

Morning Session

Satish Kumar Iyemperumal and N. Aaron Deskins, “Cu/TiO₂ photocatalysts for CO₂ reduction to useful fuels” Worcester Polytechnic Institute

Conversion of carbon dioxide, an abundant greenhouse gas, into useful fuels can help solve issues associated with both energy and the environment. Experiments have successfully shown activity for CO₂ conversion to products like CO, methane and methanol using Cu/TiO₂ photocatalysts. The oxidation state, morphology, and size of Cu can all significantly affect the photocatalytic activity. How this catalyst works and how it could be improved is an area of much research. We studied this catalyst using density functional theory (DFT) to obtain atomic level insights in the CO₂ reduction process on the catalyst surface. A key activation step in CO₂ reduction is the formation of CO₂ anion species with a bent structure. Highly dispersed small clusters of Cu were synthesized in our previous work on TiO₂ surface using a redox reaction between Cu²⁺ and Sn²⁺ [1]. We modeled small Cu_x (x=1-4) clusters on a TiO₂-anatase surface. Our results show that Cu is able to activate CO₂ into a bent configuration that can be further reduced. Charge analysis indicates that CO₂ does indeed become negatively charged in a bent configuration, but not in a linear adsorption mode. We analyzed charge on Cu to assign its oxidation state, as well as calculating adsorbed CO vibrational modes, a common experimental method to assign oxidation state of supported metals. The Cu dimer especially stabilized the bent CO₂ through strong C-Cu bonds. Our results however show that formation of the Cu dimers on the anatase surface is kinetically and thermodynamically unfavorable. A synthesis method that could create Cu dimers could lead to very active photocatalysts, and may be a promising direction for experimentalists to pursue. Our results identify how Cu clusters on TiO₂ surfaces may activate CO₂. Such knowledge is crucial towards refining and designing better catalysts for CO₂ conversion.

[1] C. Liu, S. K. Iyemperumal, N. A. Deskins, G. Li, J. Photonics Energy 2016, 7, 12004.

David Gamliel and Julia A. Valla, “Mesoporous Nickel Incorporated USY Zeolites for Hydrodeoxygenation of Lignin-derived Pyrolysis Oil Model Compounds”, University of Connecticut

Pyrolysis of biomass and agricultural wastes is a readily achieved and feedstock-independent method for production of sustainable fuels and platform chemicals. Raw pyrolysis oil is not suitable for combustion fuel applications due to poor stability and low heating value. Hydrodeoxygenation (HDO) of the oil fraction is a common method for removal of pyrolysis oil oxygen, which is eliminated in the form of water, thus preserving atomic carbon in the pyrolysis oil. Here, we propose ultra-stable Y (USY) zeolite supported Ni catalysts for liquid-phase HDO of anisole, a common product formed from lignin pyrolysis. A variety of mesoporous USY zeolites were created using top-down methods, and impregnated with Ni co-catalyst. Each Ni-impregnated catalyst was tested for liquid-phase HDO of Anisole. Analysis of fitted kinetic parameters for showed that the larger mesoporous zeolites enhanced access of reactant anisole to Ni sites for more efficient hydrogenation of the aromatic ring, whereas acid-catalyzed deoxygenation of the hydrogenated intermediate was about an order of magnitude faster, and not aided by the presence of mesoporosity.

Hoyoung D. Park, Mircea Dinca, and Yuriy Roman-Leshkov, “Heterogeneous Epoxide Carbonylation by Cooperative Ion-Pair Catalysis in Co(CO)₄-Incorporated Cr-MIL-101”, Massachusetts Institute of Technology

Despite the commercial desirability of epoxide carbonylation to β -lactones, the reliance of this process on homogeneous catalysts makes its industrial application challenging. Here we report the preparation and use of a Co(CO)₄-incorporated Cr-MIL-101 (Co(CO)₄Cr-MIL-101, Cr-MIL-101 = Cr₃O(BDC)₃F, H₂BDC = 1,4-benzenedicarboxylic acid) heterogeneous catalyst for the ring-expansion carbonylation of epoxides. We ascribe the observed performance to the unique cooperativity between the postsynthetically introduced Co(CO)₄ and the site-isolated Lewis acidic Cr(III) centers in the metal-organic framework (MOF). The catalytic performance of this system is on par with that of the reported homogeneous catalysts, attesting to the potential applicability of the heterogeneous epoxide carbonylation strategy.

