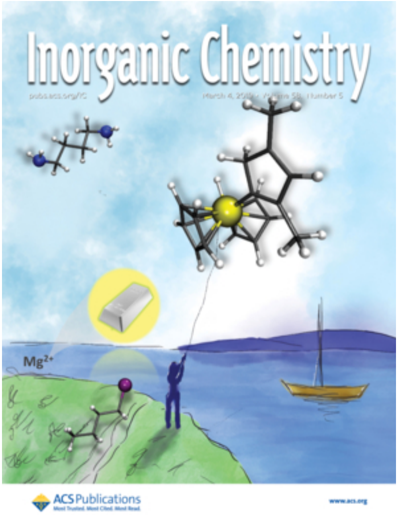


Figure 52. Catalyst design including use of co-solvent for alkyl-Li regeneration was elucidated by means of ab initio molecular dynamics.

Seawater represents a practically unlimited source of Mg, which is in high demand due to its use in car and aircraft industry. Industrially, it is produced by molten salt purification and electrolysis at significant costs. In the catalyzed organo-metathetical (COMET) process, a low-energy pathway is proposed that converts $MgCl_2$ (extracted from seawater) and alkyl-Li to alkyl-Mg. While MgR_2 can thermally decompose to Mg(s), a catalyst is needed to regenerate RLi (in our case Butyl-Li). A three-step catalytic cycle was proposed based on a catalyst of the general formula Cp_2MClL catalyst (M = Ti, Zr; L = select organic ligands) that can catalyze the necessary steps of hydrometalation and transmetalation to produce RLi. Free energy estimates from density functional based molecular dynamics in explicit solvent (tetrahydrofuran) reveal a high affinity of Li to Cl and N-containing ligands (L) that leads to catalyst deactivation. Our simulations further proposed that addition of an amine co-solvent further facilitates alkyl-Li formation and the catalyst regeneration.

Vehicle Emission Control Research

Feng Gao, Jamie Holladay, Abhi Karkamkar, Juan Lopex Ruiz, Ken Rappe, Mark Stewart, Janos Szanyi, 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, optimizing systems, and enabling new combustion strategies.

We conduct this work with collaborators at several universities: Bill Schneider (Notre Dame University); Fabio Ribeiro, Raj Gounder, and Nick Delgass (Purdue University); Hristiyan A. Aleksandrov and Georgi N.Vayssilov (Sofia University, Bulgaria); Franklin Tao (University of Kansas); and Jean-Sabin McEwen (Washington State University). We also collaborate with people at several companies: Alex Yezerets, Karishna Kamasamudram, and Neal Currier (Cummins, Inc.); Christine Lambert (Ford Motor Company); Hai-Ying Chen (Johnson Matthey); Craig DiMagio (FCA); Saeed Alerasool, Pascaline Tran, Xinyi Wei, Jeff Hoke (BASF); Randal Goffe (PACCAR); and Se Oh and Wei Li (General Motors).

Recent highlights. Lean combustion gasoline and diesel engines provide substantially higher fuel efficiency, reduced CO_2 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.

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

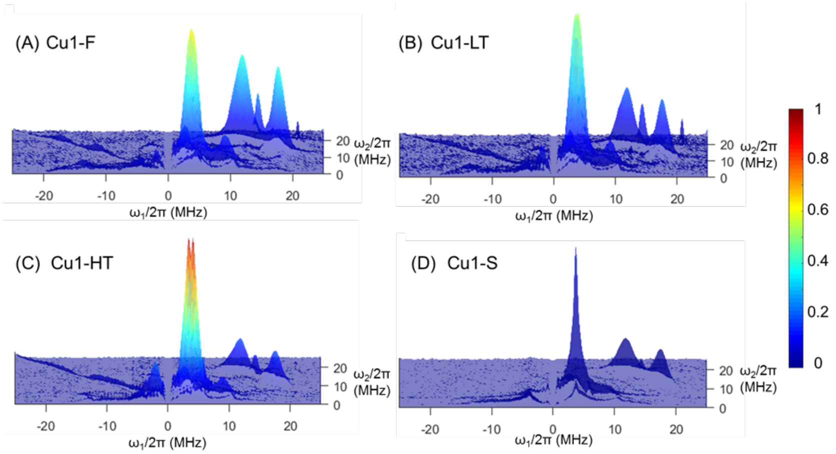


Figure 53. Surface plots of hyperfine sublevel correlation experimental spectra for hydrated (A) Cu1-F (freshly prepared, dried and calcined), (B) Cu1-LT (hydrothermally treated at 70°C), (C) Cu1-HT (hydrothermally treated at 800°C) and (D) Cu1-S (stored in a typical ambient lab environment) samples. All spectra are normalized by experimental signal intensity/videogain/mass, with Cu1-S "symmetrized".

order to provide guidelines to the synthesis of catalysts with optimized balance in low-temperature activity, selectivity, and long-term durability.

