Catalysis Club
of
Chicago

2023 Young Scientist Symposium

January 13, 2023
9:30 AM – 5:00 PM CDT

Virtual Meeting, Held via Zoom

2023 Young Scientist Symposium Program

all times listed in CDT

Main Zoom Link
To be shared with valid registrants

Poster Session Link
To be shared with valid registrants

First Session

9:30 **Opening Remarks**

9:35 **Tuning Active Site Distributions in Zeolite Catalysts for Regioselective Toluene Methylation to para-xylene**
Sopuruchukwu Ezenwa, Purdue University

10:00 **Oxidation by Reduction: Electrocatalytic Reduction of Peroxydisulfate for Efficient and Selective Oxidation of Alcohols**
Mayank Tanwar, University of Minnesota

10:25 **Technical Keynote**

Catalysis at Subvalent Nitrogen Fragments
David Powers, Texas A&M

11:05 **Break**

Second Session

11:10 **The Dependence of Olefin Hydrogenation and Isomerization on Zirconium Metal-Organic Framework Structure**
Kenton Hicks, Northwestern University

11:35 **Upcycling of Polyolefins using Supported Catalysts**
Jessica Lamb, Argonne National Laboratory

12:00 **Plasma-Assisted Approaches for the Direct Conversion of Natural Gas to Liquid Products**
Deanna Poirier, University of Notre Dame

12:25 **Lunch**

Third Session

12:40 **Poster Session 1: Even Numbers**
Gather Town

1:35 **Poster Session 2: Odd Numbers**
Gather Town

2:30 **Break**

Fourth Session

2:35 **Polyethylene in Dead-End Silica Nanopores: Forces and Mobility from Non-Equilibrium Statistical Mechanics and EXSY NMR**
Ziqiu Chen, University of Illinois at Urbana-Champaign

3:00 **Elucidation of Mechanistic Origins of Strong Metal Support Interactions by Bridging the Gap Between Surface Science and Technical Catalyst Environments**
Kaustubh Sawant, Purdue University

3:25 **Connection Between Framework Composition and Formation of Active Sites in Cu-CHA Zeolites for Partial Methane Oxidation to Methanol**
Jose Rebolledo-Oyarce, University of Notre Dame

3:50 **Career Pathways Panel Discussion: Careers in Industrial and National Lab R&D**
Cory Phillips, Air Company
Max Delferro, Argonne National Laboratory

4:50 **Closing Remarks**
Announcement of Prizes

Acknowledgements

The Catalysis Club of Chicago would like to thank the following people for their generous contributions to the success of the 2023 Young Scientist Symposium, including:

- Saumil Chheda (University of Minnesota at Twin Cities)
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2023 Young Scientist Symposium Abstracts

Oral Presentations (in order of appearance)

Note: All oral presentations will be hosted via the main symposium Zoom link.

Oral #	Title & Speaker
1	**Tuning Active Site Distributions in Zeolite Catalysts for Regioselective Toluene Methylation to para-Xylene** Sopuruchukwu Ezenwa, Purdue University
2	**Oxidation by Reduction: Electrocatalytic Reduction of Peroxydisulfate for Efficient and Selective Oxidation of Alcohols** Mayank Tanwar, University of Minnesota
Technical Keynote **Catalysis at Subvalent Nitrogen Fragments** David Powers, Texas A&M	
3	**The Dependence of Olefin Hydrogenation and Isomerization on Zirconium Metal-Organic Framework Structure** Kenton Hicks, Northwestern University
4	**Upcycling of Polyolefins using Supported Catalysts** Jessica Lamb, Argonne National Laboratory
5	**Plasma-Assisted Approaches for the Direct Conversion of Natural Gas to Liquid Products** Deanna Poirier, University of Notre Dame
6	**Polyethylene in Dead-End Silica Nanopores: Forces and Mobility from Non-Equilibrium Statistical Mechanics and EXSY NMR** Ziqiu Chen, University of Illinois at Urbana-Champaign
7	**Elucidation of Mechanistic Origins of Strong Metal Support Interactions by Bridging the Gap Between Surface Science and Technical Catalyst Environments** Kaustubh Sawant, Purdue University
8	**Connection Between Framework Composition and Formation of Active Sites in Cu-CHA Zeolites for Partial Methane Oxidation to Methanol** Jose Rebolledo-Oyarce, University of Notre Dame
Career Pathways Panel Discussion: Careers in Industrial and National Lab R&D Cory Phillips, Air Company Max Delferro, Argonne National Laboratory	

Poster Presentations

Note: Poster presenters should be at their poster for one of the two sessions; even numbers will present at 12:40 pm CDT and odd numbers will present at 1:35 pm CDT

Poster Session Link: To be shared with valid registrants

Poster #	Title & Authors
1	**Investigation of Cu-CHA Catalyst Composition and Structure on Catalytic Partial Methane Oxidation** Andrew D. Mikes, Rajamani Gounder
2	**Probing Plasma-Catalyst Interactions using In Situ/Operando Transmission Infrared Spectroscopy** Russell J. Clarke and Jason C. Hicks
3	**Electrostatic Manipulation of Lewis Acidity in Ultrathin Oxides via Catalytic Condensers** Sallye R. Gathmann, Tzia Ming Onn, C. Daniel Frisbie, and Paul J. Dauenhauer
4	**Elucidating Plasma-Catalytic Interactions through Plasma-Temperature Programmed Reactions** Hope O. Otor, Patrick M. Barboun, Hanyu Ma, Anshuman Goswami, William F. Schneider, and Jason C. Hicks
5	**Production of Aromatics via Plasma-Assisted Methane Dehydroaromatization over Mo/H-ZSM-5** Gerardo J. Rivera-Castro, Ibukunoluwa Akintola, David B. Go and Jason C. Hicks
6	**Thermal-Electro-Chemical Synthesis of Ammonia Over Molybdenium Oxynitrides** Arthur J. Shih, Dylan Bardgett, Elise A. Goldfine, Louis S. Wang, Ben Yu, Grace Xiong, Paul Chery, Trevor Worthy, Sarah Bogan, Tiffany Miao, Sossina M. Haile
7	**Effects of Acid Site Proximity in CHA Zeolites on Kinetics of Protolytic Propane Cracking and Dehydrogenation** Bereket T. Bekele, Rajamani Gounder
8	**Mechanistic Insights into the Hysteresis Phenomena during NH_3 Oxidation on Pt/Al_2O_3 Catalysts for NH_3 Slip Applications** Brandon K. Bolton, Hanyu Ma, Amish Chovatiya, Rohil Daya, Dylan S. Trandal, Krishna Gunugunuri, Krishna Kamasamudram, William F. Schneider, Rajamani Gounder
9	**Localized Structural and Compositional Kinetic Effects on Single Ni^{2+} Sites for Light Olefin Oligomerization** Yoonrae Cho, Allen Oliver, and Jason C. Hicks

10	**Quantifying the Kinetics of Framework Dealumination during Hydrothermal Aging of Proton-Form CHA Zeolites** Tania L. Class Martínez, Subramanian Prasad, Ahmad Moini, and Rajamani Gounder
11	**Investigating the influences of different Si and Al sources on accelerating the kinetics of interzeolite conversion of FAU to CHA** Ricem Diaz Arroyo, Stacey I. Zones, and Rajamani Gounder
12	**Continuous Flow Electrochemical Alkene Epoxidation Kinetics** Richa Ghosh, Drew W. Hollyfield, Andrew A. Gewirth, and David W. Flaherty
13	**Investigation of Selective Cu-Ga-Zr Catalysts for CO_2 Hydrogenation to Methanol** Abdullah J. Al Abdulghani, Edgar E. Turizo-Pinilla, Ryan H. Hagmann, Theodore O. Agbi, Maria J. Fabregas-Angulo, Diana M. Aponte-Claudio, Paola N. Fargas-Lopez, Faysal Ibrahim, Morgan Kraimer, Yomaira J. Pagan Torres, Ive Hermans
14	**Non-Mean Field Approaches for Surface Catalysis: Analytical Description of Adsorbate-Adsorbate Interactions** Purva Paranjape and Jeff Greeley
15	**Carbon Deposits as Possible Active Sites for Non-Oxidative Methane Coupling Reactions** Luke Nunzio Pretzie and Dr. Jeffrey Greeley
16	**Structural Changes to Molybdenum and Brønsted Acid Sites on Mo-MFI during Methane Dehydroaromatization Reaction-Regeneration Cycles** Ángel N. Santiago-Colón, Rajamani Gounder
17	**First-Principles Analysis of the Ammonia Decomposition Reaction on High Entropy Alloy Catalysts** Zuhal Cakir, Liangbing Huand, Chao Wang, and Jeffrey Greeley
18	**Sulfated Zirconium Metal–Organic Frameworks as Well-Defined Supports for Enhancing Organometallic Catalysis** Zoha H. Syed, Mohammad Rasel Mian, Roshan Patel, Haomiao Xie, Zihan Pengmei, Zhihengyu Chen, Florencia A. Son, Timothy A. Goetjen, Alon Chapovetsky, Kira M. Fahy, Fanrui Sha, Xingjie Wang, Selim Alayoglu, David M. Kaphan, Karena W. Chapman, Matthew Neurock, Laura Gagliardi, Massimiliano Delferro, and Omar K. Farha