Hong Je Cho, Limin Ren, Vivek Vattipalli, Yu-Hao Yeh, Nicholas Gould, Bingjun Xu, Raymond J. Gorte, Raul Lobo, Paul J. Dauenhauer, Michael Tsapatsis and Wei Fan, “Renewable p-xylene from 2,5-dimethyl furan and ethylene using phosphorus-containing zeolite catalysts”, University of Massachusetts Amherst

p-Xylene is a major commodity chemical and precursor in the production of the most widely used polyester, polyethylene terephthalate (PET). Due to the rapid growth in the global market of PET (6-8% per year), its replacement with a renewable feedstock is highly desirable, and there are ongoing research and development efforts to produce p-xylene from biomass feedstocks. Diels-Alder cycloaddition of 2,5-dimethylfuran (DMF) and ethylene with subsequent dehydration of the cycloadduct intermediate to produce renewable p-xylene is an attractive reaction pathway for its production from biomass feedstocks. To date, the most selective catalysts reported are acidic zeolites with large micropores (7.5 Å), which primarily catalyze the dehydration reaction. However, they also catalyze the formation of alkylated and oligomerized byproducts. Due to these side reactions, the highest yield to p-xylene previously achieved was 75%. In this talk, we report that phosphorous-containing siliceous zeolites can selectively catalyze the dehydration reaction from the furan-ethylene cycloadduct to p-xylene, without catalyzing reactions producing alkylated and oligomerized products. In particular, the phosphorous-containing zeolite Beta (P-BEA) and hierarchical self-pillared pentasil, P-SPP, are active, stable and selective catalysts for this reaction with an unprecedented p-xylene yield of 97%. This catalytic behavior is distinct from that of Al-containing zeolites and establishes a commercially attractive process for renewable p-xylene production.

Chunxiang Zhu and George M. Bollas, “Intensified and selective Fischer-Tropsch Synthesis”, University of Connecticut

The need for energy independence and security has refocused research on Fischer-Tropsch Synthesis (FTS) and its capability to selectively produce short and branched hydrocarbons. In this work, FTS selectivity to gasoline-range products was explored as a catalysis and process engineering problem. Novel structured catalysts for in situ upgrading of FTS products to gasoline-range hydrocarbons were successfully synthesized by coating controlled-thickness ZSM-5 films on the surface of Co/Al₂O₃/monolith structured catalysts. These catalysts were synthesized on the

premise that the monolith serves as an efficient mass and heat transfer structure, while the ZSM-5 layer functions as a hydrocarbon cracking and isomerization agent. Compared to traditional diesel-selective FTS, considerably higher quantity and quality of gasoline-range products were achieved with these bi-layered/bifunctional catalysts. Oil products with gasoline yield higher than 65 wt.% and selectivity to isomers and olefins greater than 70 wt.% were formed at relatively high temperature (230 °C) and intermediate pressure (12 bar), without compromising CO conversion, which remained as high as 79 %.

Maksim Tyufekchiev, Michael T. Timko, Marion Emmert, Pu Duan and Klaus Schmidt-Rohr, Sergio Granados-Focil, “Limitations of Chloride Based Bifunctional Polymer Solid Acid Catalysts for Cellulose Hydrolysis”, Worcester Polytechnic Institute

