New England Catalysis Society
Spring Meeting 2016
Brown University

Meeting Location

85 Waterman Street, Providence, RI.
(Building named “BERT”: Building for Environmental Research and Teaching)
Other info, such as parking, available at brown.edu/go/necs2016

Agenda

08:30 Coffee & pastries, nametag pickup

09:00 Welcome / introduction

09:05 Maria Milina, Massachusetts Institute of Technology
"Self-Assembly of Noble Metal Monolayers on Transition Metal Carbide Nanoparticle Catalysts"
09:22 Cédric BARROO, Harvard University
"Reaction-induced nanoporosity of a bulk catalyst: an extreme case of surface reconstruction"
09:39 Dequan Xiao, University of New Haven
"Drive the discovery of green catalysts for biomass conversion using inverse molecular design approaches"
09:56 Yogesh Surendranath, Massachusetts Institute of Technology
"Designer Interfaces for Energy Catalysis"
10:13 Alex Maag, Worcester Polytechnic Institute
"Liquid-Phase Stability of ZSM-5: Role of De-Alumination and De-Silication"

10:30 Break / dues payment

10:50 Jin-Hao Jhang, Yale University
"Model studies on rare earth oxide thin films beyond ceria"
11:07 Greg Hutchings, Yale University
"Nanoporous Cu-Al-Co alloys for selective furfural hydrodeoxygenation to 2-methylfuran"
11:24 Sanjubala Sahoo, University of Connecticut
"Ethane activation by second row transition metal carbides"
11:41 Christoph Rose-Petruck, Brown University
"High-efficiency CO2 up-conversion with clathrate hydrate electrolytes"

11:58 Lunch break / poster preview

13:10 Vivek Vattipalli, University of Massachusetts Amherst
"Experimental studies on molecular transport in hierarchical porous materials"
13:27 Franklin Goldsmith, Brown University
"Computer-automated generation of microkinetic mechanisms"
13:44 Pratap Rao, Worcester Polytechnic Institute
"High Light Absorption and Charge Separation Efficiency at Low Applied Voltage from Sb doped SnO2/BiVO4 Core/Shell Nanorod-Array Photoanodes"
14:01 Junjun Shan, Tufts University
"Selective dehydrogenation of ethanol to acetaldehyde and hydrogen on a highly diluted NiCu alloy"
14:18 Matthew Montemore, Harvard University
"Oxygen dissociation for selective oxidation on gold: Effect of alloying and geometrical structure"
14:35 Kevin Lee, University of Connecticut
"Adsorption Application for Desulfurization of Transportation Fuels Using Bifunctional Zeolites"

14:52 Posters / wine & cheese reception

16:00 Keynote
Graeme Henkelman, University of Texas at Austin
"Computational methods for simulating long time scales and for catalyst design"

17:00 Wrap-up / elections

Keynote Abstract

Presenter: Graeme Henkelman, University of Texas at Austin

Title: **Computational methods for simulating long time scales and for catalyst design**

Abstract: A computational method will be presented for simulating the dynamics of atomic systems on time scales much longer than can be accessed with classical molecular dynamics. In this adaptive kinetic Monte Carlo approach, possible reaction mechanisms available to the system are found by exploring the potential energy surface from minima to find nearby saddle points. Reaction rates are then calculated using harmonic transition state theory, and the system is propagated stochastically in time. Our algorithm is sufficiently efficient to model the evolution of systems at the density functional level of theory. I will show a few examples, including surface diffusion and chemical reactions at surfaces. Using the calculated reaction pathways for a catalyst we can then start to design new catalysts computationally. Specifically, I will show recent results from a collaborative effort with an experimental group to design, synthesize and test new nanoparticle catalysts for the oxygen reduction reaction.

Presentation Abstracts

Presenter: Maria Milina, Massachusetts Institute of Technology

Title: **Self-Assembly of Noble Metal Monolayers on Transition Metal Carbide Nanoparticle Catalysts**

Authors: Sean T. Hunt, Maria Milina, Ana C. Alba-Rubio, Christopher H. Hendon, James A. Dumesic, Yuriy Román-Leshkov

Abstract: Noble metal (NM) catalysts critically enable many existing and emerging technologies, such as catalytic converters, reforming, and fuel cells. However, their scarcity and high cost necessitate the development of catalytic systems with significantly reduced NM loadings, increased activity, and improved durability. Here, we present a high-temperature self-assembly method to synthesize transition metal carbide nanoparticles coated with atomically-thin noble metal monolayers by carburizing mixtures of noble metal salts and transition metal oxides encapsulated in removable silica templates. This approach allows for precise control of the final core-shell architecture, including particle size, monolayer coverage, and heterometallic composition. The resulting core-shell nanostructures achieve superior catalytic activity, improved stability, and reduced NM loadings compared to state-of-the-art commercial catalysts for a number of electrochemical applications. They are also sinter-resistant, and the core-shell structure remains stable at high temperatures under various atmospheres.

Presenter: Cédric BARROO, Harvard University

Title: **Reaction-induced nanoporosity of a bulk catalyst: an extreme case of surface reconstruction**

Authors: Cédric Barroo, Nare Janvelyan, Branko Zugic, Matthew Montemore, Andrew P. Magyar, Austin J. Akey, Efthimios Kaxiras, Juergen Biener, Cynthia M. Friend, David C. Bell