Oral 1 - Tuning Active Site Distributions in Zeolite Catalysts for Regioselective Toluene Methylation to para-Xylene

Sopuruchukwu Ezenwa,[1] Deng-Yang Jan,[2] Rajamani Gounder[1,*]

1. Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN
2. Honeywell UOP, Des Plaines, IL

Zeolites are aluminosilicates with diverse micropore sizes and shapes that have enabled controlling reactivity and selectivity by imposing constraints on reactant and product diffusion or on transition state formation; yet, even a given zeolite can show catalytic diversity because of differences in the distribution of proton (H^+) active sites among distinct void environments.[1] During zeolite synthesis, organic and inorganic structure directing agents (SDA) influence aluminum (Al) substitution at distinct framework tetrahedral sites, motivating synthetic approaches to tune Al distribution (and associated H^+ sites) to influence reaction pathways.[2] During toluene methylation (573–773 K), MFI zeolites produce *para*-xylene (*p*-X) in supra-equilibrium quantities because of contributions from intracrystalline transport phenomena and side reactions.[3] Here, we investigate how synthetic approaches can bias the distribution of active sites within MFI zeolite voids and demonstrate the consequences for regioselective toluene methylation to *p*-X under low-temperature conditions (<433 K) free of influences of external acid sites, intracrystalline residence times, and reactor-bed residence times.

MFI samples with fixed Al content were synthesized with conventional and non-conventional organic SDAs and further evaluated for toluene methylation in a packed-bed reactor. On the suite of MFI prepared using conventional SDAs, the xylene isomer selectivity (*p*-X/*o*-X ~ 0.4–0.5) was consistent with electrophilic aromatic substitution patterns governed by stabilization of kinetically relevant transition states and intermediates *via* resonance and inductive effects. However, the *para*-regioselectivity (*p*-X/*o*-X ~ 3–7) of the second suite of MFI samples synthesized by non-conventional SDAs could not be explained solely by such effects. Furthermore, initial xylenes formation rates (per H^+) on the first MFI suite were 4–10× higher than those on the second MFI suite. Rates were zero-order in dimethyl ether (DME) pressures (>25 kPa) and transitioned from first-order to zero-order dependence in toluene pressures (0.2–8.8 kPa), which reflect increasing coverages of co-adsorbed toluene on DME-derived intermediates that subsequently react *via* kinetically relevant C–C formation.[4] Although toluene adsorption constants (K_C) were similar on both MFI subsets, toluene methylation rate constant (k_X) and xylenes formation rate constant ratios (k_{pX}/k_{oX}) differed between MFI subsets respectively by up to 9× and 14×. Kinetic investigations on aluminosilicates (TON, MFI, BEA, MCM41) with acid sites located within varying void sizes (0.53–3.0 nm) revealed that rate and selectivity differences among the MFI catalysts reflect the consequences of transition states confined within distinct MFI voids. Our findings indicate that the SDAs used to crystallize MFI result in different active site distributions that influence kinetically controlled rates and selectivities during toluene methylation. Taken together, the ability to tune active site distributions to manipulate reaction pathways has broader implications in catalyst design for the selective upgrading of chemical feedstocks from fossil and renewable resources.

References:
(1) Gounder, R.; Iglesia, E. *Chem. Commun.* **2013**, *49*, 3491.
(2) Knott, B. C.; Nimlos, C. T.; Gounder, R. et al. *ACS Catal.* **2018**, *8*, 770.
(3) Ahn, J. H.; Lercher, J. A. et al. *Microporous Mesoporous Mater.* **2015**, *210*, 52.
(4) Hill, I.; Malek, A.; Bhan, A. *ACS Catal.* **2013**, *3*, 1992.

Oral 2 - Oxidation by Reduction: Electrocatalytic Reduction of Peroxydisulfate for Efficient and Selective Oxidation of Alcohols

Mayank Tanwar,[1] Seyyedamirhossein Hosseini,[2] Jordyn N. Janusz,[2] Andrew D. Pendergast,[2] Henry S. White,[2,*] and Matthew Neurock[1,*]

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Alcohol oxidation is often carried out under harsh catalytic conditions using organometallic complexes as catalysts. Electrochemical oxidation of alcohols typically requires large overpotentials to overcome the sluggish kinetics for C-H activation. Mediators such as 2,2,6,6-Tetramethylpiperidinyloxyl (TEMPO) have been successfully employed to reduce these large overpotentials.[1] Unfortunately, these mediators are relatively expensive, unsuitable for large-scale reactions, and show limited modularity. Baran and coworkers developed N-ammonium ylide mediators to help resolve the modularity issue.[2] However, oxidation with ylide mediators still requires large positive overpotentials.

Herein, we discuss a new electrochemical synthetic method developed by the White group in which reduction activates an organic or organometallic intermediate that can subsequently selectively oxidize substrates.[3] This reductive oxidation approach was carried out herein to reduce peroxydisulfate ($S_2O_8^{2-}$) to drive alcohol oxidation reactions. Thus, counter-intuitively, alcohol oxidation occurs due to an electrochemical reduction reaction at much lower overpotentials. First-principles density functional theory calculations and ab-initio molecular dynamics simulations, in conjunction with cyclic voltammetry and finite element difference simulations, establish the resulting reaction pathways and provide insights into the mechanism.

The electrocatalytic reduction of $S_2O_8^{2-}$ is initially carried out by a $Ru(NH_3)_6^{3+/2+}$ mediator. $Ru(NH_3)_6^{3+}$ is initially reduced at the cathode to form $Ru(NH_3)_6^{2+}$, which transfers an electron to $S_2O_8^{2-}$ in a rate-limiting electron transfer step. The reactive $S_2O_8^{3-\bullet}$ radical anion intermediate that forms has a lifetime of the order of picoseconds and concertedly disproportionates to generate SO_4^{2-} and the highly oxidizing $SO_4^{-\bullet}$. This dual-mediated strategy reduces the overpotential for the reduction of $S_2O_8^{2-}$ and homogeneously forms $SO_4^{-\bullet}$ away from the electrode surface, mitigating the direct reduction of this species. $SO_4^{-\bullet}$ then carries out subsequent hydrogen atom abstractions and proton-coupled-electron transfer steps.

Thus, alcohol oxidation is initiated by the redox-mediated electrocatalytic reduction of peroxydisulfate to generate the highly oxidizing sulfate radical anion. This strategy provides a selective synthetic route for the oxidation of alcohols to aldehydes, ketones, and carboxylic acids with up to 99% conversion yields carried out under mild conditions.

References

(1) J. E. Nutting, M. Rafiee, and S. S. Stahl, *Chem. Rev.*, **2018**, 118, 4834–4885.
(2) M. Saito et al., *J. Am. Chem. Soc.*, **2021**, 143, 7859–7867.
(3) S. Hosseini, J. N. Janusz, M. Tanwar, A. D. Pendergast, M. Neurock, and H. S. White, *J. Am. Chem. Soc.*, **2022**, 144, 21103−21115.

Technical Keynote: David Powers

Dave was born in Allentown, PA and pursued undergraduate education at Franklin and Marshall College. He earned a Ph.D. from Harvard University with Prof. Tobias Ritter and pursued postdoctoral research at the Massachusetts Institute of Technology and Harvard University with Prof. Daniel Nocera. He joined the Texas A&M faculty in 2015 and was promoted to Associate Professor in 2021. His research program focuses on the chemistry of sustainably generated reactive intermediates in catalysis and has been recognized by an NSF CAREER award, a DOE Early Career Award, and NIH MIRA, and a 2020 Sloan Fellowship.