For example, commercial Cu on Silicoaluminophosphate-34 (SAPO-34) selective catalytic reduction (SCR) catalysts have experienced unexpected and quite perplexing failure. Understanding the causes at an atomic level is vital for the synthesis of more robust Cu/SAPO-34 catalysts. We recently have shown (Figure 53), via application of model catalysts with homogeneously dispersed isolated Cu ions, that Cu transformations resulting from low-temperature hydrothermal aging and ambient temperature storage can be semi-quantitatively probed with 2-dimensional pulsed electron paramagnetic resonance. Coupled with kinetics, additional material characterizations and DFT simulations, we propose the following catalyst deactivation steps: (1) detachment of Cu(II) ions from cationic positions in the form of $Cu(OH)_2$; (2) irreversible hydrolysis of the SAPO-34 framework forming terminal Al species; and (3) interaction between $Cu(OH)_2$ and terminal Al species forming SCR inactive, Cu-aluminate like species. Especially significant is that these reactions are greatly facilitated by condensed water molecules under wet ambient conditions, causing low-temperature failure of the commercial Cu/SAPO-34 catalysts.

Another example is the development of advanced materials to address The DOE 150 Challenge. Although there has been success addressing NO_x emissions at

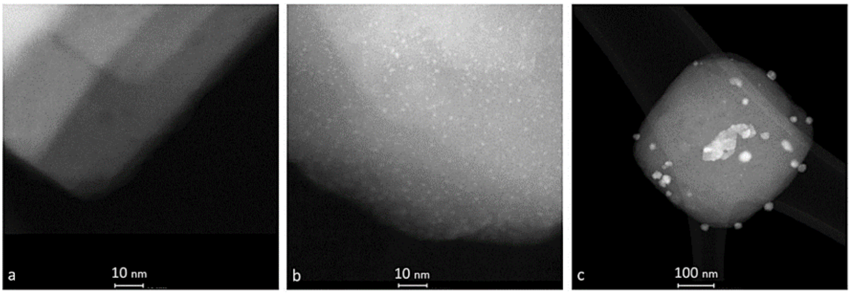


Figure 54. HAAD-STEM images of 1 wt% Pd/H-SSZ-13 a) Si/Al=6, b) Si/Al=12, c) Si/Al=30.

temperatures above 250 °C with selective catalytic reduction technology, emissions during vehicle cold start (when the temperature is below 150 °C), are a major challenge. We have recently shown that we can completely eliminate both CO and NO_x emissions simultaneously under realistic exhaust flow, using a highly loaded (2 wt%) atomically dispersed palladium in the extra-framework positions of the small-pore chabazite material as a CO and passive NOx adsorber (Figure 54). We devised a general, simple, and scalable route to prepare such materials for Pt^{II} and Pd^{II}. Through spectroscopy and materials testing, we show that both CO and NO_x can be simultaneously completely abated with 100% efficiency by the formation of mixed carbonyl-nitrosyl palladium complex in chabazite micropore.

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 selective catalytic reduction and 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.

STAFF BIOS

- Aaron Appel
- Tom Autrey
- R. Morris Bullock
- David A. Dixon
- Zdenek Dohnálek
- John Fulton
- Feng Gao
- Bojana Ginovska
- Vassiliki-Alexandra Glezakou
- Oliver Y. Gutiérrez
- Jian Zhi Hu
- Enrique Iglesia
- Andreas Jentys
- Abhijeet Karkamkar
- Bruce D. Kay
- Greg A. Kimmel
- Libor Kovarik
- Mal-Soon Lee
- Johannes Lercher
- John C. Linehan
- Nikolay G. Petrik
- Roger Rousseau
- Gregory K. Schenter
- Wendy J. Shaw
- Janos Szanyi
- Huamin Wang
- Yong Wang
- Eric S. Wiedner

Aaron Appel

Catalysis Science
Physical Sciences Division

Subtask Principal Investigator

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 chemistry with thermochemical studies to understand the limiting factors in catalytic systems, thereby identifying and controlling high-energy steps. I have incorporated bifunctionality into catalysts to avoid high-energy species and to increase catalyst performance through improved rates and energy efficiency.