Abstract: In order to improve the understanding of catalytic processes, information about the surface structure and composition of the active materials needs to be determined before and after activation and reaction. Morphological changes may occur under reaction conditions and can dramatically influence the reactivity and/or selectivity of a catalyst. Gold-based catalysts with specific architectures are currently being developed for selective oxidation reactions at low temperatures. As an example, nanoporous Au (npAu) with a composition of Au97-Ag3 are obtained by dealloying Ag70-Au30 bulk alloys. Recent studies highlight the efficiency of npAu catalysts for methanol oxidation. These studies used ozone to activate the catalysts before methanol oxidation.In this study, a bulk Ag70-Au30 catalyst is exposed to the same treatments as the npAu sample to follow morphological and compositional changes during the different steps of the catalytic process. The use of bulk samples allows probing long-range diffusion phenomena that lead to long-range changes that are difficult to observe in nanometer-sized ligaments. For this, we used FIB-SEM cross-section, XPS and EDX analysis. We found that ozone treatment of a Au-Ag catalyst induces segregation of silver as a distinct layer above the bulk sample. This segregation is accompanied by the formation of porosity at the upper part of the bulk sample. After being exposed to the reaction mixture of methanol and oxygen, this layer develops into a full three-dimensional porous network. These results are compared with the generally accepted mechanism for porosity formation in Ag-Au alloys. This study highlights the importance of ozone treatment to activate the catalyst as well as the mobility of the surface atoms under reaction conditions, which can dramatically influence the local chemistry and morphology of a catalyst.

Presenter: Dequan Xiao, University of New Haven/Chemistry

Title: **Drive the discovery of green catalysts for biomass conversion using inverse molecular design approaches**

Authors: Dequan Xiao

Abstract: Owing to the development in modern theoretical and computational chemistry (e.g., density functional theory), predicting molecular properties using accurate and efficient quantum chemistry methods becomes more and more practical. Recently, inverse molecular design approaches based on quantum chemistry have emerged as an attractive computational approach to take on the challenges in materials discovery. First, we explored the theoretical limits of reaction conditions for the hydrogenation and hydrogenolysis of biomass model compounds, using quantum chemistry calculations based on density function theory. Our results showed that thermodynamically it is indeed possible to design green hydrogenation catalysts that can work at the mildest conditions for converting biomass molecules into value-added chemicals. The thermodynamic study also helped us to understand the selectivity of an existing Cu-doped hydrotalciate catalyst in experiments. Second, we developed a new inverse molecular design method based on tight-binding electronic structure theory to search for novel hydrogenation catalysts. In this presentation, I will introduce the history of inverse molecular design method developed in my laboratory, based on the tight-binding electronic structure theory and the scheme of linear-combination-of-atomic-potential (called TB-LCAP). Our approach of inverse molecular design aims at searching for optimum points on the hypersurfaces defining the property-structure relationships, and then mapping out the molecular structures at the optimum points, leading to enhanced efficiency and success rate for materials discovery. We have applied the TB-LCAP inverse design method to successfully design nonlinear optical materials and dye-sensitized solar cells. Our results indicate that the inverse molecular design approach can be a useful tool to search for promising green heterogeneous catalysts for converting lignocellulosic biomass into value-added chemicals such as liquid fuels.

Presenter: Yogesh Surendranath, MIT

Title: **Designer Interfaces for Energy Catalysis**

Authors: Yogesh Surendranath

Abstract: The widespread utilization of renewable energy will require energy dense and cost-effective methods for storage. This challenge could be met by coupling renewable electricity to the reduction of carbon dioxide and/or protons to fuels and the oxidation of water to O2, providing, in net, a viable scheme for artificial photosynthesis. Likewise, the resulting fuels could be recombined in a fuel cell to comprise a net carbon-neutral cycle for energy storage and recovery. Realizing these goals requires the development of new electrocatalysts with enhanced selectivity, efficiency, and durability. We have developed bottom-up approaches to the design and discovery of new electrocatalysts that emphasizes controlling structure at the molecular, nano, and meso scales. The approach has led to the discovery of earth-abundant catalysts for oxygen reduction to water and the elucidation of new design principles for the efficient reduction of carbon dioxide to fuels. Our latest findings in these areas will be discussed.

Presenter: Alex Maag, Worcester Polytechnic Institute

Title: **Liquid-Phase Stability of ZSM-5: Role of De-Alumination and De-Silication**

Authors: Alex Maag

Abstract: Zeolites are microporous aluminosilicate structures commonly used for catalysis in environmental, fuel upgrading and biomass industries. Recent advances to improve process intensity and energy efficiency motivate interest in zeolite catalysis in the presence of liquid water or water-rich liquid reaction mixtures. However, many zeolites are prone to framework degradation under aqueous phase conditions. We focus our attention on ZSM-5, a commonly used zeolite for hydrothermal catalytic cracking of fatty acids and model fuels that has proven to be more robust than other zeolites such as HY and Beta. Literature studies to date have found ZSM-5 to be stable for at least 6 hours at 200°C; however many chemical reactions of interest require temperatures >250°C. In our study, we have found that ZSM-5 breaks down in the liquid phase at temperatures greater than 250 °C, allowing us to investigate the degradation mechanism and determine methods for stabilizing ZSM-5. We exposed ZSM-5 with a silica/alumina ratio of 38:1 to liquid water for three hours at temperatures ranging from 200°C to 450°C. Post-run, the catalyst was characterized with a battery of complementary techniques including XRD, IR, TEM, XPS and 27Al MQMS NMR. ZSM-5 degradation occurs due to a combination of acid site loss at intermediate temperatures followed by surface degradation at higher temperatures. Specifically, we observed improvements in the ZSM-5 backbone stability at temperatures greater than water's critical point as the familiar properties of liquid water (i.e., high dielectric and auto-ionization) shift dramatically near the critical point. Therefore, we recommend that studying ZSM-5 hydrothermal stability both above and below water's critical temperature might provide deep insight into the role of water in ZSM-5 degradation.

