Presenting our

2015 Research Review

October 7 - 8, 2015
Clayton Hall Conference Center
### Schedule of Events

#### Wednesday, October 7, 2015

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<td>9:10 a.m.</td>
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“Design of Electrolyzer Stack for CO$_2$ Conversion to Fuels and Chemicals”

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**11:50 a.m.** David Boyce ........................................................... .page 12  
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“Cross-Coupling Reactions Catalyzed by Non-Precious Metals: Ready Access to Highly Enantioenriched Organic Molecules”

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The Role of a Graphene Support in Improving Hydrogen Oxidation Activity of Supported Ni Nanoparticles

Stephen A. Giles
Advisor: Dionisios G. Vlachos and Yushan Yan

Fuel cells are an important power source for zero emission vehicles. Among low-temperature fuel cells, hydroxide exchange membrane fuel cells enable the use of non-precious metal catalysts, such as nickel, and have received increased attention from the scientific community as a result. Ni nanoparticles supported on carbon nanotubes (CNT) are shown experimentally to exhibit an order of magnitude higher exchange current density for the hydrogen oxidation reaction (HOR) than what is observed using an amorphous carbon support. Furthermore, an additional threefold increase is observed when the carbon nanotube is doped with nitrogen (N-CNT). Similar beneficial effects have been reported for other metals and metal oxide nanoparticles supported on N-CNT and N-graphene [1,2]. However, the origin of this effect is unknown.

In the current study, we employ density functional theory (DFT) along with a data-driven model to investigate both the origin of this support effect and how it impacts the electrocatalytic properties of the catalyst. Variation of the activity of the nanoparticle was studied with respect to nitrogen dopant concentration and location within the support. Upon quantifying the site-dependent activity of the nanoparticle, two primary classes of support effects were elucidated: superior immobilization and stability of the nanoparticle on certain N-doped supports, and local shifts in key electronic properties (e.g., $d$-band center) of Ni adsorption sites caused by the presence of nitrogen in the support. As a result of this investigation, we conclude that a nitrogen dopant at the edge of the nanoparticle induces the most favorable metal-support interaction for the promotion of the HOR.

Nanostructured Electrocatalysts for Carbon Dioxide Reduction

Feng Jiao
Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, E-mail: jiao@udel.edu

Due to rising energy demand and evidence of the environmental effects of CO\textsubscript{2} emissions, much research has focused on producing and storing energy from renewable sources. An efficient and selective process for the conversion of CO\textsubscript{2} to CO or other reduced products could allow for the widespread production of liquid fuels. Coupled with renewable energy sources, these processes could help solve the large scale storage issue of renewable energies while creating a carbon neutral energy source easily integrated into the current energy infrastructure. To date, researchers have identified several bulk metal catalysts such as Cu, Ag, Au, and Zn that are able to reduce CO\textsubscript{2} electrochemically in aqueous electrolytes albeit requiring significant energy from an external source (i.e. overpotential) to drive the reaction.

Nanostructured catalysts are of great interest for CO\textsubscript{2} to CO conversion due to their high catalytic surface area and unique properties relative to their polycrystalline counterparts.\cite{1} Last year we discussed our discovery of a highly active nanoporous Ag electrocatalyst, which is able to reduce CO\textsubscript{2} electrochemically to CO in a highly efficient and selective way.\cite{2} Considering the cost of Ag, we recently investigated nanostructured Zn catalyst. Using electrodeposition technique, we are able to develop a dendritic Zn catalyst, which is able to selectively reduce CO\textsubscript{2} at rates around an order of magnitude higher than bulk Zn with great long term stability.\cite{3} We characterized the behavior of the Zn catalyst during CO\textsubscript{2} electrolysis using in-situ/operando X-ray absorption spectroscopy, which provided us insight into the oxidation state and coordination of the dendritic Zn catalyst at working conditions. In addition to catalyst development, we will also discuss our recent efforts towards a practical CO\textsubscript{2} electrolyzer and the challenges associated with system level design.

References


Inexpensive Architectures for the Production of Fuels from Carbon Dioxide and Sunlight

John L. DiMeglio, Jonnathan Medina-Ramos, Rachel C. Pupillo, Stephanie Velardo, and Joel Rosenthal*

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE, 19716

The use of sunlight to power the reduction of CO$_2$ to CO provides a mechanism to store solar energy via generation of an energy rich commodity chemical that can be used for the synthesis of liquid fuels. However, there have not historically been affordable platforms to promote this transformation with high selectivity and reasonable kinetics. Moreover, the marriage of practical CO$_2$ reduction catalysts to light harvesting assemblies is not usual a trivial undertaking, which limits the practicality of schemes for the production of carbon based fuels from CO$_2$ and sunlight. It is against this backdrop that we have worked to develop inexpensive catalyst assemblies that take advantage of post-transition metal-based materials for CO$_2$ reduction. These platforms can be easily prepared using a combination of electrodeposition techniques and when used in conjunction with imidazolium-based ionic liquids, promote the electrocatalytic conversion of CO$_2$ to CO with high current densities at low overpotentials. In addition to highlighting the impressive catalytic activity of these post-transition metal-based materials we will also demonstrate that these catalysts can be easily married with light harvesting architectures, allowing for the direct conversion of CO$_2$ to CO using sunlight.
The Central Role of Bicarbonate in the Electrochemical Production of CO on Gold

Marco Dunwell
Advisor: Bingjun Xu, Yushan Yan
Committee Members: Feng Jiao, Raul Lobo