Catalysis at Subvalent Nitrogen Fragments

David Powers

Texas A&M

Direct C–H amination chemistry via electrophilic subvalent nitrogen intermediates could radically simplify access to nitrogen-containing small molecules by providing the chemical tools to selectively convert ubiquitous C–H bonds to valuable C–N bonds. At present, challenges in chemoselectivity, sustainability, and synthetic versatility prevent realization of the synthetic potential of C–H amination. This talk will describe recent efforts from the Powers Laboratory that advance 1) new strategies to structurally characterize transient intermediates in C–H functionalization reactions, 2) novel metal-free approaches to the sustainable generation of strong oxidants needed in C–H functionalization reactions, and 3) bifunctional reagent platforms that enable rapid elaboration of the primary products of C–H amination. Future directions and challenges will be discussed.

Oral 3 - The Dependence of Olefin Hydrogenation and Isomerization Rates on Zirconium Metal–Organic Framework Structure

Kenton E. Hicks,[1] Andrew T.Y. Wolek,[2] Omar K. Farha[1,2*], Justin M. Notestein[2]

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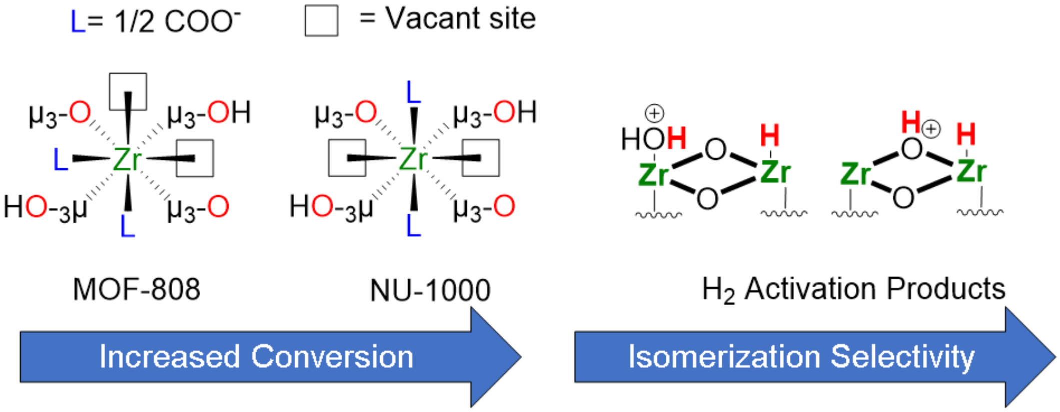
2. Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois 60208, United States

Metal–organic frameworks (MOFs) are a class of synthetically-tunable, porous materials, that are composed of metal clusters connected by organic ligands; these materials have been increasingly studied in heterogeneous catalysis due to their structural tunability and crystallinity. Of these materials, zirconium-based MOFs are most commonly studied due to their thermochemical stability and Lewis acidity. Previously, we found that the Zr_6O_8 building unit of the MOF, 'NU-1000' can heterolytically cleave H_2 over adjacent Lewis acid and base sites, leading to catalytic hydrogenation and isomerization of 1-butene, with kinetic studies suggesting the presence of parallel acid- and hydride- catalyzed pathways for olefin conversion.[1] In this presentation, these findings are expanded upon by studying the influence of thermal pretreatment and MOF topology surrounding Zr_6O_8 clusters on cluster activity for 1-butene hydrogenation and isomerization in a series of Zr-MOF catalysts sharing the same Zr_6O_8 cluster (MOF-808, NU-1000, UiO-66, NU-1000-NDC). Diffuse reflectance Infrared Spectroscopy in the presence of H_2 and pyridine shows that both thermal pretreatment and MOF topology affect the Brønsted acidity of protons generated from H_2 activation and resulting in differences in activity and selectivity for olefin hydrogenation and isomerization across catalysts and pretreatment conditions. High isomerization activity of dehydrated NU-1000 is correlated with the formation of μ_3OH species after H_2 activation. Additionally, catalytic and structural comparison across the series of Zr-MOFs shows that the geometric orientation of adsorption sites on Zr_6O_8 clusters affects butene hydrogenation activity, with wider angled orientations imbued by MOF topology performing better than others. These results indicate the importance of pretreatment in defining MOF catalytic activity and that MOF topology can affect the catalytic activity of otherwise structurally identical metal oxide clusters.



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(1) Hicks, K.E.; Rosen, A.S.; Syed, Z.H.; Snurr, R.Q.; Farha, O.K.; Notestein, J.M. *ACS Catal.* **2020**, 10, *24*, 14959.
(2) Hicks, K.E.; Wolek, A.T.Y.; Farha, O.K.; Notestein, J.M. *ACS Catal.* **2022**, 12, *21*, 13671.

Oral 4 - Upcycling of Polyolefins using Supported Catalysts

Jessica V. Lamb and Massimiliano Delferro*

Argonne National Laboratory, IL

Worldwide, over 400 million tons of plastics are generated annually, of which polyolefins constitute over half of the industrial market. Over 50% of these plastics are utilized in single-use products with over ~75% discarded annually.[1] Current plastic waste management options are limited and primarily consist of incineration, pelletizing- and molding-based recycling, and disposal to landfill (Figure 1). Furthermore, these methods often lead to hazardous emissions, downcycled products with restricted applications, and widespread environmental concerns. Therefore, there is a substantial need to seek alternative processes to chemically upcycle waste plastics into value-added products.

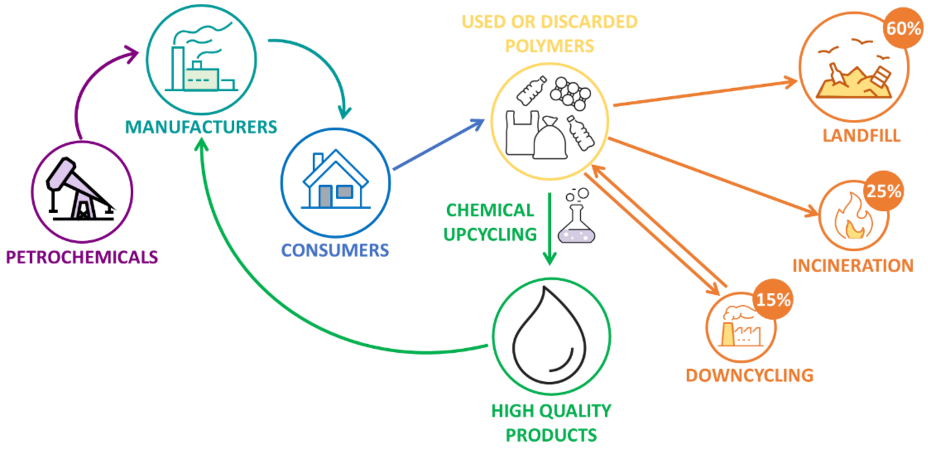

Figure 1. Current and future routes for addressing plastic waste.

This work targets the upcycling of polyethylenes using supported platinum nanoparticle catalysts selective for deconstruction via hydrogenolysis.[2-4] This process yields monodisperse liquid or wax products with significantly reduced molecular weights and increased branch density. Initial results suggest a relationship between support acidity and hydrogenolysis product properties. Furthermore, it has been found that the size and structure of the starting polymer only marginally affects the size and properties of the resulting product, allowing the potential to upcycle multiple streams of waste polyethylenes into a single product.

References:

(1) Geyer, R.; Jambeck, J. R.; Law, K. L., *Sci. Adv.* **2017**, 3 (7), e1700782.

(2) Celik, G.; Kennedy, R. M.; Hackler, R. A.; Ferrandon, M.; Tennakoon, A.; Patnaik, S.; LaPointe, A. M.; Ammal, S. C.; Heyden, A.; Perras, F. A.; Pruski, M.; Scott, S. L.; Poeppelmeier, K. R.; Sadow, A. D.; Delferro, M., *ACS Central Sci.* **2019**, 5 (11), 1795.

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(4) Hackler, R. A; Lamb, J. V.; Peczak, I.; Kennedy, R. M.; Kanbur, U.; LaPointe, A. M.; Poeppelmeier, K.; Sadow, A. D.; Delferro, M. *Macromolecules*, **2022**, 55, 15, 6801.

Oral 5 - Plasma-Assisted Approaches for the Direct Conversion of Natural Gas Streams to Value-Added Products

Deanna L. Poirier and Jason C. Hicks*

University of Notre Dame, IN

Carbon-nitrogen coupling reactions are important in the pharmaceutical and agrochemical industries.[1] However, these reactions often require high temperatures and pressures, and frequently use NH_3 as a source of nitrogen as it is easier to activate compared to the strong triple bond of N_2. In this work we demonstrate a process that utilizes nitrogen directly in the form of N_2 gas, and couples it with natural gas (i.e. methane) to produce valuable carbon and nitrogen containing products. Natural gas is an abundant source of hydrocarbons, but is difficult to activate due to the strong C-H bonds. Nonthermal plasmas are reactive mixtures of electrons, radicals, ions, and excited species that are able to activate stable molecules and perform diverse reaction chemistry at lower temperatures and pressures compared to thermal reactions.[2] Therefore, NTPs are able to activate the strong bonds of CH_4 and N_2 in order to directly produce valuable C2+ hydrocarbons and nitrogen-containing products.[3] While methane/nitrogen mixtures have been reported, less is known about how other hydrocarbons behave in the presence of nitrogen under plasma stimulation.