Presenter: Jin-Hao Jhang, Yale University

Title: **Model studies on rare earth oxide thin films beyond ceria**

Authors: Jin-Hao Jhang, Andreas Schaefer, Volkmar Zielasck, Jason F. Weaver, Marcus Baeumer

Abstract: Rare earth oxides (REOs) have shown considerable capacities for performing certain catalytic reactions. However, only ceria (CeOx) has systematically studied regarding the surface chemistry and the factors for catalytic behavior. The fundamental understanding with respect to the connections between the surface chemistry and catalytic properties of other REOs is still in a very limited scope. Here, we present the major work on the surface science studies of samaria (SmOx) conducted in ultra-high vacuum and briefly introduce the recent studies on praseodymia (PrOx), PrOx-CeOx mixed oxides, and terbia (TbOx) conducted with analytic techniques in ultra-high vacuum systems.

Presenter: Greg Hutchings, Yale University

Title: **Nanoporous Cu-Al-Co alloys for selective furfural hydrodeoxygenation to 2-methylfuran**

Authors: Gregory Hutchings and Feng Jiao (University of Delaware)

Abstract: Furfural (C5H4O2) is a biomass-derived platform chemical which may be upgraded to multiple heterocyclic and ring-opening products, through initial decarbonylation to furan, hydrogenation to furfuryl alcohol, or hydrodeoxygenation (HDO) to 2-methylfuran (2-MF, C5H6O). To date there have been few catalysts which enable selective HDO to 2-MF. In this work, we present a self-supported nanoporous Cu-Al-Co trimetallic alloy catalyst with exceptionally high vapor-phase furfural HDO activity towards 2-MF, achieving up to 66.0% selectivity and 85.0% overall conversion at 513K with a ~5 atomic % Co composition. Temperature and catalyst composition dependence studies were performed to examine optimal conditions and tune catalyst performance, and in operando X-ray absorption spectroscopy (XAS) experiments were conducted to elucidate the structure and stability of the catalyst in the reaction environment. Based on the experimental data, a mechanistic explanation for how this inexpensive, non-precious metal catalyst achieves high 2-MF selectivity is proposed.

Presenter: Sanjubala Sahoo, University of Connecticut, Storrs, CT, 06269

Title: **Ethane activation by second row transition metal carbides**

Authors: Sanjubala Sahoo, Arthur Reber, S. Suib , and S. N. Khanna

Abstract: First-principles studies are performed for C–C bond activation of ethane by 4d transition metal (TM) atoms and TMC (transition metal carbide) molecules. It is found that addition of carbon to TM atoms lead to large variations in the activation barrier depending on the TM species. For MoC, the activation energy reduces significantly. Molecular orbitals analysis shows that the changes in reactivity is mainly governed by the location and filling of 5s and 4d orbitals of TM. The two orbitals control different aspects of reactivity. The s-orbital controls the initial binding of ethane, with a strong anti-correlation between the ethane binding and the s-orbital occupation, while the 4dz 2 orbital controls the activation barrier and hence the reactivity for C-C activation. The work has been published in reference [1]. Reference: [1] S. Sahoo et al., J. Chem. Phys. A 119, 12855 (2015)

Presenter: Christoph Rose-Petruck, Brown University

Title: **High-efficiency CO2 up-conversion with clathrate hydrate electrolytes**

Authors: D. DeCiccio, S. T. Ahn, S. Sen, F. Schunk, G.T.R. Palmore, C. Rose-Petruck

Abstract: We report on the use of clathrate hydrates in water as electrolyte fluid in the electrochemical reduction of carbon dioxide. The Electrolyte has the appearance of snow slush. Fluids containing 10%mass THF with and without CO2 containing clathrate hydrates were investigated with a copper-foam working electrode. Our results show that at -0.44 V vs RHE the Faradaic efficiency for the production of CO and further reduced carbonaceous products is 80% with clathrates vs 20% with non-clathrate electrolytes of identical chemical composition at nearly equal temperature. The clathrates nearly completely suppress the hydrogen evolution reaction.

Presenter: Vivek Vattipalli, University of Massachusetts Amherst

Title: **Experimental studies on molecular transport in hierarchical porous materials**

Authors: Vivek Vattipalli, Xiaoduo Qi, Peter Monson, David Ford, Wei Fan

Abstract: Hierarchical porous materials are an emerging class of porous materials with both microporous (< 2 nm) and mesoporous (2 – 50 nm) structures, and are a subject of active investigation for a number of prospective applications such as catalysis, gas separations, sensors and drug delivery [1]. While these applications are based on the high adsorption capacities and fast molecular transport properties of such materials, the nature of molecular transport in them has been elusive for decades due to the complexity involved – the presence of multiple sizes of pores leads to the simultaneous occurrence of different diffusion phenomena such as configurational diffusion, surface diffusion and Knudsen diffusion. The evidence on the existence of structural “surface barriers” which hamper molecular transport also adds to the complexity in understanding the process [2-4]. Rational development of these materials for desired applications requires a good fundamental understanding of molecular transport in such materials.In this study, mesoporous SBA-15 silica samples and hierarchical zeolites of varying microporosity and mesoporosity were synthesized and the diffusion of different probe molecules in them was studied using the Zero Length Column (ZLC) technique. Our results demonstrate that the dominant molecular transport mechanism in MCM-41 is surface diffusion while that for SBA-15 and hierarchical zeolite is configurational diffusion, mainly because of the presence of microporous structures in the hierarchical zeolite as well as in SBA-15. For the diffusion of the larger probe molecule (1-methylnaphthalene) in SBA-15, two temperature-dependent regimes, limited by surface diffusion and configurational diffusion respectively, were observed. In the case of cyclohexane diffusion in SBA-15, our results indicate that the effective diffusion length in these materials might be much longer than what was previously thought and that the effective diffusivities of cyclohexane are determined by the extent of microporosity of the adsorbent. References1.Davis, M. E., Ordered porous materials for emerging applications. Nature 2002, 417, 813-821.2.Ford, D. M.; Glandt, E. D., Steric hindrance at the entrances to small pores. Journal of Membrane Science 1995, 107, (1-2), 47--57.3.Teixeira, A. R.; Chang, C.-C.; Coogan, T.; Kendall, R.; Fan, W.; Dauenhauer, P. J., Dominance of Surface Barriers in Molecular Transport through Silicalite - 1. 2013.4.Teixeira, A. R.; Qi, X.; Conner Jr, W. C.; Fan, W.; Dauenhauer, P. J., Mechanistic Insights into Rate-Dominant Transport Barriers in MFI Structured Zeolites. In AIChE Annual Meeting, 2014.