With atmospheric CO$_2$ concentrations recently surpassing 400 ppm, electrochemical conversion of CO$_2$ for the production of renewable fuels and useful chemicals is more important than ever. Although much work has been done in the development of high performance and more stable electrocatalysts with a wide variety of product distributions, there is still little understanding of the mechanism of CO$_2$ reduction. Au is the ideal material for initial mechanistic studies due to its high selectivity toward a single product (CO). Using in-situ attenuated total reflectance – surface enhanced infrared reflection absorption spectroscopy, electrokinetic studies, isotopic labeling, and mass spectroscopy we have shown that HCO$_3^-$, not CO$_2^-$, is the species reduced at the Au electrode. Despite this, a first order dependence of the reaction rate on both HCO$_3^-$ and CO$_2^-$ concentration is observed. We propose a new reaction mechanism in which CO$_2$ acts as a hydroxide acceptor in the electroreduction of HCO$_3^-$ for the production of CO. Additionally, we propose that adsorption of metal cations at high overpotentials inhibits access of bicarbonate to the Au surface, limiting the rate of electrochemical production of CO.
Nickel-Catalyzed Cross Couplings of Amine- and Alcohol-Derived Substrates to Deliver Enantioenriched Products

Mary P. Watson

Organic chemistry is an enabling science, providing access to much-needed molecules for the development of new materials and devices, treatment of disease, and investigation of biochemical pathways. It also enables insight into the molecular level interactions that define our world. An ongoing challenge in organic chemistry is the discovery of efficient methods to synthesize target molecules. Towards the goal of highly efficient methods, the use of transition metal catalysts to provide both reactivity and selectivity has transformed the way that organic molecules are constructed. Our research program is directed towards harnessing the power of transition metal catalysts to enable new, efficient methods for the preparation of chiral molecules in highly enantioenriched form. In particular, we are discovering transition metal-catalyzed reactions of electrophiles that are not typically used with these catalysts. With this approach, we seek solutions to long-standing challenges in the synthesis of enantioenriched organic molecules, which are vital for applications in which three-dimensional molecular structure are important, such as in the study and treatment of human disease. In particular, we have focused on the discovery of enantiospecific, nickel-catalyzed cross couplings of amine and alcohol derivatives.1-5 These reactions convert widely available chiral amines and alcohols to valuable chiral products using simple, inexpensive catalysts. The optimization and scope of these transformations will be discussed, along with our mechanistic and stereochemical hypotheses and supporting experiments.

Hydrogenolysis Mechanism of Furfuryl Alcohol on Ru/RuO₂ Catalyst

Alexander V. Mironenko
Advisor: Dionisios G. Vlachos

In the recent years, substantial research effort has been directed at the development of economically viable technologies to mitigate global warming, with special emphasis placed on fuels and chemicals production from lignocellulosic biomass, regarded as the only source of renewable carbon. Recently, we have developed a low-temperature, moderate-pressure, liquid-phase catalytic transfer hydrogenolysis (CTH) process to convert furfural to 2-methyl furan (2-MF) with a yield of ~80%, utilizing secondary alcohols as hydrogen donors over a Ru/RuO₂ catalyst. 2-MF is a renewable platform chemical that can be used as a drop-in fuel or can be further converted to jet fuels, lubricants, and aromatics.

In this work we unravel the mechanism and the functionalities of hydrogenolysis in metal/oxide catalysts by combining density functional theory, microkinetic modeling, and electronic structure analysis. We find that following furfural conversion to furfuryl alcohol (FA) via the MPV mechanism over RuO₂ Lewis acid sites, FA undergoes hydrogenolysis to 2-MF mediated by RuO₂ oxygen vacancies. A radical mechanism of C-O bond hydrogenolysis is exposed in agreement with deuterium distribution, obtained in H/D labeling experiments. Crystal Orbital Hamilton Population, Born-Haber, and spin density analyses identify key factors responsible for high hydrogenolysis activity over metal/metal oxide catalysts.
Design of Electrolyzer Stack for CO₂ Conversion to Fuels and Chemicals

Jonathan Rosen
Advisor: Feng Jiao

Electrochemical conversion of CO₂ to intermediate chemicals or fuels such as CO is a valuable process for renewable energy storage and commodity chemical production using a virtually “free” carbon feedstock. For instance, the CO product can be used downstream as a feedstock in Fischer-Tropsch or gas-to-liquids technologies to produce chemicals and synthetic fuels. Major challenges facing these technologies today are a poor energy efficiency, stemming from the high energy penalty (i.e. overpotential) of over 1 Volt needed on the cathodic side, as well as low reaction rates (i.e. current densities) in scaled up devices.¹

In our lab we have looked at addressing these issues by engineering highly active and efficient nanostructured catalysts with a high density of active surface sites compared to their bulk counterparts. We have recently developed a nanoporous Ag electrocatalyst which is able to electrochemically reduce CO₂ to CO with a ~92% selectivity at a rate over 3000 times higher than polycrystalline Ag at a significantly reduced overpotential of less than 0.50 Volts.² the traditional polycrystalline silver electrocatalyst requires a large overpotential. Here we report a nanoporous silver electrocatalyst that is able to electrochemically reduce carbon dioxide to carbon monoxide with approximately 92% selectivity at a rate (that is, current Through a series of computational and experimental methods we show that nanostructured catalysts, such as nanoporous and nanoparticle Ag, are able to stabilize key reaction intermediates such as COOH_ads significantly reducing the energy penalty needed to drive the reaction.³ This improvement is likely due to their higher density of stepped surface sites found on these catalysts, which is an important consideration in future catalyst design.

In addition to engineering highly efficient CO₂ reduction catalysts, of equal importance is the integration of these catalysts into devices capable of reducing CO₂ at high rates of reaction. Therefore, we have most recently investigated the performance of these nanostructured Ag catalysts into a flow cell capable of achieving currents approaching 1 Amp. In an effort to further increase the reaction rate we have examined combining these devices into a flow cell stack consisting of six cells run in parallel.