I am leading the subtask entitled Enhancing H_2 Addition Rates by Designing the Active Site and Its Environment, which is focused on understanding and controlling the environment for hydrogenation of carbon-oxygen and carbon-carbon bonds, emphasizing the role of solvents, confining supports, organic ligands, or a bioinspired scaffold.

In addition to leading the subtask on the reduction of carbon dioxide, I lead the Catalyst Design Thrust in the Center for Molecular Electrocatalysis. My research within this center is focused on thermochemical and electrochemical studies of molecular catalysts, especially for electrocatalytic oxidation of alcohols.

Tom Autrey

Catalysis Science
Physical Sciences Division

Co-principal Investigator

Phone: (509) 375-3792
E-mail: tom.autrey@pnnl.gov

My research interest is focused on measuring the thermodynamic properties of catalytic intermediates with a goal of providing insight for the development of new catalyst materials designed for small molecule activation. Using a combination of experimental and computational approaches, we study how environmental factors such as electrostatic interactions, spatial confinement, and solvent effects enhance the kinetics and modify the thermodynamics of catalytic hydrogenation reactions. This insight provides a rational approach to understand how the reaction environment can be tuned to control selectivity and enhance reactivity in chemical transformations. Given our focus on the catalytic reduction of polar and polarizable substrates, the heterolytic activation of molecular hydrogen, which provides a catalyst-based complex containing both hydridic and protonic hydrogen, is of special interest. My colleagues and I have shown how to use in situ reaction calorimetry to obtain both kinetic and thermodynamics data simultaneously. We collaborate with the theory group to better understand the relationships between the structure and dynamical properties in these molecular complexes. These research studies will provide the foundation for the development of new catalyst materials.

R. Morris Bullock

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

Co-principal Investigator

Phone: (509) 372-6589
E-mail: morris.bullock@pnnl.gov

My research is focused on fundamental studies of the reactivity of molecular inorganic complexes and the design of molecular catalysts. A long-term focus has been on earth-abundant metal catalysts instead of precious metals. Our goal is to use the insights on reactivity and thermodynamics to design thermal catalysts and electrocatalysts based on inexpensive, earth-abundant metals.

I am the Director of the CME, an Energy Frontier Research Center. The Center includes partners at Yale University, the University of Wisconsin-Madison, MIT, the University of Washington, and Purdue University. In the CME, we use synergistic experimental and theoretical approaches to understand, predict, and control the intra- and intermolecular movement of protons in electrocatalytic multi-proton, multi-electron processes of crucial importance to energy transformations, including reduction of oxygen, oxidation of ammonia, and oxidation of alcohols. We seek to understand the fundamental principles needed for efficient interconversion of electrical energy and chemical bonds through precise control of electron and proton transfers. Our research includes synthesis, mechanistic studies, electrochemistry, determination of thermochemical properties, computations, and evaluation of catalysis performance.

David Dixon

Robert Ramsay Chair
Chemistry
University of Alabama

Co-principal Investigator

Phone: (205) 348-8441
E-mail: dadixon@ua.edu

My group's research is focused on developing and using computational electronic structure chemistry approaches to tackle a broad range of problems of interest to the DOE. The focus of the current effort is on the study of the properties of a broad range of heterogeneous and homogeneous catalysts in close collaboration with experimental efforts. We are developing and applying reliable electronic structure prediction methods at the correlated molecular orbital theory level for model catalytic systems that can serve as benchmarks for more approximate methods such as density functional theory. We are continuing our extensive studies of alcohol and water reactions on transition metal oxide nanoclusters, including the Group 4 metals. We have predicted the interactions of organics on large TiO_2 nanoclusters to provide detailed information on how to better model desorption processes. We are investigating the role of bulky ligands on transition metal sites for homogeneous catalysis for CO_2 hydrogenation and for C-C bond formation and cross-coupling reactions. We have developed an improved understanding of the properties of carbenes as ligands and have shown that there are singlet nucleophilic and singlet electrophilic types based on a broad range of properties including singlet-triplet gaps, Brönsted basicities, Lewis acidities, hardness, and electronegativity. We are exploring site-isolated metals and small clusters in heterogeneous environments to provide further insights into reactivity. An important part of the overall effort is to provide insights into enthalpic vs. entropic effects and the role of the local environment on catalytic reactions. We are continuing to generate thermodynamic and electronic structure datasets for the development of correlations across a broad range of catalytic properties.