Presenter: Franklin Goldsmith, Brown University

Title: **Computer-automated generation of microkinetic mechanisms**

Authors: Franklin Goldsmith, Richard West

Abstract: I will present recent work to develop software, RMG-Cat, that will automatically generate a microkinetic mechanism. The software is based upon similar software for gas-phase kinetics. The talk will discuss some of the challenges in porting the code from 3D (homogeneous) to 2D (heterogeneous) mechanism development. Preliminary results for CH_4 on Ni will be presented.

Presenter: Pratap Rao, Worcester Polytechnic Institute

Title: **High Light Absorption and Charge Separation Efficiency at Low Applied Voltage from Sb doped SnO_2/$BiVO_4$ Core/Shell Nanorod-Array Photoanodes**

Authors: Lite Zhou, Chenqi Zhao, Binod Giri, Patrick Allen, Xiaowei Xu, Hrushikesh Joshi, Lyubov V. Titova and Pratap M. Rao

Abstract: $BiVO_4$ has become the top-performing semiconductor among photoanodes for photoelectrochemical water oxidation. However, $BiVO_4$ photoanodes are still limited to a fraction of the theoretically-possible photocurrent at low applied voltages because of modest charge transport properties and a trade-off between light absorption and charge separation efficiencies. Here, we investigate photoanodes composed of thin layers of $BiVO_4$ coated onto Sb doped SnO_2 (Sb:SnO_2) nanorod-arrays and demonstrate a high value for the product of light absorption and charge separation efficiencies ($\eta abs \times \eta sep$) of ~ 52% at an applied voltage of 0.6 V versus the reversible hydrogen electrode, as determined by integration of the quantum efficiency over the standard AM 1.5G spectrum. To the best of our knowledge, this is the highest efficiency achieved to date at this voltage for nanowire-core/$BiVO_4$-shell photoanodes. Moreover, although WO_3 has recently been extensively studied as a core nanowire material for core/shell $BiVO_4$ photoanodes, the Sb:SnO_2/$BiVO_4$ nanorod arrays generate larger photocurrents, especially at low applied voltages. In addition, we present control experiments on planar Sb:SnO_2/$BiVO_4$ and WO_3/$BiVO_4$ heterojunctions, which indicate that Sb:SnO_2 is more favorable as a core material. These results indicate that integration of Sb:SnO_2 nanorod cores with other successful strategies such as doping and coating with oxygen evolution catalysts, can move the performance of $BiVO_4$ and related semiconductors closer to their theoretical potential.

Presenter: Junjun Shan, Tufts University

Title: **Selective dehydrogenation of ethanol to acetaldehyde and hydrogen on a highly diluted NiCu alloy**

Authors: Junjun Shan, Nare Janvelyan, Hang Li, Jilei Liu, Tobias M. Egle, Jianchao Ye, Monika M. Biener, Juergen Biener, Cynthia M. Friend, and Maria Flytzani-Stephanopoulos

Abstract: The development of catalysts with a high dispersion of an active site for the production of targeted products selectively is a timely subject. Various highly diluted alloys or single atom catalysts have been reported to be highly active for a variety of catalytic reactions. For example atomically dispersed Au species supported on ZnZrOx oxides can catalyze the dry ethanol dehydrogenation reaction.[1] PtCu single atom alloy catalysts exhibit high activity for several selective hydrogenation and dehydrogenation reactions.[2,3] Moreover, nanoporous Au materials modified with highly dispersed Ag species exhibit unique catalytic performance in the oxidative coupling of alcohols to esters.[4]Here we report on the selective dehydrogenation of ethanol to acetaldehyde and hydrogen, an important industrial reaction to produce acetaldehyde which is an important commodity chemical, and also valuable hydrogen, using the single atom alloy strategy. Ni-containing Cu nanoparticles (NiCu NPs) and nanoporous Cu (np-NiCu) materials were found very active and selective for this reaction. Although monometallic Cu catalysts are also active, deactivation of Cu was observed. Adding a small amount of Ni to Cu forming NiCu highly diluted alloys dramatically increases the catalytic activity of copper. The kinetic studies show the apparent activation energy decreases from ~70 kJ/mol for Cu to ~45 kJ/mol for NiCu highly diluted alloys. Furthermore adding a small amount of Ni to Cu also significantly improves the stability of these catalysts, likely due to the stabilization of Cu against sintering. Our characterization data show that Ni is highly dispersed or even atomically dispersed on the Cu surface. Such highly dispersed Ni or isolated Ni atoms play a key role in the dehydrogenation of ethanol. This work opens a new route for the use of highly diluted alloys for alcohol dehydrogenation reactions. Furthermore the comparison of the catalytic performance of highly diluted alloy NPs with nanoporous materials is used to guide the design of the novel mesoporous catalyst architectures for selective dehydrogenation or oxidation reactions. References1. C. Wang, G. Garbarino, L. F. Allard, F. Wilson, G. Busca, M. Flytzani-Stephanopoulos, ACS Catal., 2016, 6, 210–218.2. F. Lucci, J. Liu, M. Marcinkowski, M. Yang, M. Flytzani-Stephanopoulos, C. E. H. Sykes, Nat. Commun. 6, 8550 (2015).3. J. Shan, F. R. Lucci, J. Liu, M. El-Soda, M. D. Marcinkowski, L. F. Allard, C. E. H. Sykes, M. Flytzani-Stephanopoulos, Surface Science (2016), DOE: 10.1016/j.susc.2016.02.010.4. Branko Zugic, Stavros Karakalos, Kara J. Stowers, Monika M. Biener, Juergen Biener, Robert J. Madix, and Cynthia M. Friend, ACS Catal., 2016, 6, 1833–1839.