References
Methane to Methanol Conversion on Copper-Containing Small-Pore Zeolites

Bahar Ipek
Advisor: Raul F. Lobo

Direct conversion of methane to chemicals and fuels has been a long-standing challenge for the field of catalysis. The large energy barrier for homolytic cleavage of the C-H bond of methane in contrast to the lower energy of the C-H bonds in the desired products—methanol and formaldehyde—renders the selective conversion of methane very difficult; facile over-oxidation of the products is unavoidable at the conditions where methane activation is possible. Copper exchanged zeolites (Cu-ZSM-5\(^1\) and Cu-mordenite\(^2\)) were found to convert methane to methanol selectively following a 3-step cyclic process: (i) oxidation of the Cu-zeolite with O\(_2\) at relatively higher temperatures (450 °C) to create reactive copper-oxo species, (ii) methane activation at moderate temperatures (120–200 °C) and (iii) admission of a solvent to extract methanol from the surface. The reactive copper species on Cu-ZSM-5\(^3\) and Cu-mordenite\(^4\) was found to be a mono-μ-oxo-dicopper complex ([Cu—O—Cu]\(^{2+}\)) based on an absorption feature at 22,700 cm\(^{-1}\) in UV–vis spectra and several unique features in resonance-enhanced Raman spectra.

We show here that copper exchanged small-pore (8-membered ring) zeolites (Cu-SSZ-13, Cu-SSZ-16 and Cu-SSZ-39) produced more methanol on a mole of methanol per gram (as high as 39 μmol methanol/g\(_{\text{zeolite}}\)) and mole of methanol per mole of Cu basis (up to 0.09) when compared to Cu-ZSM-5 and Cu-mordenite.\(^5\) Absence of evidence for the mono-μ-oxo-dicopper complex in Cu-SSZ-13, Cu-SSZ-16 and Cu-SSZ-39 and the corroborated presence of an extra-framework oxygen-copper bond vibration upon O\(_2\) activation of the samples points toward a reactive Cu\(_x\)O\(_y\) species distinct from the mono-μ-oxo-dicopper(II) complex in these zeolites with a higher reactivity towards methanol formation.

Electrochemical CO\textsubscript{2} Reduction to Formate by Bismuth Based Materials in the Presence of Non-Imidazolium Ionic Liquids

David Boyce, John L. DiMeglio, and Joel Rosenthal*
*University of Delaware, Department of Chemistry and Biochemistry, Newark, DE, 19716

A wide variety of cathode materials and modified electrode assemblies have been developed to promote the electrochemical reduction of CO\textsubscript{2} to fuels and other value added commodity chemicals. On-going research in the diverse field of CO\textsubscript{2} conversion applications is focused on the development of robust, affordable, energy-efficient systems with excellent electrocatalytic activity. To this end, our research group has developed bismuth-containing cathode materials that when used in combination with imidazolium based ionic liquids can selectively catalyze the conversion of CO\textsubscript{2} to CO with high current densities and selectivity at low overpotentials. Through optimization and further extension of this platform to other post-transition metal catalysts, such as Sn and Pb, it became apparent that interactions between the cathode surface, ionic liquid, and CO\textsubscript{2} were all critical to the observed catalysis. In subsequent studies, we have determined that the protic functionality of the imidazolium cation enables the ionic liquid to serve as a promoter for the 2e/2H\textsuperscript{+} reduction of CO\textsubscript{2} to CO. Evaluation of non-imidazolium based ionic liquids that are also protic in nature in combination with our bismuth-containing cathode materials, revealed that selectivity for HCO\textsubscript{2}\textsuperscript{-} (FE\textsubscript{FA} \sim 70\%) could be promoted with suppression of CO production (FE\textsubscript{CO} \sim 20\%). As selectivity for CO production (FE\textsubscript{CO} \sim 80-90\%) had been exclusively observed through the use of imidazolium ionic liquids, our current findings highlight the versatility of bismuth materials for the electrochemical reduction of CO\textsubscript{2} and will further guide our efforts towards developing future catalyst systems.
Cross-Coupling Reactions Catalyzed by Non-Precious Metals: Ready Access to Highly Enantioenriched Organic Molecules

Corey Basch
Advisor: Mary Watson

Transition metal-catalyzed cross coupling reactions to form carbon-carbon and carbon-heteroatom bonds have been a long-standing area of research in synthetic organic chemistry. Efforts to lower cost by utilizing naturally abundant non-precious transition metals have sparked a rapid growth in a variety of catalytic reactions. Among such reactions are those that afford enantioenriched materials. Enantiopure organic compounds can exhibit profound differences in bioactivity compared to their racemic counterparts. It is therefore necessary to develop methods for accessing either enantiomer in high optical purity.

Our research is focused on employing non-precious transition metals, particularly nickel, to deliver highly enantioenriched organic molecules from readily available stating materials in a stereospecific fashion. In this regard, we have shown that amines, which can be obtained in high enantiopurity by a variety of methods, are suitable substrates for these transformations. Efforts in our lab have focused on the development of nickel catalyzed Suzuki-Miyaura cross-couplings and Miyaura borylations to afford optically pure products with newly formed carbon-carbon and carbon-boron bonds, respectively.
NO Oxidation Reaction Mechanisms Over Microporous Materials