In this work we have studied the plasma activation of nitrogen and hydrocarbons to form C_xH_y, $C_xH_yN_z$, and H_yN_z species. We begin by studying a mixed feed ($CH_4/C_2H_6/C_3H_8/N_2$) representative of a natural gas mixture, and demonstrate that it can be upgraded to valuable gas, liquid, and solid products. More detailed studies were conducted to understand the influence of each hydrocarbon individually reacted with nitrogen, as well as the influence of parameters such as power input and feed composition (C_xH_y/N_2 ratio). Studies have focused on ethane, the second largest component of natural gas, and the insights gained will be applied to future studies on methane, which is more difficult to activate. For the C_2H_6/N_2 reaction, as the amount of dehydrogenation products (C_2H_4 and C_2H_2) increases by increased power input or increased hydrocarbon feed composition, the ammonia production also increases. This indicates that the hydrogen being liberated from these reactions is able to react with activated nitrogen to form ammonia. Although increasing the power increased the consumption and production rates of the reaction, the selectivity to C_2H_4 and C_2H_2 decreased, while methane selectivity increased as the dissociation pathways was favored. When varying the composition, the formation of liquid and solid products is observed in these nitrogen rich regions. Electrospray ionization mass spectrometry (ESI-MS) was used to identify the composition of these products. Evidence of -CH_2- and -HCN- chain growth was seen, as well as various levels of H_2 saturation. ATR-FTIR, XPS, and various NMR techniques were used to identify nitrile and amine functionalities in the products. This non-catalytic reaction shows the ability to produce valuable products from a hydrocarbon and nitrogen feed, and work is ongoing to shift the selectivity of this reaction by operating in different regimes and by use of a catalyst.

References:

(1) Ruiz-Castillo, P.; Buchwald, S. L. *Chem. Rev.* **2016**, *116*, 12564−12649.

(2) Mehta, P.; Barboun, P.; Go, D. B.; Hicks, J. C.; Schneider, W. F. *ACS Energy Lett.* **2019**, *4*, 1115–1133.

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Oral 6 - Polyethylene in Dead-End Silica Nanopores: Forces and Mobility from Non-Equilibrium Statistical Mechanics and EXSY NMR

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2. US DOE, Ames National Laboratory, Ames, IA, USA.
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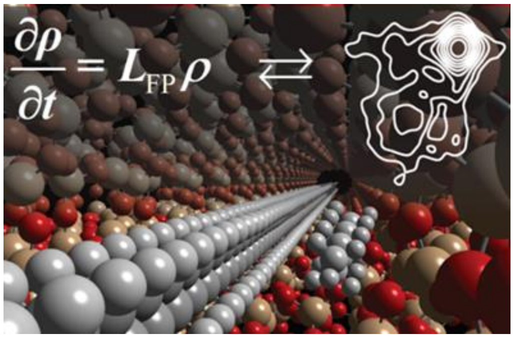

Billions of tons of plastic have been produced and only a small fraction of this has been recycled. Tennakoon et al.[1, 2] developed a catalyst that repeatedly cleaves C10-C30 hydrocarbons from the end of a polyethylene chain. The reaction occurs at a Pt nanoparticle at the base of a cylindrical silica mesopore with a diameter of 2 nm and a length of 110 nm. Portions of the polymer situated inside the pore can be differentiated from those outside using 13C NMR, allowing the dynamics and extent of polymer threading to be monitored using 2D EXSY NMR. We construct a Fokker-Planck equation for the polymer dynamics by assuming a reptation diffusivity and a graduated adsorption free energy that depends linearly on the depth of polymer penetration in the pore. The solutions allow us to predict the intensities of the 2D NMR resonances as a function of time. We use the solutions to extract a polymer diffusivity at each temperature and estimate the per-segment desorption free energy, enthalpy, and entropy. Random and systematic errors are examined to test key assumptions in the theory and interpretation of the experiments.

References:

(1) Tennakoon, A.; Wu, X.; Paterson, A. L.; Patnaik, S.; Pei, Y. C.; LaPointe, A. M.; Ammal, S. C.; Hackler, R. A.; Heyden, A.; Slowing, I. I.; Coates, G. W.; Delferro, M.; Peters, B.; Huang, W. Y.; Sadow, A. D.; Perras, F. A., Catalytic upcycling of high-density polyethylene via a processive mechanism. *Nat. Catal.* **2020,** *3*, 893-901.

(2) Wu, X.; Tennakoon, A.; Yappert, R.; Esveld, M.; Ferrandon, M. S.; Hackler, R. A.; LaPointe, A. M.; Heyden, A.; Delferro, M.; Peters, B.; Sadow, A. D.; Huang, W., Size-Controlled Nanoparticles Embedded in a Mesoporous Architecture Leading to Efficient and Selective Hydrogenolysis of Polyolefins. *J. Am. Chem. Soc.* **2022,** *144,* 5323-34.

Oral 7 - Elucidation of Mechanistic Origins of Strong Metal Support Interactions by Bridging the Gap between Surface Science and Technical Catalyst Environments

Kaustubh J. Sawant,[1] Junxian Gao[1], Zhenhua Zeng[1], Dmitry Zemlyanov[1,2], Jeffrey T. Miller[1] and Jeffrey P. Greeley[1, *]

1. Davidson School of Chemical Engineering, Purdue University, IN
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Ultrathin (hydroxy)oxide films on transition metal substrates serve as an important model system for oxide-metal interfacial interactions in heterogeneous catalysis, such as the strong metal support interaction (SMSI) and have been extensively studied under both surface science and technical catalyst conditions. However, in spite of these efforts, few general principles governing SMSI phenomena have been elucidated, and molecular-level models to predict the conditions under which SMSI is expected to occur do not exist. A significant challenge in developing such models is, in turn, the difficulty of constructing a thermodynamic framework that permits extrapolation of DFT predictions to both ultra-high vacuum conditions and technical catalyst environments. Since experiments under both sets of conditions have been used to explore the SMSI, having a flexible DFT/thermodynamic model of this type would be a significant benefit in interpreting these measurements and identifying general principles underlying SMSI behavior.

In this talk, we begin by introducing a novel mixed canonical – grand canonical scheme to permit rigorous comparison of Density Functional Theory (DFT) calculations, describing many different ultrathin film structures and stoichiometries, with UHV single crystal measurements. The predictions of the scheme match well with, and provide important structural and chemical details describing, ZnO_xH_y and TiO_xH_y films on a number of different metal substrates. Based on these results, we develop linear scaling relationships (SRs) between the (hydroxy)oxide film formation energies and simple adsorption energies of the corresponding cations and anions. The SRs permit efficient prediction of the stability of a variety of ultrathin films without the cost of DFT calculations. Next, we demonstrate that, by changing the thermodynamic ensemble under which the computational results are analyzed, the predictions can be extrapolated to conditions relevant to heterogeneous as well as electro-catalytic reactions. We use these insights to estimate which transition metals, under what conditions, are likely to exhibit SMSI behavior, as well as the molecular structure of the associated films. Finally, we discuss how SMSI overlayer formation for irreducible oxides like ZnO is connected to hydroxylation of ultrathin films. This observation is, in turn, mechanistically different from the SMSI overlayer formation in traditional SMSI systems like TiO_2, where the reduction of the support cation (Ti) is necessary. These molecular understandings facilitate the possibility of developing new catalytic active sites through rational exploitation of SMSI-like phenomena.

In order to analyze how these structures, affect important real-world chemistries and identify key descriptors that influence their reactivity we briefly looked at ZnO and $Zn_6O_5H_5$ model catalysts over metal surfaces. We found that the graphite-like ZnO interacts weakly with metal surface and barely affects the surface electronic properties. On the other hand, the honeycomb-like $Zn_6O_5H_5$ can contribute negative charge to the metal atoms confined within the zinc hydroxy rings and tune the adsorption behavior of common adsorbates like CO with little sacrifice of the total number of active sites. Such studies allow us to formulate design principles for metal nanoparticle catalyst coated with surface oxides since these systems play a crucial role in industrially relevant reactions.