Zdenek Dohnálek

Catalysis Science
Physical Sciences Division
Deputy Director
Institute for Integrated Catalysis

Subtask Principal Investigator

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 and CO_2 hydrogenation. The primary goal of the surface science approach used in my lab is to achieve a detailed, site-specific, molecular-level understanding of the kinetics and dynamics of elemental reaction steps on well-defined surfaces and monodispersed clusters. Comprehensive experimental studies involve both atomically resolved imaging and ensemble averaged spectroscopies to determine the catalyst structure and identify reaction intermediates and products. Novel deposition methods are developed and employed to prepare clusters and films of model metal and metal oxide catalysts with tailored chemical properties. Studies are complemented by collaborative theoretical investigations to achieve detailed generalizable structure-reactivity relationships. Systems recently investigated include anatase(101) and rutile(110) TiO_2 and RuO_2(110) surfaces and supported WO_3, MoO_3, CeO_2, and TiO_2 clusters.

John 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 XAFS 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, specifically the understanding of structure-function relationships on well-defined catalytic systems using in situ spectroscopies and reaction kinetics. In Thrust 1 of the BES program, my role is to lead the research on synthesis of facet-specific early transition metal oxide catalysts, and their use in the conversion of bio-derived molecules to value-added chemicals and/or energy carriers through solid-gas catalytic reactions. Our current focus is utilizing facet-specific CeO_2, TiO_2, and ZrO_2 as catalysts or catalyst supports for oxygen removal, C-C coupling, and oxidative dehydrogenation reactions.

My research team also conducts research associated with diesel engine exhaust cleaning, supported by DOE Energy Efficiency and Renewable Energy, Vehicle Technologies Office. We work on developing novel zeolite-based catalysts for use in SCR and passive NO_x adsorber processes, and on understanding fundamental catalytic chemistries involved in these processes. Our research group was the first to suggest two catalytic centers in Cu/SSZ-13, an industrial SCR catalyst, and to prove the mobile nature of catalytic active centers under reaction conditions. In 2015, our group contributed to the first comprehensive overview of small pore materials as SCR catalysts in *Chemical Society Reviews*. We also collaborate with industrial partners, including Cummins, Inc., Johnson Matthey Inc., Fiat Chrysler Automotive, and PACCAR, to provide solutions to their practical problems.

Bojana Ginovska

Catalysis Science
Physical Sciences Division
Phone: (509) 375-5979
E-mail: bojana.ginovska@pnnl.gov

My research interests focus on theoretical investigation and modeling of enzymes and biomimetic catalysts for energy applications using a variety of methodologies, including quantum mechanical calculations, classical and quantum mechanics/molecular mechanics simulations, and enhanced sampling techniques. Specifically, my work focuses on understanding the role of the outer coordination sphere on catalysis in enzymes and biomimetic transition metal-based molecular catalysts. I am exploring the effects of structural flexibility, allosteric regulation, and electrostatic changes on the thermodynamic and kinetic properties of biocatalysts, as well as accurate characterization of reaction pathways. The work extends to modeling and designing protein scaffolds with synthetic molecular catalysts for CO_2 conversion to products suitable for chemical energy storage. My research on biocatalysts focuses on fundamentally understanding the mechanism of enzymatic interconversion of small molecules and extracting design principles from enzymes that can be applied to the development of bioinspired catalysts. My research portfolio also includes the development and characterization of hydrogen storage materials and hydrogen carriers.

Vassiliki-Alexandra Glezakou

Basic and Applied Molecular Foundations
Physical Sciences Division

Co-principal Investigator

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
- Studies of CO/CO_2 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.
- Theoretical investigations of functionalized graphene membranes for reactive separations
- Solvent and confinement effects on catalytic centers
- Modeling of complex solid/liquid, liquid/liquid interfaces
- Data science approaches for catalysis and separations