Jason A. Loiland
Advisor: Raul F. Lobo

The catalytic NO oxidation is an industrially important reaction currently investigated in the context of emissions control technologies to abate the release of nitrogen oxides (NO\textsubscript{x}), particularly in the selective catalytic reduction of NO\textsubscript{x} with ammonia (NH\textsubscript{3}-SCR) using zeolite catalysts. Fe- or Cu-exchanged zeolites are efficient catalysts for SCR technology. The kinetic importance of NO oxidation in SCR over zeolites is unclear and seems to depend on the catalyst, as sometimes it has been implicated as the overall rate-determining step (RDS) [1], while in others cases it has been shown to not be the RDS [2]. NO oxidation rates were measured as a function of temperature from 298-623 K over H-, Na-, and siliceous CHA materials to observe the effects that aluminum atoms and the extra-framework cation (H\textsuperscript{+}, Na\textsuperscript{+}) have on reactivity (Figure 1). The materials exhibit two reaction regimes as a function of temperature, as indicated by the V-shape curve in Figure 1. Below a temperature of approximately 423 K, all materials display substantial catalytic reactivity and reaction rates decrease with increasing temperature, resulting in negative apparent activation energies (-24.9 to -37.5 kJ mol\textsuperscript{-1}). The catalytic rates at low temperatures are attributed to a confinement effect in the materials' micropores that accelerate a homogeneous-like reaction by stabilizing a N\textsubscript{2}O\textsubscript{4}‡ transition state inside the zeolite crystals. The trend with temperature changes above 423 K, and reaction rates over H-SSZ-13 and Na-SSZ-13 increase with increasing temperature (left-hand side of V curve), a clear indication that a different reaction mechanism occurs above 423 K. The reaction rates over siliceous CHA are low and unaffected by temperature above 423 K, indicating that the material has minimal catalytic activity in this temperature window and that framework aluminum atoms with exchanged cations are necessary to observe activity. In-situ FTIR studies reveal that NO\textsuperscript{+} is the only observable N\textsubscript{x}O\textsubscript{y} species present in measurable concentrations on the alumino-silicate zeolites at high temperatures, and we have proposed plausible mechanisms for the formation of NO\textsuperscript{+} at framework aluminum positions within the zeolite pores.

![Figure 1. Arrhenius plots of the forward NO oxidation rates (1,000 ppm NO + 5% O\textsubscript{2}, 100 sccm, 0.1 g catalyst) at 298-623 K over SSZ-13 (CHA) materials.](image)

References
Access to Unsaturated Lactams via Transition Metal Catalysis: Development of an Aza-Heck Reaction

Scott Shuler
Advisor: Professor Donald Watson

Unsaturated lactams are important and interesting compounds that can be found in many natural products and bioactive molecules. In addition, they are rich synthetic intermediates that can be derivatized in a plethora of ways. To this end, we wished to synthesize these compounds in a general and efficient manner. By taking advantage of hydroxamic acid derivatives as an electrophilic nitrogen source, we are able to synthesize numerous unsaturated lactams using an easily-reduced palladium(II) source and an extremely cheap, commercial ligand.
Recent experimental studies have indicated the efficacy of bifunctional catalysts such as HZSM-5 supported Ni clusters containing metal and acid sites towards the hydrodeoxygenation reaction of lignin-derived compounds. In order to better understand the utility of these catalysts, we employ electronic structure calculations to elucidate the catalytic pathways by modeling a zeolite-supported nickel tetramer cluster (Ni₄-ZSM-5). Hydrogenation of acetone to isopropanol followed by dehydration to propene have been investigated as model reactions on the metal and acid sites, respectively. In Ni₄-ZSM-5, we observe a reverse hydrogen spillover, whereby the Brønsted hydrogen migrates from the zeolite active site to the metal cluster. Consequently, the zeolite-supported metal cluster becomes electron-deficient, facilitating the hydrogenation reaction. In contrast, studies conducted on the dehydration reaction pathways indicate that the Brønsted acid catalysis in HZSM-5 is preferred over the metal catalyzed pathway in the Ni₄-ZSM-5 system, again as a result of the electron-deficient nature of the metal species.
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Examining the Role of Imidazolium Ionic Liquids in the Proton-Coupled Electron Transfer Promoted Conversion of CO$_2$ to CO on Bismuth Based Materials

John DiMeglio
Advisor: Joel Rosenthal

Heterogeneous electrochemical reduction of CO$_2$ to CO can be coupled to liquid fuel production and provides a strategy to address current issues in solar energy storage. Recently, our lab developed a bismuth carbon monoxide evolving catalyst (Bi-CMEC) that can efficiently promote the reduction of carbon dioxide. The kinetics and efficiency with which Bi-CMEC drives electroreduction of CO$_2$ is comparable to that observed using expensive precious metals, with Faradaic efficiencies and current densities for CO production of $\text{FE}_{\text{CO}} \sim 90\%$ and $j_{\text{CO}} \sim 5-30 \text{ mA/cm}^2$, respectively at applied over potentials as low as 200 mV. Through a series of voltammetric, electrochemical impedance and surface analysis experiments, we have worked to reveal the primary factors that lead to CO generation by this system. These experiments suggest that the preorganization of imidazolium ([Im]$^+$) ions at the catalyst/electrolyte interface serves to reduce the resistance associated with charge transfer to CO$_2$ at the electrode surface. Moreover, impedance measurements provide evidence that the [Im]$^+$ assists in the formation and stabilization of charge separated adsorbates of the type Bi–CO$_2$---[Im]$^+$. In addition, the imidazolium cations can also provide the protons necessary to drive CO evolution via a proton-coupled electron transfer process. These findings help shape our understanding of the complex dynamics attendant to activation of CO$_2$ at Bi-CMEC and continue to shape our efforts to develop new architectures for electrocatalytic energy conversion.
Modeling the Oxygen Evolution Catalysis of Fe$_3$O$_4$ Nanoparticles

Stephen A. Giles
Advisor: Dionisios G. Vlachos and Yushan Yan

One of the most important roadblocks for the realization of a renewable energy grid is the catalysis of the oxygen evolution reaction (OER). The mechanism is typically regarded as a four-step, four-electron process, and requires a large overpotential to achieve an appreciable current density. Moreover, a platinum (Pt) catalyst is typically regarded as optimal; therefore, the process is both energy-intensive and cost-prohibitive. Recently, however, a number of earth-abundant metal oxides have been proposed to be efficient OER catalysts [1]. Experiments have shown, in particular, that Fe$_3$O$_4$ nanoparticles become more active with decreasing size. The origin of these size effects has hitherto only been speculated.