Oral 8 - Connection Between Framework Composition and Formation of Active Sites in Cu-CHA Zeolites for Partial Methane Oxidation to Methanol

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The increase in the production of natural gas has led to increased efforts to make better use of this steam and add more value to its components[1,2]. Methane (CH_4) is majority presence in natural gas[3]. Due to this reason, research groups are trying to develop ways to convert methane to higher-value products such as long-chain alkanes or methanol[1,3]. Liquid methanol would reduce the storage and transportation costs of methane[1]. Many groups have been focused in the direct reaction of methane to methanol ($CH_4 + 0.5O_2 \rightarrow CH_3OH$) through understanding of the active site and the reaction mechanism[3].

Inspired by methane monooxygenase (MMO) enzymes that contain a transition metal as active site(s) (such as iron or copper), the direct conversion of methane can be performed by ion-exchange zeolites[4]. Among the possible exchange metals, Cu-exchanged zeolites have been vast study due to the high production of methanol in MOR, MFI, ZSM-5 or CHA[1,3,5]. However, the nature of the active site(s), it is still a mystery due to the complexity of measure in UV-vis-NIR spectroscopy for the overlapping of different type of active sites presence in one sample[6].

To avoid this problem, it is possible to group different type of active sites and determinate when these appear depending on Cu and Al loading in the zeolite sample. In this work, through a controlled process to add aluminum and copper to CHA samples, the fraction of Cu monomers (Z_2Cu and ZCuOH) and Cu dimers (e.g., mono-(μ-oxo)dicopper) was determined using a titration model[7] that considers the presence of dimers and the possibility of avoiding the presence of 2Al in the same - membered-ring[8].

These copper species were treated by different stream gas like CO or CH_4 to reduce them. This reduction confirmed that Z_2Cu is inactive on partial methane oxidation (PMO) and depending on Cu and Al loading different fraction of Cu dimers (O-bridged and O_2-bridged) are presence, and these species impact the reactivity of the sample in the PMO reaction. DFT calculations determined the impact of the Al arrangement on the formation of different Cu dimers and concluded a preference for 8MR 4NN and 8MR 3NN as mono-(μ-oxo)dicopper, however this Cu dimer exhibits different reactivity depending on the location in the framework.

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Poster 1 - Investigation of Cu-CHA Catalyst Composition and Structure on Catalytic Partial Methane Oxidation

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Copper-exchanged zeolites catalytically convert methane to methanol (533-573 K) with high selectivity (50-100%) at low conversions (<0.1%)[1]. Prior studies have determined that increasing the framework Al content and decreasing the extraframework Cu content increased the selectivity towards methanol but have not identified how these bulk compositional variables affected the number and structure of active Cu sites formed during steady state catalysis[2-3]. Herein, we studied how the distribution of Cu active sites in CHA was affected by increasing the extraframework Cu site density and altering the arrangement of framework Al atoms in chabazite (CHA) zeolites and their effect on continuous partial methane oxidation (PMO) kinetics, apparent reaction orders, and apparent activation energies. The number of 6-MR paired Al sites in CHA was varied using previously reported methods to use different combinations of organic and inorganic structure-directing agents during crystallization and quantified through Co(II) titration. All Cu-CHA samples showed PMO rates that were nearly first-order in methane pressure, consistent with prior reports that suggest C-H activation in methane is the rate limiting step. Cu-CHA samples with different framework Al arrangements showed that formation rates of over-oxidation products (e.g., CO_2) had different apparent reaction orders in O_2, implying differences in the Cu active sites formed during reaction. The number of redox-active Cu sites were quantified through linear combination fitting of XANES spectra collected under *in-situ* and transient conditions after reactant (O_2) cut-off. Characterization of Cu sites using *in-situ* and transient XAS and UV-vis indicate different types of binuclear oxo-bridged Cu active sites are formed during reaction and are influenced by the arrangement of framework Al atoms in CHA zeolite. This investigation highlights the effect of Al siting in zeolites on the structures of extraframework Cu complexes that form and, in turn, on partial oxidation rates and selectivity.

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Poster 2 - Probing Plasma-Catalyst Interactions using In Situ/Operando Transmission Infrared Spectroscopy

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In recent years, the prospect of combining nonthermal plasma with a heterogeneous catalyst to perform difficult and energy intensive chemical transformations at mild conditions has received widespread interest in the catalysis community. The highly energetic ions, radicals, and excited species generated by the non-equilibrium plasma react with increased activity over ground-state species, and subsequent coupling with certain catalytic materials has been observed to improve the activity further by largely unexplored mechanisms. The lack of knowledge about the complex role of the catalyst under plasma stimulation is owed to a shortage of versatile and accessible instrumentation capable of probing the plasma-catalyst interface *in situ*. Thus, we have developed a plasma-enabled FTIR transmission cell that utilizes a unique ring-electrode configuration to generate a dielectric barrier discharge-like plasma capable of interacting with a catalyst wafer. In addition to being simple to construct and adaptable to different configurations (e.g., for post-plasma catalysis for studying interactions with long-lived species), the IR cell is able to simultaneously interface with both OES and mass spectrometry to collect *operando* data on the plasma-phase, catalyst surface, and reactor effluent concurrently. The ability of the design to both induce and detect interactions between the plasma and a surface was verified by studying the plasma oxidation of aminosilica, which revealed a pathway to form nitrosilica that is not thermally accessible. Additionally, the cell was used to observe N_2 activation over Pt nanoparticles, highlighting the ability to observe species bound to metal active sites. These results emphasize the broad scope of foreseeable applications for this design and give merit to its usefulness as a tool for studying plasma-catalyst interactions.

Poster 3 - Electrostatic Manipulation of Lewis Acidity in Ultrathin Oxides via Catalytic Condensers

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We have proposed a new strategy for increasing catalyst performance, dynamic catalysis, in which the reaction coordinate changes with time to promote desired reactions.[1] Recently, we developed a method for synthesizing oxide-based catalytic condensers, a type of “programmable” catalyst that can be used to implement dynamic catalysis.[2,3] In these devices, an externally-applied electrical bias, V_{CAT}, condenses charge (e^- or h^+) into an ultrathin catalyst film, allowing for temporal manipulation of active site electron density. Herein, we describe the fabrication and characterization of an alumina-graphene catalytic condenser (**Fig. 1a**).

Our central result is that the alumina-graphene catalytic condenser can stabilize up to ~0.1 h^+/site, which then reduces the activation energy of isopropanol dehydration by ~16 kJ/mol. While bulk Al_2O_3 is an insulator with a large band gap (E_g ~8 eV), our ultrathin (4 nm) amorphous alumina film behaves like a poor semiconductor with E_g ~5 eV and gap states present near the Fermi level, allowing for conduction of holes (h^+). We conducted fixed-V_{CAT} temperature programmed surface reaction (TPSR) experiments of isopropanol dehydration and calculated the activation energy (E_a) by fitting TPSR data to a first-order Polanyi-Wigner equation (**Fig. 1b**). At no applied bias (V_{CAT} = 0 V, charge neutral), the alumina-graphene condenser reactivity is consistent with that of γ-Al_2O_3 (E_a of 115 kJ/mol vs. 117 kJ/mol, respectively). In comparison, at V_{CAT} = +3 V (~0.1 h^+/site), the condenser was significantly more Lewis acidic (E_a ~99 kJ/mol). These changes to the film’s activity were reversible, and no Ohmic heating was observed. Future work will utilize this device platform to demonstrate, fundamentally understand, and optimize charge-based dynamic catalysis.

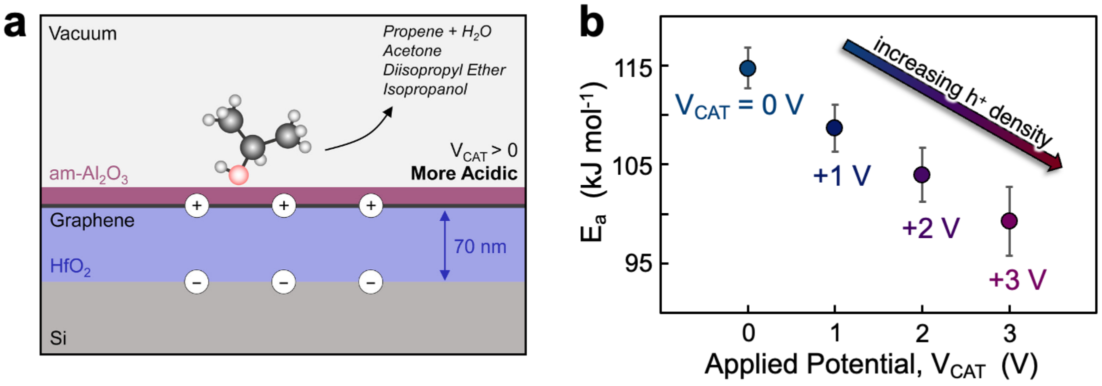

Figure 1. **(a)** Schematic of the alumina-graphene catalytic condenser. **(b)** Isopropanol dehydration TPSR demonstrates a monotonic decrease in E_a with increasing potential, V_{CAT}.