Solid acid catalysts have been proposed as a viable alternative to liquid acids and enzymes for cellulose hydrolysis for the recovery of glucose and other valuable compounds. A dominant hypothesis in the literature suggests that introduction of specific binding groups to the catalyst structure in addition to strong acidic groups increases the interaction time between cellulose and the catalyst resulting in increase of hydrolysis rate. Materials that possess chlorinated groups as a binding site, thought to interact with cellulose by forming a hydrogen bond with a hydroxyl group, have shown remarkable activity towards cellulose hydrolysis to glucose and levulinic acid. However, the mechanism of catalysis involving such bifunctional solid acid catalysts and cellulose solid particles has not been elucidated. In this work, we investigated the structure-related catalytic activity by detailed structure characterization and series of hydrolysis tests. The material of interest was commercially available cross-linked chloromethyl polystyrene that was functionalized by a well-known synthesis procedure to introduce sulfonic acid groups to the structure. Structural characterization revealed lack of chloride on the external surface of the catalyst, which suggests that chlorine is not participating in hydrogen bonding with cellulose. The catalytic activity of the partially sulfonated solid acid catalysts showed that it was highly active towards cellobiose and cellulose hydrolysis. Analysis of the structure of the catalyst after hydrolysis revealed that the chloromethyl group is being replaced by hydroxyl groups. This suggested that liquid hydrochloric acid was generated that could be responsible for the catalytic activity. This was supported by a control study of unmodified chloromethyl polystyrene hydrolysis of cellulose that revealed it was also able to hydrolyze cellulose. Ion chromatography analysis and pH measurements revealed that acid was generated and its concentration was consistent with the concentration of chloride ions. The results of this study suggest that degradation of carbon chloride bond and formation of aqueous hydrochloric acid could explain the high catalytic activity of chloride based bifunctional solid acid catalysts for cellulose hydrolysis.

Sanjubala Sahoo, Steven L. Suib, and S. Pamir Alpay, “Reactivity of graphene-supported single transition metal atom (Cr, Mn, Fe and Co) catalysts”, University of Connecticut

Single-atom catalysis is a relatively new concept to enhance catalytic activity of transition metal atoms through proper choice of support. The interest in such systems is due to the fact that both the quantum size effect and support-catalyst interactions may lead to unique electronic structures that may enhance catalytic properties. This allows for the design of materials systems at the atomic scale, tailored for specific reactions. Utilizing this concept, we investigated theoretically free and graphene supported single Cr, Mn, Fe and Co atoms for the activation of methane where we have

identified the catalytically active centers. To do this, we employed density functional theory taking into account the generalized gradient approximation as the exchange-correlation treatment. Our results show that graphene-supported TM systems have a high binding energy for methane relative to free ones. The binding can be further enhanced by the presence of defects in graphene. Our analysis shows that the TM-C bonds, the charge transfer between the TM-support and the d-density of states play significant role in the catalytic activity.

Jin-Hao Jhang, Chao Zhou, Gregory S. Hutchings, Omur E. Dagdeviren, Udo D. Schwarz, Eric I. Altman, “Atomic View of Acid Zeolite Chemistry: Surface Chemistry Studies on 2D Silicate Materials”, Yale University

Two-dimensional (2D) silica and aluminosilicate recently have been discovered and successfully fabricated on different substrates in ultrahigh vacuum conditions. The discovery of these new 2D materials leads to many scientific interests because silicate-based materials are extensively used in optics, electronics, catalysis, etc. Particularly in catalysis, aluminosilicate frameworks named zeolites are essentially in charge of numerous catalytic reactions. However, it has been a long-term challenge to understand how surface properties of zeolites promote catalytic reactions. The 2D silicate materials are key to making surface science approaches possible for understanding zeolite chemistry from an atomic view. Both 2D silica and aluminosilicate can be stabilized as a bilayer-structure in which corner-sharing TO₄ (T=Si and Al) tetrahedra construct as two mirror-image layers. In this work, we first performed a structural study of 2D silica and aluminosilicate bilayers grown on Pd(111) with low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), and density functional theory (DFT). Our results reveal how the interplay among lattice strain, doping, and charge transfer determine the structure of metal-supported 2D silicate bilayers. Second, we seek to establish that 2D silicates are capable of promoting acid catalyzed reactions in a manner analogous to 3D zeolites, therefore, a surface chemistry study on both 2D silica and aluminosilicate was performed via temperature programmed desorption (TPD). The probe molecule 2-propylamine reacts through a deamination process and produces propene on the 2D aluminosilicate indicating the existence of acid sites capable of catalysis. In contrast, no propene or other products were detected on the 2D silica surface. We also generated atomic deuterium (D) on both silica and aluminosilicate by a D₂-plasma treatment and a D₂-recombination feature at 540 K assigned to the decomposition of surface OD groups was only observed from the aluminosilicate sample. These findings show the similarity between the 2D aluminosilicate and the acid zeolites which allows us to consider the 2D material as a zeolite model to explore zeolite chemistry.