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

Oliver Y. Gutiérrez

Catalysis Science
Physical Sciences Division

Co-principal Investigator

Phone: (509) 371-7649
E-mail: oliver.gutierrez@pnnl.gov

My research aims to build a bridge between molecular description of catalytic reactions and rational design of novel catalysts and catalytic processes. Thus, my work focuses on fundamental aspects of heterogeneous catalysis covering topics in industrial and emerging processes for the production of chemical energy carriers. Specifically, catalytic target reactions have included hydrodefunctionalization and hydrogenation of hydrocarbons, bio-oil conversion, and photocatalytic H_2 generation. Accordingly, I have mainly investigated bulk and supported transition metal sulfides, and supported metal nanoparticles. The properties of these materials, in stages of preparation and during/after sorption and catalysis, have been studied making use of rigorous kinetics and advanced characterization methods, e.g., in situ infrared, Raman, and X-ray absorption spectroscopy (XAS); XRD; and temperature-programmed reactions. Currently, my work centers on the phenomena at the interface between electrocatalysis and thermal catalysis for the transformation of oxygenated molecules. Another topic of my current research is the cooperative effects between metal sites and acid sites and the associated reaction mechanisms for the conversion of polar molecules to fuels. We aim at structure-activity correlations for designing new catalysts and catalytic routes with enhanced activity and selectivity.

David Heldebrant

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 the 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 reactive separations and chemical conversions, and 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, SOx, 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) and polymers. My experimental approach of these systems includes the 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 ‘captured’ CO_2 and assessing its reactivity within CO_2 capture solvents to develop more energy and cost-efficient catalytic systems for renewable energy storage or value-added products from CO_2.

Jian Zhi Hu

Catalysis Science
Physical Sciences Division
Phone: (509) 371-6544
E-mail: jianzhi.hu@pnnl.gov

I have extensive research experience in solid-state and liquid-state NMR spectroscopy and magnetic resonance imaging with more than 200 peer-reviewed publications, h-index of 41, about 5700 web of science citations, two R&D 100 awards, and 11 US Patents. I have developed or originated a range of slow and ultra-slow magic angle spinning or magic angle turning NMR techniques for enhanced spectral resolution in solids, semi-solids, and biological materials. Recently, I have developed the combined high-temperature and high-pressure magic angle spinning NMR for *in situ* studying of the reaction mechanisms associated with catalytic reaction and materials synthesis.

My current research interests and expertise include the following:

- *In situ* and *ex situ* NMR characterization of heterogeneous 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 temperature and high-pressure magic angle spinning NMR capabilities at magnetic fields ranged from 7.4 to 19.97 Tesla with sample spinning rate up to 15 kHz or more.
- Computational modeling of NMR to link the experimental NMR results to detailed molecular structures at the solid surface or solid-liquid interface and the solvation structures of the species inside the liquid.

Enrique Iglesia

Department of Chemical Engineering
University of California at Berkeley

Co-principal Investigator

Phone: (925) 323-5559
E-mail: Iglesia@berkeley.edu

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

His group addresses the synthesis and the structural and functional characterization of solids used as catalysts for production of fuels and petrochemicals, for conversion of energy carriers, and for improving the energy and atom efficiency and the sustainability of chemical processes. His work combines synthetic, spectroscopic, theoretical, and mechanistic techniques to advance novel concepts and applications in heterogeneous catalysis. He has co-authored more than 340 publications and 40 U.S. patents.

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

Abhi Karkamkar

Multiscale Synthesis
Physical Sciences Division

Co-principal Investigator

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 Kay

Chemical Physics and Analysis
Physical Sciences Division

Co-principal Investigator

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 $TiO_2(110)$ and supported oxide catalysts based on cyclic $(WO_3)_3$ and $(MoO_3)_3$ clusters. Current efforts are focused on small molecule adsorption and catalytic reactions on single metal atoms on Fe_3O_4 (001).

Gregory Kimmel

Chemical Physics and Analysis
Physical Sciences Division

Co-principal Investigator

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 surface scientists involved in the program. We use ultrahigh vacuum surface science techniques to study thermal and non-thermal reactions on model oxides surfaces such as $TiO_2(110)$. Recently, we have investigated the photooxidation of carbon monoxide, and the adsorption and reactivity of carbon dioxide on $TiO_2(110)$. We have also investigated hydrogen reactivity on highly hydroxylated $TiO_2(110)$. Currently, we are investigating the photooxidation of acetone on $TiO_2(110)$. 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

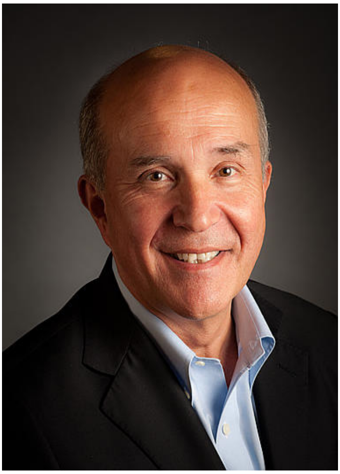
Microscopy Group
Environmental Molecular Sciences Laboratory
Phone: (509) 375-4377
E-mail: libor.kovarik@pnnl.gov

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 understating 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. 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 methods to study the bonding environment of massively reconstructed low-index surfaces of δ-Al_2O_3 and θ-Al_2O_3.