Presenter: Matthew Montemore, Harvard University

Title: **Oxygen dissociation for selective oxidation on gold: Effect of alloying and geometrical structure**

Authors: Matthew M Montemore, Cynthia M Friend, Robert J Madix, Efthimios Kaxiras

Abstract: Au is capable of selectively and efficiently catalyzing oxidation reactions, such as methanol coupling to methyl formate. However, many of these reactions require atomic oxygen to be adsorbed on the surface in order to proceed, which is a challenge since Au cannot normally dissociate O2. Here, we use density functional theory and thermodynamic modeling to examine two routes for dissociating O2 while maintaining high catalytic selectivity. First, we examine AgAu alloys, motivated by the excellent catalytic performance of nanoporous Au, which is a nanostructured material with a small amount (~2%) of Ag. Using atomistic thermodynamics, we find that, under oxidation reaction conditions, the surfaces of dilute AgAu alloys have Au terraces and AgAu bimetallic steps. These bimetallic steps are likely responsible for O2 dissociation, and the calculated barrier on the AgAu(211) structure that we find in the thermodynamic calculations has a low activation barrier for O2 dissociation that is in agreement with experiment.We also show that the reconstruction of Au surfaces that occurs spontaneously plays an important role in preventing O2 dissociation. For example, the barrier for O2 dissociation on an unreconstructed Au(100) surface is lower than Ag(111) and Ag(110), both of which dissociate O2 easily. Therefore, by preventing surface reconstruction, Au surfaces that can dissociate O2 can be created. This may play a role in the activity of small Au nanoparticles.

Presenter: Kevin Lee, University of Connecticut

Title: **Adsorption Application for Desulfurization of Transportation Fuels Using Bifunctional Zeolites**

Authors: Kevin x. Lee, Julia A. Valla

Abstract: Adsorptive desulfurization of transportation fuels is receiving significant attention as it has shown to be highly advantageous over conventional hydrodesulfurization process. Y zeolites have shown to be promising sorbent material for their large surface area and unique pore structure. However, the natural state of these zeolites can impose diffusion limitations and low sulfur selectivity especially when diesel-based refractory sulfur compounds are present. In order to overcome these challenges, mesoporosity has been introduced to allow easy access for sulfur compounds with large kinetic diameter to adsorption sites. Two top-down methods were used to create mesopores in the parent Y: 1) desilication (DS) and 2) surfactant-assisted method (SA). To enhance selectivity for the aforementioned compounds, active metals such as Ce and Cu have been incorporated in the parent Y via the ion-exchange method. These metals provide additional adsorption sites by forming two new complexes with sulfur compounds. CuY can undergo π-complexation while CeY can form strong σ-bond with the sulfur rings. The objective of this study is to understand the role of mesoporosity and active metals in Y zeolites on the adsorption of thiophenic compounds from liquid fuels.The capacity and selectivity of the prepared zeolites were tested in a dynamic fixed-bed adsorption column. 100 ppmw S of each sulfur compound (thiophene (TP), benzothiophene (BT) and dibenzothiophene (DBT) in n-octane) was used as sulfur feed. Effluents were collected periodically, analyzed and plotted to generate breakthrough curves. Results indicated that CuSAY exhibits the highest capacity for DBT by producing 125 mL/g of sulfur-free fuel. This is a result of highly accessible pores and strong sulfur-metal interaction provided by the bifunctional zeolites. For the desulfurization of model fuel containing TP, BT and DBT, CeSAY was the best sorbent due to high selectivity features for refractory sulfur compounds. Theoretical studies confirmed the strong adsorption energy between metal-exchanged zeolites and sulfur compounds.Finding the optimum balance between the pore structure and metals in a bifunctional zeolite is essential for adsorptive desulfurization of hydrocarbon fuels. By combining the two aforementioned functionalities, bifunctional zeolites can offer energy- and cost-efficient and highly effective desulfurization processes.

Poster Abstracts

Presenter: Satish Kumar Iyemperumal, Worcester Polytechnic Institute

Title: **Comparison of Solvent Models for Metal Surface Chemistry using Density Functional Theory**

Authors: Satish Kumar Iyemperumal and N. Aaron Deskins

Abstract: Aqueous phase reactions play a crucial role in applications like heterogeneous catalysis, electrochemistry, and biomass reforming. The presence of solvents such as water can have profound effects in altering the reaction rate, pathway, and selectivity of products. Using experimental techniques, studying reactions over catalyst surfaces in an aqueous environment is very challenging. Hence, Density Functional Theory is often used to model such interfaces to provide useful insights. However, across literature, the use of different solvent models has lead to inconsistent conclusions. In our present work, we systematically compare three different solvent models: implicit (solvent described by a background continuum), explicit (solvent molecules modeled at DFT level), and hybrid (a combination of explicit and implicit). We considered structures with various number of water molecules (single water molecules to multiple layers). Using these solvent models, we determine the effect of solvent on the adsorption of several species and several model reactions like oxygen reduction (ORR) on Pt(111). The factors affecting the implicit or explicit solvation effects are identified. We find that an explicit solvation model consisting of at least 3 ice-bilayers are required for stable determination of solvation energy. The explicit solvation effect is largely dominated by the number of hydrogen bonds between the adsorbate and the surrounding explicit water. The implicit solvation predicts a solvation effect that is comparable to that of explicit solvation only when there are no hydrogen bonds between adsorbate and explicit water. However, the thermodynamics of the oxygen reduction reaction predicted using implicit solvation is close to that obtained by explicit or hybrid solvation. The effect of hybrid solvation is small in general. However, it helps in converged solvation effects with increase in solvation shell thickness. Our work provides valuable insights in order to choose a suitable solvation model that can be used in modeling reactions at metal-water interface in a consistent manner.