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Poster 4 - Elucidating Plasma-Catalytic Interactions through Plasma-Temperature Programmed Reactions

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Plasma enhanced catalysis is a growing field that leverages the contributions of both plasma and a heterogeneous catalyst in facilitating transformation of reactant molecules. Most plasma processes to date have relied upon the utilization of conventional thermally active catalysts. However, the design of materials that can effectively harness the plasma-catalyst synergy depends on the fundamental understanding of relevant plasma activated surface reaction pathways. Moreover, in these plasma-catalytic systems, plasma phase reactions can dominate, which often complicates the analysis and contribution of the catalyst surface reactivity to the overall product yields.[1]

In this presentation, we will discuss our recent efforts in utilizing sequential plasma driven experiments and temperature programmed reactions to probe the reactivity of plasma activated nitrogen on metal catalysts surfaces. By sequentially activating nitrogen using plasma prior to thermal reaction with a reactant gas (H_2 or O_2), we study the reactivity of plasma activated nitrogen under reductive and oxidative conditions. Our results show the formation of NH_3 over different supported metals catalyst (Fe, CO, Ni and Pt) after a plasma activated nitrogen surface is thermally treatment with H_2.[2] Thus, when N_2 activation is facilitated by plasma, the metal catalyst surface can facilitate subsequent hydrogenation to produce NH_3. Using microkinetic modelling simulations, we show that the NH_3 peak temperature scaled with the activation energy of the hydrogenation step, indicating that the hydrogenation ability is critical in elucidating reactivity trends from plasma stimulation. Further, we demonstrate the reactivity with O_2 over plasma-activated N_2 on Pt, Pd, Au and Ag. Here, we observed the formation of NO and N_2O, with the product selectivity dependent on the metal and metal dispersion. Overall, these studies highlight the importance of the metal surface reactivity under plasma stimulation and guides material selection and system design for plasma-activated processes.

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Poster 5 - Production of Aromatics via Plasma-Assisted Methane Dehydroaromatization over Mo/H-ZSM-5

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Methane dehydroaromatization (MDA) is a non-oxidative, direct approach to selectively convert methane to a mixture of transportable aromatics[1]. However, this reaction is thermodynamically limited, requiring elevated temperatures (>700 ^oC) to achieve significant methane conversions. Under these conditions, coke formation is favored leading to rapid catalyst deactivation. These drawbacks suppress potential applications for this process at an industrial scale.

Non-thermal plasmas have emerged as a promising alternative route to facilitate the activation of stable molecules (i.e. CH_4, CO_2, N_2) to value-added fuels and chemicals, including MDA. The highly reactive environment created in a plasma allows for endothermic reactions to take place at temperatures close to ambient. In this presentation, we show that utilization of a dielectric barrier discharge plasma can lead to enhancements in the methane conversion and aromatic production under typical thermal conditions (700 ^oC). Furthermore, we found that the plasma can 1) facilitate methane activation over Mo/H-ZSM-5 at temperatures as low as 500 ^oC and 2) promote the formation of aromatics under these low-temperature conditions. We will discuss our current understanding of this complex plasma-catalytic chemistry with a focus on how the plasma facilitates the direct conversion of methane to valuable aromatics.

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Poster 6 - Thermal-Electro-Chemical Synthesis of Ammonia over Molybdenium Oxynitrides

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NH_3 is a critical global resource for fertilizers and chemical intermediates and can also serve as an easily transported hydrogen vector in support of a green hydrogen economy[1]. Applied electric potentials allow us to thermodynamically circumvent pressurization of the system, potentially enabling the reduction of capital costs, decrease in energy consumption, and facilitating NH_3 synthesis at smaller scales than the incumbent high-pressure approach (the Haber-Bosch process)[2,3].

In this work, we synthesized molybdenium oxynitrides (MoO_xN_y) as a promising cathode catalyst for ammonia synthesis [4,5]. Our ammonia synthesis electrochemical cell consisted of MoO_xN_y at the cathode [5], cesium dihydrogen phosphate (CsH_2PO_4) as the protonic electrolyte [6,7], and platinum nanoparticles supported on acetylene black as the anode (cathode reaction conditions of 38% H_2O, 62% N_2 at -0.7 V_{OCV}, anode reaction conditions of 38% H_2O, 62% H_2, both at 1 atm total pressure and 250°C). We will discuss our efforts in excluding incidental NH_3 in our system [8] and our findings that NH_3 is only produced at the cathode over MoO_xN_y. We further posit that a significant fraction of the produced NH_3 originate from lattice nitrogen atoms in the MoO_xN_y rather than N_2.

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Poster 7 - Effects of Acid Site Proximity in CHA Zeolites on Kinetics of Protolytic Propane Cracking and Dehydrogenation

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Brønsted acid sites (H^+) in zeolites catalyze monomolecular alkane cracking and dehydrogenation through protolytic mechanisms involving carbocationic transition states.[1] In parallel with the protolytic dehydrogenation pathway, propane dehydrogenation is catalyzed via H-transfer routes with product-derived carbonaceous deposits, which form in H_2-deficient regions of catalyst beds during reaction.[2] The H-abstraction capacity of these extrinsic carbonaceous residues depends on their H_2 deficiency; therefore, co-feeding excess H_2 suppresses their number and reactivity, allowing for the sole measurement of protolytic dehydrogenation rates.[2] In the chabazite (CHA) zeolite framework, first-order cracking rate constants (per H^+) have been reported to increase with the fraction of six-membered ring (6-MR) paired H^+ sites.[3] Previous studies report alkane cracking rates are higher at paired than isolated H^+ sites[3–5], possibly because carbocationic transition states are entropically stabilized by electrostatic interactions from spectating H^+ sites.[3] Herein, we investigate the effect of H^+ proximity on monomolecular propane dehydrogenation rates. CHA zeolites with varying 6-MR paired H^+ sites were synthesized using previously reported methods, where the compositions of structure directing agents (SDAs) was varied.[6] First-order apparent rate constants (per H^+) for propane cracking and dehydrogenation linearly increased with six-membered ring (6-MR) paired H^+ site content. Assuming measured rates reflect the weighted-average contributions from independent paired and isolated site ensembles, propane cracking and dehydrogenation rate constants (748 K) were estimated to be ~7–10× higher at paired sites. Rate measurements at different temperatures (728–778 K) allowed estimating apparent cracking and dehydrogenation activation enthalpies that were the same for both site ensembles ($\Delta H^{\ddagger}_{app,crack.}$ ~180 kJ mol^{-1}; $\Delta H^{\ddagger}_{app,dehyd.}$ ~ 205 kJ mol^{-1}), while activation entropies were systematically less negative at 6-MR paired H^+ sites (~15-20 J mol^{-1} K^{-1} higher for paired sites). The increase in activation entropy appears to reflect an attenuated ion-pair interaction between the carbocationic transition state and the anionic framework charge, likely via stabilization of the anionic lattice charge by the spectating H^+ site. These insights further our understanding of the consequences of H^+ site proximity and multi-ion-pair interaction in acid catalysis.

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Poster 8 - Mechanistic Insights into the Hysteresis Phenomena during NH_3 Oxidation on Pt/Al_2O_3 Catalysts for NH_3 Slip Applications

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NH_3 emissions are predominantly caused by diesel engine vehicles and denitrification units of coal-fired power plants. For diesel engine vehicles to meet stringent nitrogen oxide (NO_x) emission regulations, NH_3 is introduced into diesel engine aftertreatment systems containing selective catalytic reduction (SCR) units, with downstream ammonia slip catalysts (ASC) responsible for removing residual NH_3 from the exhaust stream. ASCs are dual-layer materials consisting of a top-layer NO_x SCR catalyst (e.g., Cu-chabazite zeolites; Cu-CHA) and a bottom-layer NH_3 oxidation catalyst comprising platinum supported on gamma alumina ($Pt/\gamma\text{-}Al_2O_3$). During vehicle operation, ASCs experience wide operating conditions that influence Pt oxidation state and structure, and cause differences in observed NH_3 oxidation kinetics and selectivities [1]. During heating and cooling of the ASC under NH_3 oxidation conditions, rates differ during ignition and extinction cycles to show a hysteresis in oxidation behavior, with higher NH_3 oxidation rates observed for the extinction branch. This hysteresis phenomena has been observed for other oxidation reactions of other compounds (e.g., NO, CO, CH_4) over $Pt/\gamma\text{-}Al_2O_3$; however, the mechanistic origins underlying this phenomena remains debated [2-4]. In this work, we combine steady-state and transient kinetic measurements and theoretical calculations to elucidate the kinetic and mechanistic details of NH_3 oxidation on $Pt/\gamma\text{-}Al_2O_3$ powder samples of different Pt particle size and pretreatment history. Supplemental characterization including H_2 temperature-programmed reduction (TPR) and in situ spectroscopic techniques (X-ray absorption, CO DRIFTS) were used to determine the Pt oxidation state and structure in a range of reaction-relevant conditions. Experimental data are connected to DFT predicted states of the catalyst surface and expected reaction kinetics as a function of catalyst particle size. The understanding of the kinetic and mechanistic factors that give rise to a hysteresis in oxidation behavior from these techniques can provide guidance on how to design ASC catalysts for real-world applications.