Afternoon Session

Travis J. Omasta, Xiong Peng, Yufeng Zhang, and William E. Mustain, “Approaching 2 W·cm⁻² AEMFCs through Electrode Engineering and Controlling the Cell Water Content and Balance”, University of Connecticut

In recent years, advances in alkaline exchange membrane fuel cells (AEMFCs) with anion exchange membrane (AEM) solid polymer electrolytes have gained traction due to their distinct – and potentially game-changing – advantages over proton exchange membrane fuel cells. However, AEMs and AEMFCs are at a significantly less mature stage in their developmental than proton

exchange membrane fuel cells (PEMFCs), and have experienced limitations specifically in the area of stability, carbonation, and achievable current and power densities, exhibiting a sizable performance gap vs PEMFCs.¹ This talk will focus on several fundamental and engineering advances that have enabled the creation of AEMFCs that are able to achieve up to 1.9 W·cm⁻² peak power (> 2.5 W·cm⁻² iR-corrected) and 100's of hours of stable operation, bringing AEMFCs much closer to the incumbent PEMFC technology, and opening the way to overcome the cost barrier that has slowed the growth and large scale market implementation of fuel cells in the transportation sector.² One of the largest contributors to the challenges faced in AEMFCs is the cell water content and balance, where the role of water has an impact on the anode (generation through the hydrogen oxidation reaction), cathode (consumption through the oxygen reduction reaction), and movement from the cathode to anode through electro-osmotic drag. This results in a significantly larger current-driven movement of water than PEMFCs, where less water required for the transport of the protons and there is no electrochemical consumption, and a need to provide adequate water to maintaining proper ionomer and membrane hydration while avoiding catalyst layer flooding or dry-out. Back diffusion of water from anode to cathode in the AEMFC, which is coupled to the membrane conductivity, is a promising way to decrease the extreme water gradient, and simplify the water balance problem in AEMFCs.³ In this study, we will discuss the influence of the membrane, ionomer and gas diffusion layer as well as the flow rate and dew points of the anode and cathode gases on AEMFC performance. Using a hydrophilic gas diffusion layer without a microporous layer increases membrane hydration, but also increases the possibility for flooding. Catalyst layer engineering – through adjusting the carbon/ionomer/catalyst loadings, adjusting hydrophilicity/hydrophobicity, manipulating electrode thickness and porosity, etc. – is investigated. We will also discuss controlling the total amount of water fed to the AEMFC through the gas feeds, as well as the water balance between the anode and cathode. Water back diffusion from the anode to the cathode likely plays an important role in membrane hydration and hydroxide transport through the membrane. Finally, we will discuss Pd-Cu catalysts as a high performing alternative to platinum for oxygen reduction at the AEMFC cathode.

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Raymond Gasper, Ashwin Ramasubramaniam, “Behavior of the Methanol Decomposition Reaction on defective graphene supported Pt13: a DFT study”, University of Massachusetts Amherst

Defective graphene has been shown experimentally to be an excellent support for transition-metal electrocatalysts in direct methanol fuel cells. Prior computational modeling has revealed that the improved catalytic activity of graphene-supported metal clusters is in part due to increased resistance to catalyst sintering and to CO poisoning, but the increased reaction rate for the methanol decomposition reaction (MDR) is not yet fully explained. Using density functional theory, we

investigate the adsorption and reaction thermodynamics of MDR intermediates on defective graphene-supported Pt₁₃ nanoclusters with realistic, low-symmetry morphologies. We find that the support-induced shifts in catalyst electronic structure correlate well with an overall change in adsorption behavior of MDR intermediates, and that adsorption energy scaling relationships perform well on the low-symmetry surface. We also investigate the reaction kinetics and thermodynamics, including testing the effectiveness of scaling relationships for predicting reaction barriers (such as the BEP relationship) on the nanoclusters.