Thus, in the current study, we combine experimental results with density functional theory (DFT) calculations to examine the OER occurring on Fe$_3$O$_4$ nanoparticles. On the basis of microscopy, the nanoparticles are known to adopt a cuboctahedral geometry. Therefore, modeling the two terraces and connecting edge as (100), (111), and (211) periodic surfaces, we are able to study the variation of overpotential as a function of size. Our DFT results indicate that the edge sites are active for the OER. The high activity of the Fe$_3$O$_4$ edge sites is due in part to the adsorbates being bonded in a bridge configuration. As a result, the traditional scaling relations that have been demonstrated for the reactive intermediates of OER can be violated.

Solvent Effects in Biomass Conversion: Pyridine Adsorption on Zeolites

Nicholas Gould
Advisor: Bingjun Xu

Pyridine adsorption has been extensively studied in vacuum to characterize the presence of Bronsted and Lewis acid sites in zeolites. However, biomass conversion often deals with highly oxygenated reactants that require reactions be carried out in liquid phase. But the fundamentals of solvent competition for active sites and solvent affecting the binding energy of adsorbed reactants are still unclear due to a lack of a convenient experimental technique. Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) is capable of studying the catalyst-solvent interface and can be coupled with Temperature Programmed Desorption (TPD) for qualitative binding energy measurements. The binding energy of pyridine to Lewis sites is solvent dependent and is decreased compared to the corresponding gas phase experiment. Pyridine is easily removed from Lewis sites at room temperature in all solvents studied with the exception of water, where pyridine remains adsorbed at room temperature, but is easily removed at 100°C. Binding energy on Bronsted sites remains to be studied. Accessibility studies were carried out using 2-methylpyridine and 2,6-dimethylpyridine on zeolites with varying pore sizes (BEA, ZSM-5, CHA). Initial studies suggest accessibility is solvent independent but temperature dependent.
In this piece of work, we study the electrochemical reduction of CO$_2$ on copper electrodes at low overpotentials. This reduction was probed utilizing surface enhance infrared absorption spectroscopy (SEIRAS) to identify adsorbed species and gas chromatography/nuclear magnetic resonance for quantification of products. Evidence suggests that previously undocumented H$_{\text{ads}}$ peaks occur on the copper surface at low overpotentials, and its loading is unaffected when the surface is doped with CO. Isotopic studies further the validity of these peak assignments using the kinetic isotope effect. This study provides initial data on surface adsorption on copper and creates a stepping stone for further SEIRAS study on copper films.
Lewis acidic zeolite Beta catalyst for the Meerwein-Ponndorf-Verley reduction of furfural

Molly Koehle
Advisor: Raul F. Lobo

The catalytic properties of tin-, zirconium- and hafnium-containing siliceous Beta zeolite were investigated in the Meerwein-Ponndorf-Verley reduction of furfural using a liquid-phase plug-flow microreactor at temperatures between 328–358K. Catalytic rates varied widely with the highest turnover frequency observed on Hf-Beta (4.6 min⁻¹), followed by Zr- and Sn-Beta (1.8 min⁻¹ and 0.51 min⁻¹, respectively). The lowest activation energy was observed on Hf-Beta (49.6 kJ/mol) while Zr- and Sn-Beta showed higher but similar activation energy (60.7 and 60.4 kJ/mol, respectively). The catalysts deactivate with time on stream (with a half-life of 3.5 hours or longer) and are poisoned by the reaction product furfuryl alcohol. Deactivation is caused, at least in part, by polymerization of reactants and products that are retained in the zeolite and block access to active sites, but operation at higher temperature (408K) slows the rate of deactivation significantly. The catalytic properties of the materials can be regenerated by calcination in air.
Fe/γ-Al₂O₃ and Fe-K/γ-Al₂O₃ as Reverse Water-Gas Shift Catalysts

Jason A. Loiland
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The reverse water-gas shift (RWGS) reaction can effectively transform CO₂, an anthropogenic greenhouse gas, to CO, which is a useful chemical intermediate [1]. Various metals and metal oxides are known to catalyze the RWGS reaction [2], with Fe- and Cu-based materials being most commonly used. However, currently available catalysts require very high temperatures, and driving the reaction to completion is a significant challenge [3].

In this report, the RWGS reaction was investigated over Fe/γ-Al₂O₃ and Fe-K/γ-Al₂O₃ catalysts at temperatures between 723 K and 753 K and atmospheric pressure. Both materials exhibited fast catalytic CO formation rates and high CO selectivity (>99%). Reaction rates displayed a strong dependence on H₂ partial pressure (reaction orders of 0.58 and 0.54 over Fe/γ-Al₂O₃ and Fe-K/γ-Al₂O₃, respectively), and a weak dependence on CO₂ partial pressure (reaction orders of 0.37 and 0.21, respectively) under equimolar CO₂:H₂ flows. Iron, on both catalysts, was found to reduce to the +2 oxidation state under H₂ flow, and oxidize to the +3 oxidation state under CO₂ flow based on in situ XANES. Iron is mostly in the +2 oxidation state under continuous equimolar flow of CO₂ and H₂. The catalysts were stable under excess H₂ but deactivated slowly under an equimolar mixture of CO₂ and H₂ (1-2%/hr of the overall reaction rate). Addition of potassium to the Fe/γ-Al₂O₃ material (Fe/K mass ratio = 1.24) leads to a threefold increase in reaction rate, but also doubles deactivation rate (CO₂:H₂ = 1:1). Gas-switching experiments (CO₂ or H₂ only) and DRIFTS spectra collected in situ showed that stable intermediates are formed on Fe-K/Al₂O₃ but not Fe/Al₂O₃. This suggests, but does not prove, that a redox mechanism is the only reaction pathway on the Fe/Al₂O₃ catalyst, and is the predominant pathway on the Fe-K/Al₂O₃ catalyst. The potassium promoter activates a secondary pathway for CO formation, which may be the so-called associative pathway.