Presenter: Sourav Biswas, University of Connecticut

Title: **Cooperative catalysis of Cu and Mn in alkyne coupling**

Authors: Sourav Biswas, Angelo R. Rossi and Steven L. Suib

Abstract: Synergistic–cooperative catalysis involving two metals is an exciting phenomenon in those organic transformations which cannot be accomplished by individual metal catalyst. Joint participation of dual metals having distinctive properties is often required for acquiring high activity. The biggest challenge in this field is to exploit the relative compatibility of the two metals in the same reaction medium. Herein, we introduce Cu incorporated mesoporous manganese oxide (meso Cu/MnOx) as an effecient catalyst in aerobic oxidative self and cross coupling of terminal alkynes to produce 1,3-diyne derivatives. Use of air as the sole oxidant, avoidance of any kind of additives, ease of product separation, great functional group tolerability, wide synthetic scope, and superior reusability (up to 8th cycle) are the notable features of our catalytic protocol. While elucidating the reaction mechanism, a synergistic cooperative effect between the copper and manganese has been established, which is responsible for superior catalytic activity. The labile lattice oxygen of the meso Cu/MnOx played a vital role in deprotonation of the alkyne proton as supported from the TPD and TGA studies. Moreover, for the first time, we designed model complexes for the active sites of the catalyst by DFT calculations and provided a qualitative description of the coupling mechanism, which supports the experimental findings.

Presenter: Lida Namin, Worcester Polytechnic Institute

Title: **Modeling alloys for ethanol oxidation in fuel cell applications**

Authors: Lida M. Namin and N. Aaron Deskins

Abstract: Our goal for this project is to develop realistic atomic models of alloys for use in the ethanol oxidation reaction (EOR) in direct ethanol fuel cells (DEFCs). DEFCs can be an efficient way of energy production if they utilize effective catalysts. The conventional catalyst for fuel cells, platinum is highly expensive and is not effective in breaking carbon-carbon bond in DEFCs. Platinum-based DEFCs also suffer from CO-poisoning. To resolve these problems, alloying platinum with other transition metals has been widely investigated in the literature due to the fact that alloying a catalyst with other transition metals has shown to increase the catalytic activity. Synthesizing all possible alloys experimentally is a burdensome task which is not economically feasible. As a result, our research focuses on modeling different alloys by means of density functional theory (DFT) which is a computational chemistry method and solves the equations that describe the electrons and nuclei of many-body systems such as atoms and molecules. In the first part of this project, we modeled innovative platinum-based alloys and compared their activities with pure platinum. An alternative way to resolve the problems associated with Pt-based catalysts is to substitute platinum with other transition metals such as iridium. As a result, in the second part of this project, the application of iridium and iridium-based alloys as catalysts in DEFCs has been investigated. Finally the platinum-based alloys and iridium-based alloys have been compared. Our results show that these alloys are really effective in the EOR.

Presenter: Dan Liu, Brown University

Title: **Electrochemical Reduction of CO2 on Cu Foam**

Authors: Dan Liu, Tayhas Palmore

Abstract: We report the electrochemical reduction of CO2 at copper foams with hierarchical porosity. We show that both the distribution of products formed from this reaction and their faradaic efficiencies differ significantly from those obtained at smooth electropolished copper electrodes.

Presenter: Hongbo Shi, University of Massachusetts Amherst

Title: **Structure–Function Relationships for Graphene-Supported Pt Nanoclusters**

Authors: Hongbo Shi, Scott M. Auerbach, and Ashwin Ramasubramaniam

Abstract: Platinum-based catalysts play an important role in energy conversion technologies, particularly, in hydrogen-based or methanol-based proton exchange membrane fuel cells (PAFC). Graphene-supported Pt nanoclusters were recently found to be promising catalysts due to their enhanced catalytic activity and tolerance to CO poisoning, as well as their long-term stability toward sintering. However, structure–function relationships that govern the improved electrocatalytic activity in these materials are still not well understood. . Here, we employ a combination of empirical potential simulations and density functional theory (DFT) calculations to investigate the structure–function relationships of small Ptn (n=2-80) clusters on model carbon (graphene) supports.. A Tersoff-Brenner style empirical potential, was employed within a Genetic Algorithm to investigate the global-minimum structures of Pt clusters in the size range of N=2-80 on pristine as well as defective graphene supports. Point defects in graphene strongly anchor Pt clusters and also appreciably affect geometries of small clusters, which we characterize via various structural metrics such as the gyration radius, average bond length, and average coordination number. Through selected ab initio studies, we find a consistent trend for charge transfer from Pt clusters to defective graphene supports resulting in the lowering of the cluster d-band center. This lowering of the cluster d-band center has been shown previously to result in weaker CO adsorption as well as reduced barriers for CO oxidation. By varying the cluster size, we also identify an optimal range of cluster sizes over which the support effect can play a role in modulating the activity of the cluster, thereby providing guidance for practical applications of graphene-supported Pt nanoclusters in electrocatalysis.

Presenter: Eunsuk Kim, Brown University

Title: **Bio-inspired Molecular Catalysts for O-Atom Transfer Chemistry**

Authors: L. Taylor Elrod and Eunsuk Kim

Abstract: Nature utilizes high-valent metal oxo species to carry out a wide variety of critical catalytic processes, including nitrate and carbon dioxide reduction. Dimethylsulfoxide reductase (DMSOR) family of oxotransferase enzymes efficiently catalyze oxygen atom transfer (OAT) reaction through Mo and W centers. Herein, we present our recent advances in the development of bio-inspired molecular OAT catalysts using discrete Mo and W complexes, which highlights the importance of the secondary coordination environment of the catalytic active site. The catalytic reaction of nitrate to nitrite is studied using IR, UV-Vis, and NMR spectroscopic characterizations of the reaction products, along with cyclic voltammetry and isotopic labeling studies.