Lida M. Namin, N. Aaron Deskins, “Determination of Iridium Bimetallic Alloy Properties from Electronic Structure Calculations”, Worcester Polytechnic Institute

Alloys can have a number of structures, such as ordered, fully mixed, segregated, shell-core, or near surface. The alloy structure in turn determines the electronic and catalytic properties of the alloy. Iridium-based alloys have shown promise in a number of catalytic applications, including ethanol oxidation [1, 2], oxygen reduction [3], hydrogen generation [4], and biomedical science and engineering [5, 6]. Iridium alloys are especially important as they possess high melting point, high corrosion and oxidation tolerance, and excellent mechanical properties which broaden their applications. Our goal was to provide a systematic understanding of realistic iridium alloys, including their stability and electronic properties at various temperatures and synthesis conditions. Identifying how structure affects stability and electronic properties is key to predicting catalyst performance. We used density functional theory (DFT) calculations to study these alloys. Statistical methods, such as the cluster expansion approach, were also combined with DFT to model a large number of possible bimetallic configurations. In the present study we studied iridium-platinum alloys as a model bimetallic system. We have identified viable structures of these alloys at various composition levels (Ir(x)Pt(1-x); $0 < x < 1$), and shown how these metals prefer to segregate at low temperature. While identification of the most thermodynamically stable alloy 0 K structures can be straight-forward, real working catalysts often have not reached equilibrium. Monte Carlo simulations at finite temperature (600 K+) indicate that disordered iridium-platinum structures occur with larger degree of mixing. We have examined how the electronic structure (e.g. density of states) changes at various compositions and structures (e.g. segregated versus mixed), and potential implications of these changes on catalysis. We have also modeled a large number of other iridium alloys with various metals, including Pd, Rh, Sn, Cr, Fe, etc. This systematic study of iridium alloys provides details on which bimetallic systems are stable, their expected electronic properties, and how to realistically model these catalysts. Our results show how theoretical methods can advance alloy development and potential new catalysts.

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Aaron Garg, Maria Milina, Madelyn Ball, Daniela Zanchet, Sean T. Hunt, James A. Dumesic, and Yuriy Román-Leshkov, “Transition Metal Nitride Core-Noble Metal Shell Nanoparticles as Highly CO Tolerant Catalysts”, Massachusetts Institute of Technology

Core-shell architectures offer an effective way to tune and enhance the properties of noble metal catalysts. Here, we demonstrate the synthesis of Pt shell on titanium tungsten nitride core nanoparticles (Pt/TiWN) by high temperature ammonia nitridation of a parent core-shell carbide material (Pt/TiWC). X-ray photoelectron spectroscopy revealed significant core-level shifts for Pt shells supported on TiWN cores, corresponding to increased stabilization of the Pt valence d-states. The modulation of the electronic structure of the Pt shell by the nitride core translated into enhanced CO tolerance during hydrogen electrooxidation in the presence of CO. The ability to control shell coverage and vary the heterometallic composition of the shell and nitride core opens up attractive opportunities to synthesize a broad range of new materials with tunable catalytic properties.

Dr Rajamani Gounder,

Larry and Virginia Faith Assistant Professor of Chemical Engineering, Charles D. Davidson School of Chemical Engineering, Purdue University

“Mobilizing single atoms to form multinuclear copper sites dynamically during NOx selective catalytic reduction with ammonia in Cu-zeolites”

Poster Session

Meredith Allen, Thomas J Schwartz and William Gramlich, “Functionalization of 5-Hydroxymethylfurfural by Selective Etherification”, University of Maine

There is a desire to use biomass to replace oil as the feedstock for modern chemicals and products. In this study, we seek to create tunable polymers using 5-hydroxymethylfurfural (HMF) as a renewable platform chemical. The properties of the final polymer can be tuned by modifying the side-chain of the monomer, which is added by the etherification of HMF. Several different catalysts with a variety of active sites and pore structures were evaluated for their activity in the etherification reaction. We have also evaluated the interplay of R-group identity and active site structure on the etherification kinetics. Catalysts possessing Brønsted acid sites showed the highest selectivities to the ether product. Catalysts without Brønsted sites were an order of magnitude less active and selective than those with Brønsted sites. The improved selectivity observed for H-BEA-Zeolite, compared with Amberlyst-15, is hypothesized to be due to the ability of the zeolite to stabilize reaction intermediates. When the rate of production of the ether product was evaluated for BEA Zeolite and Amberlyst-15 it was found that although the consumption rates were comparable, the ether

production rate depends on catalyst identity. Increasing the size of the alcohol decreases the production rates, and the rate of production of all ether products was consistently higher for H-BEA Zeolite for all alcohols tested. Based on these results, we hypothesize that the structure of H-BEA Zeolite leads to improved activity for etherification. We suggest that Brønsted acidity is needed for etherification, and catalyst morphology may also be significant.