Mal-Soon Lee

Basic and Applied Molecular Foundations
Physical Sciences Division
Phone: (509) 372-4404
E-mail: malsoon.lee@pnnl.gov

My research interest is in the fundamental understanding of materials properties including structure, spectroscopy, and reactivity at elevated temperature and/or pressure. My recent research focuses on the phase behavior and reactivity at complex interfaces for porous materials in the areas of thermal and electrochemical catalysis, CO_2 sequestration, and nuclear waste disposal. To understand the properties of these heterophase materials, large-scale high-performance computing techniques, such as ab initio molecular dynamics simulations, ab initio electronic structure calculations, and enhanced sampling techniques are employed. With these simulations, materials properties such as structure, energetics—including enthalpy and entropy of reaction, spectroscopy such as infrared, XRD, neutron scattering, and XAS spectroscopy—are studied using a variety of statistical mechanical tools that can be directly compared with experimental observations. The current focus of my work is on thermochemical and/or electrochemical catalysis for biomass conversion to biofuels at solid/liquid interfaces or porous materials, in collaboration with experimental groups to provide an atomic-scale understanding of reaction properties.



Johannes Lercher

Director
Institute for Integrated Catalysis
Principal Investigator
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 multifunctional catalysts. Specifically, my team is addressing fundamental aspects of industrially relevant catalyzed reactions to understand the reaction steps on the surface of solid catalysts on an elementary level. This knowledge is used to design and synthesize nanoscopically well-defined chemically functionalized surfaces and materials. The synthesis and modification of the target materials is controlled on the level of the individual chemical reactions during the genesis of the (nanoscopic) particles and the assembly of the pre-functionalized entities. The materials explored primarily include highly structured micro- and meso-porous materials containing protons, metal ions, metal, and metal oxide clusters. Advanced characterization methods (in situ XRD, XAS, IR, Raman, and inelastic neutron scattering spectroscopy) are used to characterize these materials in stages of preparation and during/after sorption and catalysis. Catalytic target reactions are the low-temperature, acid-catalyzed activation, functionalization, and transformation of alkanes; the oxidative activation of light alkanes, including CH_4; and the hydrogenation and hydrodefunctionalization of biogenic and fossil feedstocks (such as lignin and aromatic molecules containing oxygen, nitrogen, and sulfur). The elementary steps and selective control of sorption and diffusion in molecular sieves is another significant focus of my work outside the catalysis area.

John Linehan

Catalysis Science
Physical Sciences Division

Co-principal Investigator

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 NMR, Fourier transform infrared, and XAFS structure—are used to interrogate the metal catalyst species prevalent during catalysis. Meanwhile, the substrates and products also are investigated so that catalytic rates can be correlated with the metal-containing catalytic species present in a time-dependent manner. In collaboration with my colleagues, we have developed the fastest first row transition metal catalyst for CO_2 hydrogenation to formate using thermodynamic principles and operando spectroscopy. This new catalyst efficiently operates at room temperature and at 1 atm total pressure. Both properties are unusual for any CO_2 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.

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 thermal and non-thermal processes at surfaces and interfaces, including heterogeneous thermal- and photo-catalysis, adsorption, desorption, surface and bulk diffusion, defects and reactions induced by energetic electrons, and others. I am interested in kinetics and dynamics of reactions at interfaces, involving electronic excitations, such as electrons, holes, and excitons. The goal is to understand basic mechanisms of the interfacial non-thermal processes to optimize their efficiency. I use well-characterized metallic and metal oxide substrates (e.g., Pt(111), rutile $TiO_2(110)$, anatase $TiO_2(101)$, α-$Al_2O_3(0001)$) and a wide spectrum of inorganic and organic adsorbates, from simple molecules (CO_2, CO, O_2, H_2O, etc.) to more complicated organic alcohols, ketones, acids, and hydrocarbons. An experimental approach involves basic surface science techniques and ultrahigh vacuum chambers equipped with sources of ultraviolet photons, low-energy electron guns, reflection absorption Fourier transform infrared spectroscopy, a mass spectrometer for angular- and time-resolved desorption measurements, a molecular beam doser, and other state-of-the-art capabilities. My current studies include understanding thermal and non-thermal processes effects in catalysis, the role of charged point-defects in adsorption, chemical transformation and photodesorption, the correlation of the structure of the adsorption complex with reactivity on metal oxide surfaces, and the role of surface diffusion in surface reactions.