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Poster 9 - Localized Structural and Compositional Kinetic Effects on Single Ni^{2+} Sites for Light Olefin Oligomerization

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Previously, Cho et al. has shown that isolated nickel ions anchored on the lacunary defects of the polyoxometalate structures could serve as potentially stable, single sites capable of facilitating ethylene oligomerization.[1] Due to outstanding tunability of polyoxometalates, the similar approach of defect driven site isolation can be implemented on polyoxometalates with different molecular structures and elemental composition. There have been several studies investigating the trend in overall redox properties or acidity of transition metal substituted polyoxometalate with different structures or elemental compositions.[2–4] However, the localized kinetic effects specifically done on isolated Ni active sites has not been thoroughly investigated to our knowledge.

In this work, we have successfully isolated single Ni active sites on Keggin structures with different internal heteroatoms (P and Si). Successful synthesis of desired materials were confirmed through ^{31}P nuclear magnetic resonance spectroscopy (NMR) and single crystal x-ray diffraction pattern (XRD). The structural effect on kinetic behavior was evaluated by observing dimeric butene selectivity to from the product stream of ethylene oligomerization done at 200°C and 20 bar. The resembling product distribution was observed once it was compared to that of Ni substituted Wells Dawson phosphor-tungstate. Once, internal heteroatoms were changed within Keggin polyoxometalates from P to Si, Ni active sites showed subtle catalytic differences. Selectivity toward terminal 1-butene decreased approximately by 15% with Ni substituted Keggin silico-tungstate. In addition, apparent activation barrier of Ni active sites on Keggin silico-tungstate was measured to be 87 kJ/mol which is nearly 30 kJ/mol higher than that of Ni substituted Keggin phosphor-tungstate.

In summary, we highlight the tunable kinetic nature of Ni single sites which are isolated on lacunary defects by perturbing overall structure and elemental compositions of mother polyoxometalate.

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Poster 10 - Quantifying the Kinetics of Framework Dealumination during Hydrothermal Aging of Proton-Form CHA Zeolites

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Aluminosilicate zeolites are used as Brønsted acid catalysts in their H-forms and for the selective catalytic reduction of nitrogen oxides (NO_x) in their Cu-exchanged forms, and are typically regenerated in oxidative environments at high temperatures to remove carbonaceous deposits. Yet, exposure to water-containing environments (~10 kPa H_2O) at high temperatures (>823 K) causes hydrothermal aging, characterized by the hydrolysis of framework Al-O bonds that eventually leads to removal of framework Al (Al_f) atoms to form extraframework Al (Al_{ex}) species in dealumination events. Empirical observations indicate that, in their Cu-form, small-pore (eight-membered ring; 8-MR) cage-window zeolite topologies such as chabazite (CHA) show improved resistance to dealumination and framework degradation compared to medium- and large-pore zeolites after exposure to hydrothermal aging conditions.[1] The total Al content (e.g., Si/Al),[2] Al distribution (e.g., among different T-sites)[3,4] and structural defects (e.g., silanol groups)[5] are reported to influence dealumination kinetics (723-873 K, 5-35 kPa H_2O) on H-form MFI zeolites. However, the kinetics and mechanisms of framework dealumination, and their dependence on material properties including Al density and local arrangement, are difficult to determine in low symmetry frameworks such as MFI. Here, we synthesized H-form CHA zeolites, a high-symmetry (one T-site) framework, with varying Al content (Si/Al = 12-22) and percentages of 6-MR paired Al sites (2-28%) at fixed composition (Si/Al = 11-12) using previously reported methods[6] to study the influence of zeolite material properties on the kinetics of dealumination during hydrothermal aging. Samples were exposed to hydrothermal aging conditions (923 K, 10 kPa H_2O) for varying amounts of time in a packed-bed reactor. The number of Al_f sites after each treatment was determined by quantifying the number of H^+ sites by NH_3 TPD[7] and used to determine kinetic models for Al_f removal as a function of time, temperature, water pressure, and other material properties (e.g., active site density and proximity). The decrease in Al_f content with time was best-described by a first-order kinetic model that approaches a fixed value of Al_f at infinite times (Al_∞). Estimated first-order dealumination rate constants and Al_∞ were compared among materials of different properties. Preliminary results suggest that the intrinsic dealumination rate in CHA zeolites is not influenced by proximity but depends on the total Al content. Altogether, this study developed new approaches to quantify the kinetics of dealumination in zeolites, which can be applied generally to study materials of varying bulk and atomic properties, to gain fundamental insights into the kinetics and mechanisms of dealumination under hydrothermal aging conditions.

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Poster 11 - Investigating the Influences of Different Si and Al Sources on Accelerating the Kinetics of Interzeolite Conversion of FAU to CHA

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The synthesis of high silica CHA (SSZ-13) has been widely investigated due to its high thermal stability and use in selective catalytic reduction of NOx.[1] In conventional hydrothermal synthesis, soluble sources of the inorganic reagents, organic structure directing agent (SDA) and high amounts of hydroxide are used to form CHA. Interzeolite conversion (IZC), a route where a crystalline zeolitic source is used to form another zeolite, has displayed faster crystallization rates than conventional synthesis. In FAU-to-CHA IZC, the composition of the FAU reagent influences the rate and product selectivity.[2] CBV720 (FAU) has demonstrated to have the fastest rate of conversion to CHA at 135 °C[2] compared to other FAU reagents, but the underlying reasons for faster IZC kinetics are not well understood. Using N,N,N-trimethyl-1-adamantammonium as the OSDA, we studied CHA crystallization kinetics using FAU reagents with different Si/Al ratio and using non-FAU reagents, at fixed synthesis conditions (SDA/SiO_2 0.14, H_2O/SiO_2 40, OH/SiO_2 0.6, SiO_2/Al_2O_{3gel} 30). Interzeolite conversion was verified by XRD and accompanied by a pH jump indicative of CHA formation. Temperature plays a crucial factor in slowing down or stopping the interzeolite conversion for certain FAU reagents. To understand if these differences in rates are due to incongruencies in dissolution, FAU reagents of different composition were introduced into a high alkaline solution. CBV720 (Si/Al_{FAU} 15) was denatured at a faster rate than CBV100 (Si/Al_{FAU} 2.5) but was not completely dissolved, thus it is easier to be attacked by hydroxides in solution. Denatured CBV720 was investigated in similar conditions as FAU (135 °C) and formed CHA at similar times than fully crystalline CBV720. Denatured CBV720 was amorphous, as confirmed by XRD and no micropore volume; surprisingly, ^{27}Al MAS NMR showed mostly tetrahedral AlO_4. CBV720 ion-exchanges more OSDA than other FAU reagents before reaction, which could correlate to the faster rate. In contrast, the denatured CBV720 has almost no OSDA exchanged. These findings indicate that denatured CBV720 is just as reactive and the amount of OSDA exchanged is not the main factor influencing the rate. Another ammonium SDA (inhibitor) was added into the synthesis at similar conditions to study the competition for ion-exchange or surface nucleation in IZC kinetics. The conversion of CBV720 and non-FAU synthesis slowed down. ^{13}C MAS NMR peaks were broader when the inhibitor was present indicating hindered mobility of OSDA inside cages. These results may indicate a steric hinderance to form nuclei instead of ion-exchange competition during IZC.