Presenter: Maksim Tyufekchiev, Worcester Polytechnic Institute

Title: **In-Situ Raman Microspectroscopy Reactor for Monitoring of Acid Catalyzed Cellulose Hydrolysis**

Authors: Maksim Tyufekchiev, Geoffrey Tompsett, Michael Timko

Abstract: A custom microreactor was designed and built for in situ monitoring acid catalyzed cellulose hydrolysis using Raman microscopy. The reactor consists of top and bottom parts tightened by six screws and sealed with a gold plated copper o-ring. Both parts can be demounted from one another allowing for solid sample removal after reaction and study by off-line instrumentation. The reaction chamber, machined in the bottom part of the reactor, has a 50-microliter volume and is fit with a quartz window to allow for optical and spectroscopic access. The window and the top part of the reactor are sealed using a Teflon o-ring. Both parts of the reactor are gold plated to prevent acid corrosion. The reaction chamber has an inlet and outlet for liquid (or gas) flow. The top part of the reactor is water-cooled braised-on copper tubing, to prevent thermal damage to microscope lenses. In this view-cell microreactor, we used Raman microscopy to monitor crystallinity changes during acid-catalyzed cellulose hydrolysis. Specifically, we monitored cellulose crystallinity at over a range of reaction temperatures and acid concentrations showing that highly crystalline cellulose does not decrystallize even at acidic conditions and temperatures as great as 200° C. We take this as evidence of hydrolysis occurring without decrystallization. Conversely, the crystallinity of cellulose with bulk initial crystallinity of approximately 50% increased with increasing reaction time, suggestive of preferential hydrolysis of amorphous cellulose. This study demonstrates the potential of the microreactor for studying a wide range of liquid-solid reaction chemistries. Future work will use this method to study depolymerization and decrystallization of cellulose and synthetic polymers under thermal, solvo-thermal, and catalytic conditions.

Presenter: Azadeh Zaker, Worcester Polytechnic Institute

Title: **Catalytic Cracking of Dodecane in Supercritical Water**

Authors: Azadeh Zaker, Patricia Guerra, Geoffrey Tompsett, Michael T. Timko

Abstract: Catalytic Cracking of Dodecane in Supercritical Water

Presenter: Patricia Guerra, Worcester Polytechnic Institute

Title: **Catalytic Cracking of Dodecane in Supercritical Water**

Authors: Azadeh Zaker; Patricia Guerra; Geoffrey Tompsett; Michael T. Timko

Abstract: Catalytic Cracking of Dodecane in Supercritical Water

Presenter: David Gamliel, University of Connecticut

Title: **Effects of Catalyst Properties on Biomass Conversion by Catalytic Fast Pyrolysis and Hydropyrolysis**

Authors: David P. Gamliel, Laura Wilcox and Julia A. Valla

Abstract: Biomass is a clean and renewable carbon source, capable of providing sustainable carbon for conversion to fuels and platform chemicals. Catalytic fast pyrolysis (CFP) of biomass is the thermochemical conversion of biomass to liquid bio-oil, gas and char under inert atmosphere at intermediate temperatures and high heating rate. Recently, catalytic pyrolysis of biomass under a hydrogen atmosphere at elevated pressure, termed hydropyrolysis, has been studied as an effective method for production of deoxygenated high-value bio-oil with plentiful aromatic and aliphatic hydrocarbons. The objective of this work is to determine how catalyst properties correlate to CFP and hydropyrolysis product yields, and propose the ideal catalyst for the production of value-added products from biomass resources. A wide variety of catalysts were prepared and characterized for this study, such that the effects of transition metal choice, metal loading, support type and support acidity could be determined. Each catalyst was completely characterized using a variety of techniques to find the surface area, morphology, pore structure, metal oxidation state and crystal structure. Pd, Ru and Ni were chosen as candidate metals due to their high activity for deoxygenation and hydrogenation. These metals were deposited via dry impregnation on a variety of alumino-silicate supports including alumina, silica and ZSM-5 zeolite. Furthermore, the Si/Al ratio of the ZSM-5 support was varied in order to determine the effects of acidity on the CFP and hydropyrolysis product distribution.

Presenter: Azadeh Zaker, Worcester Polytechnic Institute

Title: **Catalytic Cracking of Dodecane in Supercritical Water**

Authors: Azadeh Zaker, Patricia Guerra, Geoffrey Tompsett, Michael T. Timko

Abstract: Catalytic Cracking of Dodecane in Supercritical WaterAzadeh Zaker, Patricia Guerra, Geoffrey Tompsett, Michael T. TimkoDepartment of Chemical EngineeringWorcester Polytechnic InstituteWorcester MA 10609An abstract to be submitted to the National Meeting of the AIChE (2016)Technical Session: Reaction Engineering of Biomass and Hydrocarbons in Supercritical WaterSponsored by: Catalysis and Reaction Engineering DivisionIn this work, we investigated dodecane cracking in supercritical water (SCW) using ZSM-5 as an acid catalyst. We studied the reaction in the presence and absence of water by tracking reaction progress in a batch reactor held at 400°C and 24.1 MPa. For the same catalyst loading (5 wt. % oil-based), addition of water reduced formation rates of gas, liquid, and solid products. We identified and quantified liquid products using GC/MS and GC×GC chromatography. GC/MS was used primarily to track production of specific compounds, including toluene, xylenes, and ethylbenzene. GC×GC was used to monitor both individual compounds as well as classes of compounds: aliphatics, 1-ring aromatics, 2-ring aromatics, and 3-ring aromatics. SCW changes the observed product distribution of dodecane cracking, with increased production of aliphatics observed in the presence of water compared to increased production of aromatic compounds in its absence. Furthermore, in the absence of water, GC×GC analysis indicates increased yields of 2-ring and 3-ring products, including molecules such as naphthalene and alkyl-naphthalene. In addition to liquid phase analysis, we characterized the coke deposited on the catalyst using Temperature Programmed Oxidation (TPO) technique. Water reduces coke formation by an order of magnitude and alters its chemical characteristics. Coke deposited in the presence of water is mostly soft coke while coke formed in the absence of water is mostly graphitic hard coke. Finally, we developed a reaction network model to interpret our results. The reaction network consisted of aliphatic, aromatic, gas, and coke products. Future work will investigate catalysts other than ZSM-5 and more sophisticated molecular reaction networks.