Simone Raugei

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

My activity focuses on the development and application of computational and theoretical methodologies for the study of chemical and biochemical processes using high-performance computing. I am the principal investigator (PI) of the Basic Energy Sciences Biophysical Sciences Program at PNNL. This is a highly interdisciplinary program that focuses on uniquely characterized 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, CH_4 coenzyme M reductase, and nitrogenase using a variety of computational and experimental approaches. I am the PI for the crosscutting theory tasks in of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center (Director: R. Morris Bullock), where I am leading a theoretical effort for the design of electrocatalysts for energy storage and energy delivery. In particular, I am focusing on the theoretical characterization of novel electrocatalysts, based on inexpensive transition metals, for dihydrogen production/oxidation, dioxygen reduction, dinitrogen reduction, and ammonia oxidation.

Roger Rousseau

Basic and Applied Molecular Foundations
Physical Sciences Division

Subtask Principal Investigator

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 C_2-oxygenate synthesis from syngas and steam reforming of biomass-derived tars, thermal and electrochemical upgrading of bio-oils to fuel precursors; design of CO_2 capture solvent systems for flue-gas cleanup; and the role of anharmonicity on the free energetics of confinement in zeolites and reactivity at solid-liquid interfaces. A hallmark of our team is that we develop and test modern simulation techniques on well-defined model systems in direct comparison with concurrent experiments as represented by our activities on the core Basic Energy Sciences program. These methods are then adapted and deployed on projects relevant to the U.S. Department of Energy's technology offices where we have active programs in applied catalysis and materials.

Gregory Schenter

Chemical Physics and Analysis
Physical Sciences Division

Co-principal Investigator

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 activation in molecular complexes composed of Lewis acid-Lewis base pairs. We combine experimental and computational approaches to study how tunable environmental factors—such as electrostatic interactions, nano confinement, and pressure—enhance the kinetics and modify the thermodynamics of hydrogen release and uptake in condensed phases. 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

Director
Physical Sciences Division

Co-principal Investigator

Phone: (509) 375-5922
E-mail: wendy.shaw@pnnl.gov

My research focuses on learning from enzymes to develop a mechanistic understanding of the outer coordination sphere of molecular catalysts. 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 the environment around the active site
- Role of the positive charge on the transition state
- Physical-chemical characteristics of the active site pocket

We have evaluated the impact of an amino acid outer coordination sphere on CO_2 hydrogenation catalysts. We found that a pendant amine improved catalytic activity, while the impact of the functional groups in the outer coordination sphere depended upon the rate-limiting step of the catalyst. There was a clear effect of the outer coordination sphere based on the different relative reactivity of three analogous complexes with only first coordination spheres modified. We are currently trying to provide in-depth mechanistic insight using computational methods. We are also moving our studies to a structured outer coordination sphere. By covalently attaching our complexes into a structured protein scaffold, we can induce catalytic activity and are now mutating residues to increase the positive charge near the metal to establish whether the positive charge helps to stabilize the transition state. Both computational and experimental studies suggest that it is. Further studies will focus on mechanistically understanding if it is the specific location of the charge or the overall charge being felt at the metal atom that increases activity.

János Szanyi

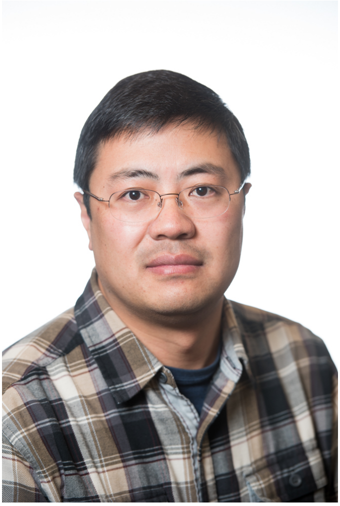
Catalysis Science
Physical Sciences Division

Subtask Principal Investigator

Phone: (509) 371-6524
E-mail: janos.szanyi@pnnl.gov

My research is aimed at understanding the structure-reactivity relationships of heterogeneous catalytic reaction systems by combining spectroscopy and kinetic studies.