Xiaoduo Qi, Vivek Vattipalli, Paul Dauenhauer and Wei Fan, “Understanding diffusion pathway of cyclohexane through nanoscale MFI zeolite”, University of Massachusetts Amherst

Zeolites have been widely used in the fields of shape selective catalysis and separation due to their unique molecular sieving property. During catalytic reactions, reactants diffuse into pore network, react at active site, and diffuse out of pore network. To minimize the effects of internal mass transfer limitation on the overall reaction rate, nanoscale zeolite crystals have been designed and synthesized. However, within small zeolite crystals, diffusion study has shown that the apparent diffusivity appears to be orders of magnitude smaller than that for large zeolite crystals. This discrepancy of apparent diffusivity has led to the phenomena called “Surface Barrier”, which is a general term to describe a mass transfer resistance near the surface of zeolites. For large zeolite particles, since the internal micropore diffusion is dominant, such a surface resistance is often negligible. While for small zeolite particles, the surface resistance can contribute significantly to the overall mass transfer rate.

To explain the origin of the surface barrier, pore blockage and pore narrowing mechanisms have been proposed². However, with such hypotheses, Kinetic Monte Carlo simulation suggested 99.9% of the micropores on external surface have to be blocked³. In this presentation, we propose a new “Pore Re-entry” mechanism. According to this mechanism, molecules undergo a surface diffusion on the external surface during the desorption step. The surface diffusion is much slower than the Knudsen diffusion. Diffusion on the external surface might lead to re-entering of micropore openings, which significantly increase apparent diffusion length for the molecules. In order to demonstrate the existence of such effects, silicalite-1/silica nanoparticle mixtures were developed where silicalite-1 particles were isolated from each other by 35 nm solid silica nanoparticles. Mass transport study using cyclohexane suggested that the diffusion of cyclohexane is still controlled by the micropore diffusion with the same activation energy, but much faster in the mixtures, providing a strong evidence for the existence of the Pore Re-entering effect. The observation provides critical information for the rational synthesis of hierarchical porous materials for the applications in separation and catalysis.

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Xiong Peng, Travis J. Omasta, William A. Rigdon, Lianqin Wang, John R. Varcoe and William E. Mustain, “Catalyst and Electrode Advances for High Performing PEM and AEM Fuel Cells”, University of Connecticut

Recent advances in polymer electrolyte membrane fuel cells have brought the technology extremely close to finally fulfilling its promise as a high efficiency, sustainable energy source for transportation applications^{1,2}. An overwhelming amount of work in this area has focused on the proton exchange membrane fuel cell (PEMFC), where high performance has been achieved. However, proton-based systems still suffer from very high materials cost of both the membrane and catalysts, and the need to drive costs down by reducing material loading generally leads to accelerated degradation of otherwise stable systems as well as increased sensitivity to water due to the reduced water capacity with thinning catalyst layer thickness. To overcome these limitations, our group has developed an air-assisted cylindrical liquid jets spraying system that allows for the precise control of the catalyst layer microstructure, leading to high-performance catalyst-coated membranes. The system design and influence of operating parameters on PEMFC performance will be shown. On the materials side, our team has produced Ni-rich PtNi alloys and Pt₃Ni alloy nanocages that have shown very highly activity for the oxygen reduction reaction (ORR) and excellent stability at PEMFC cathode conditions. This poster will show the structure and chemistry of the Pt-Ni catalysts as well as their in-situ and ex-situ performance. The Pt-Ni nanocage PEMFCs have shown behavior that well exceeds the DOE targets for activity and comes very close to the DOE targets for durability. From both an activity and durability perspective, these Pt-Ni nanocage catalysts considerably outperform state-of-the-art commercial Pt/C catalysts. Another low-temperature alternative to the PEMFC that has been widely discussed in recent years is the anion exchange membrane fuel cell (AEMFC). The AEMFC has an effective pK_a much higher than the PEMFC, and this basic environment has several possible advantages over the acid system, including a less corrosive environment for the catalyst and catalyst support, which opens up the periodic table with regards to possible materials to be employed. Also, it is well known that the kinetics for the ORR are more facile in alkaline media than acid media³, though the converse is true for the hydrogen oxidation reaction, which necessitates the study for advanced Pt catalysts such as PtRu⁴. Our recent work has shown that the internal water dynamics in the AEMFC is likely more complex than the PEMFC. In this poster, the influence of the membrane, ionomer and gas diffusion layer as well as the flow rate and dew points of the anode and cathode gases on anion exchange membrane fuel cell performance will be shown. After cell optimization, a peak power density of 1.2 W/cm² has been reproducibly achieved with radiation-grafted ETFE membranes and ionomers.