Presenter: Megan Jackson, MIT

Title: **Charge Transfer Properties of Graphite-Conjugated Pyrazines**

Authors: Megan Jackson, Seokjoon Oh, Sterling B. Chu, Corey J. Kaminsky, Jeffrey T. Miller, Yogesh Surendranath

Abstract: The interconversion of electrical and chemical energy requires catalysts that can efficiently transfer multiple electrons to or from small molecules. Heterogeneous catalysts have extended band structures with high densities of states at the Fermi level, allowing these surfaces to engage in concerted electron transfer and substrate activation; however, metallic surfaces contain a broad distribution of active sites that are difficult to characterize and tune at the molecular level. Recently, we have developed a new class of catalysts that incorporate molecularly well-defined, highly-tunable active sites into heterogeneous graphite surfaces. These graphite-conjugated pyrazines (GCPs) feature a unique conjugated linkage between a discrete molecular active site and the delocalized states of graphitic carbons. Edge planes of graphitic materials display high populations of o-quinone moieties that undergo site-selective irreversible condensation with substituted phenylenediamines to form robust, aromatic pyrazine linkages. Here, we probe the electronic structures and charge transfer properties of metal-conjugated GCPs by cyclic voltammetry (CV) and X-ray absorption spectroscopy (XAS). CVs of the dissolved complex tris(bipyridine)Ru(II) (Ru(II)(bpy)3) display a reversible Ru(III/II) wave, and the same wave is observed when the molecule is anchored to an electrode surface through an insulating aliphatic linkage. Remarkably, conjugating this Ru center to the graphite surface causes the redox waves to disappear. Consistent with these CVs, in-situ XAS demonstrates that applying oxidizing potentials to an electrode with aliphatically tethered Ru(II)(bpy)3 causes a change in oxidation state from Ru(II) to Ru(III), but applying the same potentials to the Ru(II)(bpy)3 GCP has no effect on oxidation state. These results suggest that the aromatic pyrazine linkage allows for strong orbital overlap between the Ru center and the large density of states of the graphite electrode, indicating that rather than just being attached to the electrode, the Ru center becomes part of the electrode in a GCC. This system provides the first example of a discrete molecular complex that is embedded within the band structure of an electrode.

Presenter: Anna Wuttig, Massachusetts Institute of Technology

Title: **Competing Pathways in Interfacial CO2-to-Fuels Catalysis**

Authors: Anna Wuttig, Momo Yaguchi, Kenta Motobayashi, Masatoshi Osawa, Yogesh Surendranath

Abstract: Renewable electricity can be stored in the energy dense bonds of carbon-based fuels via the electroreduction of CO2. CO2 reduction in aqueous electrolytes suffers efficiency losses due to the simultaneous reduction of water to H2. Rational design of selective CO2-to-fuels catalysts requires direct knowledge of the electrode surface structure during turnover and how electrons and protons couple to direct product selectivity. In this presentation, we present the results of combined in-situ surface-enhanced infrared absorption spectroscopy (SEIRAS) and electrochemical kinetic studies that probe the mechanistic basis for kinetic bifurcation between H2 and CO production on model polycrystalline Au catalysts. We uncover the complex heterogeneity in CO surface binding equilibria and the differential proton coupling requirements for CO versus H2 production. Under the conditions of CO2-reduction catalysis, electrogenerated CO species are irreversibly bound to Au in a bridging mode at a surface coverage of ~0.3 and act as kinetically inert spectators. Electrokinetic data are consistent with a mechanism of CO production involving rate-limiting single electron transfer to CO2 with concomitant adsorption to surface active sites, followed by rapid one electron, two proton transfer, and CO liberation from the surface. In contrast, the data suggest a H2 evolution mechanism involving rate-limiting single electron transfer to bicarbonate, hydronium, and/or carbonic acid to form adsorbed H species, followed by rapid one electron, one proton or H recombination reactions. We assemble the spectroscopic and kinetic data to construct a mechanistic model, which predicts that impeding proton transfer to the surface is an effective strategy for improving CO2 to fuels catalyst selectivity.

Presenter: Kai Yan, Brown University

Title: **The influence of elastic strain on catalytic activity towards the hydrogen evolution reaction (HER)**

Authors: Kai Yan, Alireza Khorshidi, Tuhina Marrk, Pradep Guduru, Andrew Peterson

Abstract: Elastic strain affects catalytic reaction rates, but is often coupled with a ligand effect. To isolate the strain effect, we subjected thin metal films on elastic substrates to uniaxial loading and investigated their activity towards the hydrogen evolution reaction (HER). Simultaneously, we performed electronic structure calculations for analogous conditions. Both theory and experiment show strain controls reactivity in a controlled manner consistent with the qualitative predictions of the HER volcano plot and the d-band theory: Ni and Pt’s activity were accelerated by compression, while Cu’s activity was accelerated by tension.