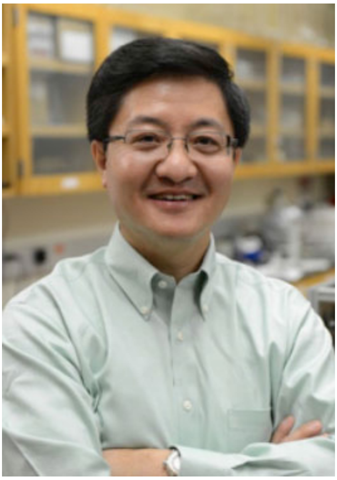
Currently, we are conducting detailed kinetics and operando spectroscopy measurements on model high surface area supported metal catalysts using flow reactors and steady-state isotopic transient kinetic analysis/Fourier transform infrared/mass spectrometry techniques. These studies provide detailed kinetic information together with surface speciation that allow us to greatly enhance our mechanistic understanding of heterogeneous catalytic systems, in particular, the activation of C=O double bonds (e.g., reduction of CO_2). Our current focus is to understand the mechanism of H_2 activation at the metal/support interface during the reverse water gas shift reaction as the metal dispersion increases (i.e., from nano-sized metal particles to single metal atoms). I am also involved in research related to the fundamental understanding of automotive emission control catalysis. In this area 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 hydrocarbon storage in zeolites.



Huamin Wang

Applied Catalysis
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 the fundamental understanding of catalytic reactions involved in these processes by experimental approaches. My recent work at PNNL has two focuses: (1) applied research for developing efficient and cost-effective catalysts and catalytic processes for biomass conversion to renewable fuels and chemicals. Specifically, I am working on hydrotreating of intermediates produced by thermochemical processing of biomass into fuels, catalytic fast pyrolysis of biomass, and catalyst deactivation mitigation for biomass conversion. 2) fundamental research for understanding atomic-level structure/function relationships of transition metal oxide and zeolitic catalysts used in various oxygenates conversion reactions in gas and condensed phases.



Yong Wang

Hydrocarbon Processing
Energy Processes & Materials Division

Co-principal Investigator

Phone: (509) 371-6273
E-mail: yong.wang@pnnl.gov

Yong Wang is Voiland Distinguished Professor in Chemical Engineering at Washington State University and a Laboratory Fellow at Pacific Northwest National Laboratory. His group's research is focused on the fundamental understanding of novel catalytic materials and reaction engineering to address the issues related to energy and atom efficiency related to the conversion of fossil fuels and biomass feedstocks to fuels and chemicals. Wang has authored >300 peer reviewed publications (H index=70 and 22,300 citations). He has co-edited 2 books and 5 special journal issues, and has given more than 200 invited presentations. He is the inventor on 286 issued patents including 108 issued U.S. patents (>90% of his patents are licensed to industries). He is elected to National Academy of Inventors and Washington State Academy of Sciences. He is a fellow of AIChE, ACS, Royal Society of Chemistry (RSC), and American Association of the Advancement of Science (AAAS). He has won numerous awards including 2019 AIChE Catalysis and Reaction Engineering Practice Award, 2017 ACS I&EC Division Fellow Award, 2006 Asian American Engineer of the Year Award, Presidential Green Chemistry Award, 3 R&D 100 Awards, Distinguished Alumni Achievement Award from WSU's Voiland School of Chemical Engineering and Bioengineering, 2 PNNL Inventor of the Year Awards, Battelle Distinguished Inventor Award, and PNNL Laboratory Director's Award for Exceptional Scientific Achievement Award. He is the past chair of the Energy & Fuel Division of the American Chemical Society, and currently serves the ACS National Award Committee and editorial board of 8 catalysis and energy related journals including ACS Catalysis and Catalysis Today.

Eric Wiedner

Catalysis Science
Physical Sciences Division
Center for Molecular Electrocatalysis

Co-principal Investigator

Phone: (509) 372-4368
E-mail: eric.wiedner@pnnl.gov

My research interests focus on the rational design of new molecular catalysts for the interconversion of electrical energy and chemical fuels. By understanding the factors that limit catalysis, whether kinetic or thermodynamic in nature, we can rationally 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 the hydrogenation of carbon dioxide and esters as part of the research thrust entitled Enhancing H_2 Addition by Designing the Metal Center and Its Environment task, and on the design of molecular electrocatalysts for dinitrogen reduction and ammonia oxidation as part of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center.

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

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