References

Diels-Alder and Dehydration Reactions of Biomass-Derived Furan and Acrylic Acid for the Synthesis of Benzoic Acid

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Routes to benzoic acid starting from furan—obtained from hemicellulose-derived furfural—and methyl acrylate are reported. These routes involve Diels-Alder and dehydration reactions of furan and methyl acrylate (or acrylic acid) in a two-step reaction protocol that minimizes side reactions. The Diels-Alder reaction of furan and methyl acrylate (or acrylic acid) was run at 298 K and was catalyzed by Lewis acidic (Hf-, Zr- and Sn-Beta) zeolite catalysts achieving a relatively high turnover frequency (~2 h\textsuperscript{-1}) with no side reactions detected. The dehydration of the product oxanorbornene was performed homogeneously at low temperatures (298 to 353 K) in mixtures of methanesulfonic acid and acetic anhydride in 96% yield. This is much more favorable than the 1.7 % yield of methyl benzoate obtained for the dehydration of the oxanorbornene in neat methanesulfonic acid. The effect of oxanorbornene concentration and stereochemistry were found not to decrease yield to aromatics while dehydration of the carboxylic acid form of the oxanorbornene led to a drop in selectivity to 43% at complete conversion in mixtures of methanesulfonic acid and acetic anhydride. This reaction sequence could be an important entry point for selectively directing high-yield, hemicellulose-derived furans to aromatic products used in the existing chemical process industry.
pH Dependence of HOR/HER Activity for PtRu/C

Jared Nash
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With fuel cells gaining favor, as seen by the Toyota Mirai, there is a necessity to reduce the catalyst cost without sacrificing activity. One possibility is the hydroxide exchange membrane fuel cell (HEMFC) in which a larger range of metal catalysts are stable and may be used. However, the activity of the hydrogen oxidation reaction (HOR) decreases by two orders of magnitude going from acid to base. In order to improve catalyst design, a more fundamental understanding of the HOR mechanism is necessary. PtRu has been shown to be one of the most active catalysts for HOR in base.\(^1\) It has been proposed that the hydrogen binding energy (HBE) is the sole descriptor for HOR activity for monometallic catalysts.\(^2,3\) A competing theory suggests that hydroxide adsorption affects the HOR activity in base which suggests that a more oxophilic catalyst would improve the activity in base.\(^4\)

In this work, we measured the activities of PtRu bimetallic using the rotating disk electrode (RDE) method with pH ranging from 3 to 13. Using cyclic voltammetry, copper underpotential deposition (Cu-UPD), and CO stripping, the HBE, surface Ru composition, and hydroxide adsorption potential were measured. Even with the relatively small surface Ru coverage-approximately 24\%, there was a significant change in the relationship between pH and activity. For monometallic catalysts, the change of activity with pH is monotonic.\(^3\) In this work, we found that the activity decreased from pH 3-9, but increased from pH 9-13. From pH 6-13, there was relatively little change in the HBE which suggests that there is an additional factor that affects the HOR activity.

Reference
Electrochemical Conversion of CO$_2$ to CO in Stacked Flow Cells

Jonathan Rosen  
Advisor: Feng Jiao  

Devices able to convert CO$_2$ to value-added fuels and chemicals are valuable technologies for reducing CO$_2$ emissions from sources such as power plants and additionally as a method of renewable energy storage and chemical production depending on the availability of inexpensive electricity. Recently much progress has been made on the development of highly efficient electrocatalysts which are able to convert CO$_2$ to value-added products such as CO, formic acid, and a variety of other C$_1$ and C$_2$ fuels. However, when scaled up from laboratory conditions to working devices these catalysts have only displayed either high energy efficiency or high activity.$^1$

The development of high performance devices able of achieving both these properties is crucial for commercialization. Recently we have focused on integrating highly active electrocatalysts, both commercial and designed in our lab, into working flow cells capable of reducing CO$_2$ at high rates. In addition to optimizing device performance such as per pass conversion, long term stability, and efficiency we have examined further process scale up from a single cell to multiple cells run in parallel. Similar to the effect seen in fuel cells, running the cells in parallel is a potential method to further increase reaction rates to more commercial levels.

References

Dehydrogenation of ethane and propane from shale gas has the potential to meet the increasing global demand for light olefins. Dehydrogenation is performed industrially on platinum or chromia/alumina catalysts [1], but platinum is expensive and chromia is toxic [2], which creates a need for alternative catalysts that are both inexpensive and non-toxic.

It is well known that metal carbides can be used as catalysts for dehydrogenation of alkanes [3]. Specifically, molybdenum carbide supported on alumina and silica reacts with numerous hydrocarbons, including propane, producing olefins [4]. Molybdenum carbide supported on H-[Al]ZSM-5 is also used to convert methane to benzene [5]. The primary product, ethylene, reacts rapidly on the zeolite acid sites to produce benzene and other aromatic species. Using H-[B]ZSM-5, a material with very weak acidic properties [6], as a support for molybdenum carbide nanoparticles, we have prepared a novel catalyst that shows high activity for C-H bond activation.

A number of pure and supported molybdenum carbides were investigated for the dehydrogenation of n-pentane. Two samples provided the highest reactivity and selectivity toward pentenes: Mo/H-[B]ZSM-5 (zeolite support) and Mo/Al2O3. These two catalysts exhibited an induction period, with the highest reaction rates observed 1 h after the start of the reaction. This increase in reactivity indicates that the most active form of the catalyst is formed in the reactor by interaction with the reactant. For both the alumina and the [B]zeolite supports, there was a slow deactivation rate occurring over the 5 h on stream investigated, but unlike the other catalyst tested, the selectivity of the dehydrogenation product from the zeolite support did not change with time on stream. The dehydrogenation of n-hexane and n-heptane were also tested on the most active catalysts.