Vivek Vattipalli and Wei Fan, “Direct fluoride-free synthesis of pure silica zeolites”, University of Massachusetts Amherst

Zeolites are widely used as adsorbents, solid catalysts and as ion exchangers, and are known to have exciting potential in separations, drug delivery and as low-k dielectric materials. Pure silica zeolites are ideally suited for these emerging applications mainly due to their high hydrothermal stability, hydrophobicity and dielectric properties. However, their synthesis remains a challenge. The International Zeolite Association – Structure Commission (IZA-SC) recognizes 232 zeolite frameworks, of which less than 50 have been made in pure silica form.

Hydrothermal synthesis with hydrogen fluoride is the most successful synthetic strategy for their synthesis, with more than 90% of the known pure silica zeolites having been synthesized by the method. However, the use of hydrogen fluoride adds significant cost and safety-related hindrances

to the commercialization of these pure silica zeolite materials. The dry gel conversion (DGC) technique has been used to make Si-MFI and Si-BEA zeolites in the absence of fluoride. In this study, we show that the DGC technique may be generalized to synthesize new pure silica zeolites without the use of hydrogen fluoride. We use it to synthesize Si-CHA and Si-STT zeolites for the first time without hydrogen fluoride. We also propose a new metric to evaluate pure silica zeolite syntheses, and which can help determine the most-suited technique to be used in their synthesis.

Sanket Sabnis, Vijesh Tanna, Chao Li, Jiabin Zhu, Vivek Vattipalli, Stephen Nonnenmann, Henning Winter and Wei Fan, “Exfoliation of 2-dimensional zeolites in liquid polybutadienes”, University of Massachusetts Amherst

Layered zeolite precursors were successfully exfoliated by briefly shearing or sonication with the assistance of commercially available telechelic liquid polybutadienes at room temperature. The exfoliated zeolite nanosheets can form a stable suspension in an organic solvent, providing an exciting potential for the fabrication of zeolite membranes, composite materials and hierarchical zeolites.

Alex R Maag, Alex D. Paulsen, Ted J. Amundsen, Paul E. Yelvington, Geoffrey Tompsett and Michael T. Timko, “Model Hydrothermal Liquefaction Chemistries using CeZrOx Catalyst”, Worcester Polytechnic Institute

Research to produce fuels and chemicals from biomass and/or biowaste feedstocks has been driven by the need to reduce our reliance on fossil fuels and find an alternative to meet our growing energy demand. Hydrothermal liquefaction (HTL) is a promising process that reacts wet organic solids at moderate temperatures and high pressures without the need for a costly biomass drying step. HTL reactions utilize water as both a solvent and reactant to form a biphasic product with a carbon rich oil phase with high heating value and a water soluble organic byproduct. It is desirable to upgrade the organics in the water phase to reduce wastewater generation. In preliminary HTL runs on food waste, it was discovered that CeZrOx increased oil yields relative to other commonly used catalysts at 300 °C and 20.7 MPa. Model HTL reactions using CeZrOx have been performed with minimal activity for catalyzing reactions involving only alcohol, carboxylic acid or ketones. In contrast, CeZrOx was highly active – and selective – for reactions involving aldehydes, with alkenes as the primary products formed. For example, pentanal self-condensation reactions under HTL conditions produced a decenone product that phase separated into an oil phase. On-going work is focused on optimizing the catalyst properties and catalytic reactor conditions.