The Mo/[B]ZSM-5 catalyst showed the highest conversion of all the catalysts investigated, while maintaining the same high selectivity towards the dehydrogenation product as Mo/Al2O3. Furthermore, by using [B]ZSM-5, the secondary bimolecular reactions observed in acidic [Al]ZSM-5, which include oligomerization and dehydrocyclization reactions, were suppressed, preserving the olefinic product.

The novel molybdenum-containing low acidity [B]ZSM-5 zeolites are capable of activating pentane and other hydrocarbons with a high selectivity towards the dehydrogenation product. This new catalyst has the potential for applications in industrial dehydrogenation or hydrotreating, particularly in the presence of species that poison metal catalysts, such as sulfur or nitrogen.

Selective Hydrodeoxygenation of Furfural to 2-methylfuran using Fe-Cu/Silica Catalyst

Huibo Sheng
Advisor: Raul F. Lobo

Furfural, derived from hemicellulose through hydrolysis and dehydration, is as a promising platform chemical for biofuels production. Furfural, however, cannot directly be used as fuel because it is oxygen rich and self-polymerize when exposed to air or light and has to be transformed into a more suitable species. Furfural can be source of numerous derivatives, which can be either substitutes of fossil fuels or be used as fine chemicals. Among these species 2-methylfuran is specially promising as a biofuel or biodiesel additive.

Supported Cu on silica is a mild hydrogenation catalyst that only hydrogenates the carbonyl group of furfural to form furfuryl alcohol. In this work, we described the properties of iron-containing Cu-based catalysts that show much higher reactivity and very high selectivity towards 2-methylfuran. Furthermore, we found that the catalyst pre-activation condition can have a large effect on the selectivity. Catalyst that calcined and pre-reduced at 210 °C will selectively produce furfuryl alcohol, while that pre-reduced at 270 °C will shift the selectivity to 2-methylfuran.

References
High-Performance Dealloyed PtCu/CuNW Oxygen Reduction Reaction Catalyst for Proton Exchange Membrane Fuel Cells

Jarrid Wittkopf
Advisor: Yushan Yan

One major barrier to fuel cell commercialization is the high cost of oxygen reduction reaction (ORR) catalysts. Current catalysts are predominantly supported Pt nanoparticles. These nanoparticles show high surface area but low specific activity and durability. A transition to unsupported catalysts possessing an extended surface should improve both specific activity and durability and in turn, cost-effectiveness when high surface area can be achieved. Platinum-coated copper nanowires (Pt/CuNW) exemplify these advantages. In this study, post-synthetic processing is used to further improve the performance of Pt/CuNW catalyst. Specifically, annealing followed by electrochemical dealloying enhances activity through geometric lattice tuning. The resultant bimetallic PtCu/CuNW catalyst yields specific and mass activities (SA and MA) of 2.65 mA cm\(^{-2}\) and 1.24 A mgPt\(^{-1}\), surpassing the respective DOE benchmarks of 0.72 mA cm\(^{-2}\) and 0.44 A mgPt\(^{-1}\). PtCu/CuNWs demonstrate enhanced durability over Pt nanoparticle catalysts by maintaining 64.1% of its active surface area after 30,000 cycles between 0.6 - 1.1 vs. RHE at a scan rate of 50 mV s\(^{-1}\) in Ar saturated 0.1 M HClO\(_4\). Post durability PtCu/CuNWs outperformed the DOE benchmarks with a SA and MA of 1.50 mA cm\(^{-2}\) and 0.477 A mgPt\(^{-1}\).
Kinetic Study of the Hydrogen Oxidation Reaction in Hydroxide Exchange Membrane Fuel Cells

Mariah Woodroof
Advisor: Dr. Yushan Yan

Hydrogen fuel cells convert chemical potential directly into electrical energy by separating the hydrogen oxidation (HOR) and oxygen reduction reaction with a solid polymer ion exchange membrane (IEM). Although the HOR on platinum catalysts is facile compared to the ORR, its activity is very dependent on the pH of the electrolyte. The HOR activity is quantified using the exchange current density (i_0), a parameter that is extracted from the kinetic current of the HOR polarization curve. The exchange current density is traditionally measured using a rotating disk electrode (RDE) in a liquid electrolyte. However, the HOR on platinum in liquid acid is so fast that the kinetic current is masked by the inherent diffusion limitations of the RDE system. To eliminate the mass transfer limitations of aqueous phase hydrogen, a hydrogen pump cell can be used in which gas-phase hydrogen is passed over the Pt catalyst that is interfaced with a solid polymer IEM. The in-situ HOR activity on platinum interfaced with a Nafion® proton exchange membrane (PEM) has previously been studied using a hydrogen pump [1].

However, the in-situ HOR activity for platinum interfaced with a solid electrolyte hydroxide exchange membrane (HEM) has yet to be reported. Although the HOR’s slower activity in base allows for the extraction of the kinetic current from RDE data, an important comparison of the HOR activity between liquid and solid electrolytes needs to be established. This work used a hydrogen pump to present the first comparison between liquid and solid base electrolytes. The exchange current densities for both electrolytes were found to be very similar. However, the locations of the hydrogen underpotential deposition (H_UPD) peaks in the cyclic voltammogram (CV) for the solid base electrolyte are shifted to lower overpotentials compared to the H_UPD peaks in the CV for liquid base.

Recent studies have shown that the H_UPD peaks on platinum shift to lower overpotentials in response to decreased pH of the electrolyte and increased HOR activity [2]. However, although the H_UPD peaks for platinum in the solid base electrolyte shifted to the left, the activity remained unchanged. This work also investigated the cause of H_UPD shifts in solid base electrolyte and found that the cationic functional groups in the HEM were interacting with the platinum surface at certain overpotentials, blocking active sites, and preventing hydrogen to adsorb onto the catalyst surface. However, the range of overpotentials where the cations are adsorbed onto the surface do not overlap with the overpotentials where platinum is active for the HOR. Therefore, this is why no decrease in HOR is observed in the solid base electrolyte system.

In Situ Formation of Cobalt Oxide Nanocubanes as Efficient Oxygen Evolution Catalysts

Yan Zhang
Advisor: Feng Jiao

Oxygen evolution from water poses a significant challenge in solar fuel production because it requires an efficient catalyst to bridge the one-electron photon capture process with the four-electron oxygen evolution reaction (OER) [1]. Here, a new strategy was developed to synthesize nonsupported cobalt oxide nanocubanes through an in situ phase transformation mechanism using a layered Co(OH)(OCH3) precursor [2]. Under sonication, the precursor was exfoliated and transformed into cobalt oxide nanocubanes in the presence of NaHCO$_3$–Na$_2$SiF$_6$ buffer solution. The resulting cobalt catalyst with an average particle size less than 2 nm exhibited a turnover frequency of 0.023 per second per cobalt in photocatalytic water oxidation. X-ray absorption results suggested a unique nanocubane structure, where 13 cobalt atoms fully coordinated with oxygen in an octahedral arrangement to form $8\text{Co}_4\text{O}_4$ cubanes, which may be responsible for the exceptionally high OER activity.

References:
Mediated electrolysis for efficient and economical regeneration of high-purity chlorine from waste hydrogen chloride gas

Yun Zhao
Advisor: Yushan Yan

Chlorine is used to synthesize numerous consumer products and useful intermediates.\[^{[1]}\] Chlorination of alkanes or aromatics is a substitution reaction with hydrogen, for which only half of the chlorine atoms are actually used to produce chloro-organics, the other half being lost as waste HCl gas or recovered as low-value HCl aqueous solution. Today, the global by-production of HCl totals 9.3 million tons per year, when only the synthesis of polyurethane, chloromethane, and polycarbonate is considered. At present, only 15% of this HCl by-product is recycled, leaving an unrealized Cl\(_2\) regeneration market of $2.4 billion per year (based on the current price of Cl\(_2\): $315/ton).\[^{[2]}\] Currently, the dominant commercial processes today are electrochemical because of the simple modular design and milder operating conditions electrolyzers offer.\[^{[3]}\] Typical processes feed waste aqueous HCl solution to the anode and utilize a hydrogen evolution (HEC, Equation 1) or oxygen depolarization (ODC, Equation 2) cathode, generating hydrogen or water, respectively, in addition to Cl\(_2\).

\[
\begin{align*}
\text{HCl} & \rightarrow \text{Cl}_2 + \text{H}_2 \quad (1) \\
4 \text{HCl} + \text{O}_2 & \rightarrow 2 \text{Cl}_2 + 2 \text{H}_2\text{O} \quad (2)
\end{align*}
\]

Despite the increasing demand for Cl\(_2\), current HCl recycling technologies are not economical enough to deploy into more of this multi-billion-dollar market. Herein, we propose an iron reduction cathode (IRC) based gaseous HCl electrolyzer system to regenerate chlorine from waste hydrogen chloride at low temperature. At the anode, HCl gas is oxidized to generate chlorine and protons, at the cathode, Fe\(^{3+}\) is electrochemically reduced to form Fe\(^{2+}\). Subsequently, Fe\(^{2+}\) is chemically oxidized to Fe\(^{3+}\) by oxygen in a reactor external to the electrolytic cell. Regeneration Fe\(^{2+}\) is recycled to the electrolyzer. Due to high standard potential (\(p^o, 0.77 \text{ V}_{\text{SHE}}\)) and fast kinetics (exchange current density, \(i_0\), of \(~10^{-2} \text{ A/cm}^2\) on glassy carbon, no catalyst was required),\[^{[4]}\] IRC offers substantial benefits over alternative commercial HEC and ODC cathodes. Taking advantage of IRC, a much lower cell voltage is achieved: 0.67 V vs. 1.16 V (with ODC) and 1.22 V (HEC) at a typical current density of 4 kA/cm\(^2\). Compared to the commercial HEC or ODC-based HCl electrolysis processes, it will save 45–50% of energy consumption approximately. Moreover, without the need for a precious metal cathode catalyst and a costly thick membrane, the captital cost can be reduced by 40%–50% (IRC: $2,640/m\(^2\) vs. HEC: $4,339/m\(^2\) and ODC: $5,034/m\(^2\), estimated with 4 kA/m\(^2\) and current materials prices).

\[^{[2]}\] ThyssenKrupp, *HCl electrolysis brochure*.
Selectivity Control in the Catalytic Dehydration of Methyl Lactate over Alkali-Metal Zeolites

Brian Murphy
Advisor: Bingjun Xu

Catalytic dehydration of lactic acid and its esters is a promising approach to renewably produce acrylic acid and its esters, which are currently derived almost entirely from petroleum. Via a combination of fundamental reactivity and in-situ transmission Fourier Transform infrared (FTIR) spectroscopic investigations, we have achieved a molecular level understanding of the dehydration reaction mechanism over zeolite NaY. Bronsted acid sites generated in-situ via surface ion exchange have been identified as the primary active sites for the dehydration pathway. The key branching point between the desired dehydration and undesired decarbonylation pathways is the dissociation of methyl lactate on NaY to form adsorbed sodium lactate and surface methyl groups. While the decarbonylation pathway to acetaldehyde dominates when methyl lactate is not dissociated, adsorbed sodium lactate may undergo dehydration catalyzed by either Brønsted or Lewis acid sites, although the former are significantly more active. In order to control selectivity, we have introduced additives into the reactant solution, and shown that basic additives reduce selectivity to decarbonylation significantly. The mechanistic understanding gained will enable rational design of catalysts for selective dehydration of methyl lactate.