Bryan E. Sharkey and Friederike C. Jentoft, “Solid Catalysts for the Deoxydehydration of Biomass-Derived Polyols to Olefins”, University of Massachusetts Amherst

Deoxydehydration (DODH) is an oxo-transition metal catalyzed reaction which can convert a vicinal diol to an olefin in a single step by a combined dehydration and deoxygenation using a reductant. This reaction is a very promising tool for upgrading biomass-derived polyols for fuels and chemicals production as it provides both selective deoxygenation and introduces alkene functionality. Deoxydehydration has been demonstrated with high yield using homogeneous rhenium catalysts. With the goal of developing robust and selective heterogeneous catalysts for the deoxydehydration reaction, solid catalysts using ReOx and MoOx active species on a range of polar oxide supports were prepared using incipient wetness impregnation. These catalysts were tested for

catalytic activity and recyclability using 1,2-decanediol as the reactant, triphenylphosphine as the reductant, and toluene as the solvent. The rhenium supported catalysts were found to be more active and demonstrated 75-90% yield of the expected alkene product, where as the solid molybdenum catalyst were found to be catalytic, but with only 15-20% yield. The most active solid rhenium catalysts were found to lose activity on subsequent runs. Leaching was found to be the primary cause of catalyst deactivation, and the parameters that control leaching behavior were investigated.

Koushik Ponnuru, Jinesh C. Manayil, Hong Je Cho, Amin Osatiashtiani, Karen Wilson, Wei Fan and Friederike C. Jentoft, “Solid Catalysts for Regioselective Aldol Condensations”, University of Massachusetts Amherst

Aldol condensation has drawn strong interest for valorization of short oxygenates in biomass-derived pyrolysis oil to produce molecules with longer carbon chains and lower oxygen content. This reaction proceeds by a C-C bond formation followed by subsequent dehydration. Although prior studies in literature examined distinct catalysts with acid, base, and cooperation of acid-base site pairs for aldol condensation, knowledge pertaining to the mechanistic detail, specifically on the regioselectivity and demarcation of the two reaction steps is limited. Furthermore, studies on solid base catalysts for aldol condensation proved that they are unstable under acidic conditions and are therefore not suitable for upgrading the bio-oil mixtures as they typically contain a high percentage of carboxylic acids. Hence, there is a need to develop selective solid catalysts that are stable in biomass-derived feedstock. In this study, we developed and tested several families of Brønsted and Lewis-acidic catalysts including sulfonic-acid functionalized SBA-15 with or without hydrophobization, sulfated zirconias, and isomorphously substituted zeolites in polar and nonpolar solvents. Benzaldehyde and 2-butanone were chosen as diagnostic reactants to elucidate the association of activity with sites on the solid catalysts. We demonstrated that both aldol reaction steps (addition and dehydration) and regioselectivity of the cross-aldol condensation involving asymmetric ketones can be controlled by tuning the nature, density, and environment of the active site.

Kevin X. Lee, George Tsilomelekis, Julia A. Valla, “Selective Removal of Refractory Sulfur Compounds from Hydrocarbon Fuels using Bimetallic Mesoporous Y Zeolites”, University of Connecticut

The biggest challenge for the deep desulfurization of transportation fuels is the heavy, refractory sulfur compounds, such as dibenzothiophene (DBT). The presence of other aromatic compounds in fuels, including those containing high energy density, makes selective removal of the sulfur compounds even more difficult. In this study we demonstrate that adsorptive desulfurization using bimetal-exchanged mesoporous Y zeolites can overcome the aforementioned challenges, by selectively targeting only the sulfur-containing molecules, while still exhibiting high sulfur adsorption capacity. The mesopores shorten the diffusion path length toward the internal active sites of the zeolite, while the metals (Ce and Cu), not only create relatively stronger bonds, but also multiple adsorption configurations. The bimetallic mesoporous Y zeolites were prepared using a templated top-down approach, followed by the introduction of the metals, Cu and Cu, via ion-exchange. The ability of each material to remove sulfur compounds was demonstrated by fixed-bed experiments. The adsorption mechanisms were further studied, at the molecular level, using in-situ DRIFTS. Our results indicate that the metals display high affinity for sulfur compounds, via either π -complexation

or σ -bond interaction. Specifically, Ce-exchanged Y zeolites exhibit multiple adsorption modes, as they can adsorb sulfur compounds via the different configurations. The mesoporosity in Y zeolites enabled the adsorption of refractory sulfur compounds, with a diffusion coefficient of 4.5x greater than the Y zeolite. In conclusion, bimetallic mesoporous Y zeolites exhibited the highest DBT removal ability due to both improved mass transfer and high adsorption energy.