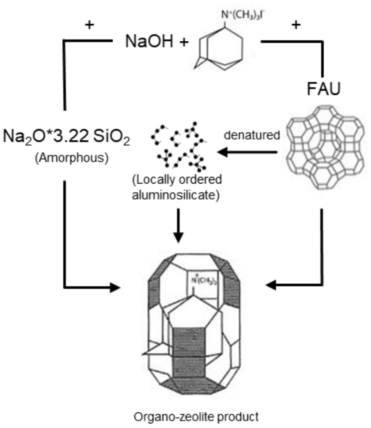

Figure 1. Synthetic routes to CHA from amorphous, ordered aluminosilicates and crystalline FAU reagents

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Poster 12 - Continuous Flow Electrochemical Alkene Epoxidation Kinetics

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Electrochemical alkene epoxidations offer a promising alternative to energy-intensive thermocatalytic industrial epoxidations that utilize costly or hazardous oxidants.[1] By applying an anodic potential (>2.0 V_{RHE}) at ambient conditions, water (H_2O) can act as the sole oxygen source for the oxidation of alkenes to epoxides. Prior studies on ethylene, propylene and C_{5+} alkene electroepoxidations utilized batch reactors and offer limited product analysis, catalyst characterization, and examination of stability.[2-4] To date, a mechanistic understanding of electroepoxidations remains elusive. Here cyclic voltammetry measurements in a custom-made flow cell reveal potentials at which the liquid-phase 1-hexene (C_6H_{12}) electroepoxidation to 1,2-epoxyhexane ($C_6H_{12}O$) on gold (Au) occurs. As [C_6H_{12}] increases on Au, the integrated oxidation peak area from 1.7-1.95 V_{RHE} increases until 25 mM and current densities at potentials greater than 2.0 V_{RHE} decrease. Both trends reflect C_6H_{12} oxidation (adsorption on Au or epoxidation to $C_6H_{12}O$), which competes with surface Au oxidation and H_2O oxidation. The areas of reduction peaks from 0.5-0.9 V_{RHE} and 1.35-1.5 V_{RHE} depend weakly on [C_6H_{12}], showing that C_6H_{12} does not desorb reversibly from the surface. Consequently, we conclude C_6H_{12} irreversibly adsorbs and then epoxidizes at potentials greater than 1.7 V_{RHE} on Au. As [H_2O] increases, the areas of oxidation peaks from 1.7-2.4 V_{RHE} decrease. The oxidation peak at low [H_2O] (< 5 M) reflects reactions between C_6H_{12}, CH_3CN, and Au, demonstrated by Au dissolution. At higher [H_2O] (> 5 M), this feature signifies C_6H_{12} epoxidation and oxidation and reconstruction of the Au surface. The current density at potentials greater than 2.3 V_{RHE} increases with [H_2O], because competing C_6H_{12} epoxidation and H_2O oxidation reactions both require O-atoms derived from H_2O. We propose that both C_6H_{12} epoxidation and H_2O oxidation have the same pathway to the required surface oxo species, Au=O.[4,5] The Au=O either reacts with a C_6H_{12} molecule to form $C_6H_{12}O$ or a second H_2O molecule to form O_2 for the epoxidation or H_2O oxidation reaction respectively.

Continuous flow kinetic measurements indicate that the Faradaic efficiency (FE) for epoxidations on most metal foils (Au, Pt, Pd, Ag, Ni) fall well below 5% and H_2O oxidation dominates in these conditions. In contrast, oxide nanoparticles or thin films composed of MnO_x give higher FE values. Bulk electrocatalytic C_6H_{12} epoxidation reactions varying reactant (C_6H_{12}, H_2O) concentration and potential will be performed to measure epoxidation turnover rates, carbon selectivity, and FE. *in situ* Raman spectroscopy will be performed to determine critical intermediates on the anode implicated by cyclic voltammetry and bulk electrolysis kinetic measurements. Insights from this study can be used to determine optimized reaction conditions for electron and carbon-selective electroepoxidations.

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Poster 13 - Investigation of Selective Cu-Ga-Zr Catalysts for CO_2 Hydrogenation to Methanol

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Upgrading CO_2 into fuels and value-added chemicals has attracted increasing attention given environmental concerns (e.g., climate change) and economic incentives (e.g., turning waste CO_2 into a carbon source). One of the proposed routes for CO_2 utilization is its hydrogenation to methanol, an important commodity produced in excess of 110 metric tons annually.[1] However, the exothermic CO_2 hydrogenation to methanol competes with its endothermic reduction to CO. Methanol selectivity at high temperatures is therefore limited. For CO_2 hydrogenation to compete with the industrial routes, the development of highly active, selective, and stable catalysts is required. We have identified CuGaZr catalysts that are more selective to methanol from CO_2 hydrogenation than the industrial CuAlZn catalyst.

A series of CuGaZr catalysts was synthesized at various ratios by coprecipitation from their nitrate salt solutions. The catalysts were tested for CO_2 hydrogenation under a WHSV of 48,000 mL / (g_{cat}•hr), a H_2:CO_2 ratio of 4:1, temperatures between 240 – 300 °C, and pressures between 1 – 35 bar. To understand the differences between the synthesized materials and the industrial CuAlZn catalyst, XRD, SEM-EDX, TPR-H_2, N_2O titration, N_2 physisorption, and XPS analyses were performed. The catalysts were investigated using *operando* DRIFTS coupled with modulation excitation (ME) spectroscopy, in which the feed composition is varied at a set frequency in order to examine the corresponding CO_2 hydrogenation mechanism and establish structure-activity relationships.

The synthesized CuGaZr materials are more selective toward methanol than the industrial catalyst under the same CO_2 hydrogenation conditions. The binary materials CuGa, CuZr, and GaZr are less active than the ternary CuGaZr system that is composed of ~20 wt% of each metal. The ternary CuGaZr materials are largely amorphous with high metal dispersion and large surface areas. XPS and XRD analysis indicate possible formation of $CuGa_2O_4$ and Cu_2O under reaction conditions. The ME-DRIFTS analysis shows that the CO_2 hydrogenation mechanism on CuGaZr is likely to occur via formate-like intermediates in agreement with published precedent.[2] The formation of the formate appears to be a fast step, but its activation is relatively slow, exhibiting a delay relative to the appearance of $CO_{2(g)}$ and being limited by the amount of surface gallium hydrides. The industrial CuAlZn under the same conditions shows no trace of formates, implying CO_2 hydrogenation goes through a direct CO cleavage.[2] This difference in reaction pathway is proposed to be essential to the differences in selectivity.

The higher selectivity of CuGaZr vs CuAlZn holds even at high temperatures despite the thermodynamic favorability of the reverse water gas shift reaction toward CO. The mechanistic investigation of these catalysts may provide important insights into the broader incorporation of CO_2 as a viable carbon source in industrial methanol synthesis.

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Poster 14 - Non-Mean Field Approaches for Surface Catalysis: Analytical Description of Adsorbate-Adsorbate Interactions

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Theoretical studies of hetero-catalytic reactions routinely utilize microkinetic models, advantageous for rationalizing experimentally observed reaction rates, effective activation barriers, and reaction orders in terms of the corresponding elementary steps. Such models rely on the mean-field assumption, where configurational entropy of adsorbates on the surface is approximated by its mean. However, interactions between the adsorbates, predominant in practical catalytic systems [1-3], cause significant deviation from the mean field configurational entropy, limiting the accuracy of this assumption.

Previous efforts to correct this approximation are either purely numerical [4,5], which result in no closed form rate equations, or employ spatially averaged analytical correction factors[6], which have limited ability to capture contributions which arise because of local configurations deviating from the average. In this work, we present a novel strategy to incorporate adsorbate-adsorbate interactions into microkinetic models as correction factors to the mean field expressions.

To arrive at the analytical corrections, Bethe-Peireles approximations to the grand canonical partition function based on the Cluster Variational Method[8] are applied. This scheme restricts the analysis to a small cluster of adsorption sites; the interactions within the cluster are examined explicitly, while an average correction factor is applied to consider interactions that would result from the adsorbates outside of the cluster. The unknown correction factor is self-consistently solved for. Utilizing the common approximation of a Most Abundant Surface Intermediate (MASI), this formalism can be readily generalized to a multi-adsorbate system, yielding analytical activities of reacting species. In the case of adsorbate-adsorbate repulsions, pertinent in most of the catalytic systems, the adsorption isotherm, as illustrated in the adjacent figure, shows clear deviation from a mean-field prediction, and, as the magnitude of repulsion is increased, a plateau is observed. This corresponds to a state wherein it is unfavorable to have any nearest neighbor adsorbates because of the strong repulsion, as seen in the high penalty required to change the coverage beyond half a monolayer. These results provide intuitive understanding of experimentally observed non-mean field structures in catalytic systems at a fundamental level. Additionally, the analytical form of these expressions will permit direct incorporation into microkinetic models, while preserving the rich physical and mechanistic insights which are readily obtained from such models.

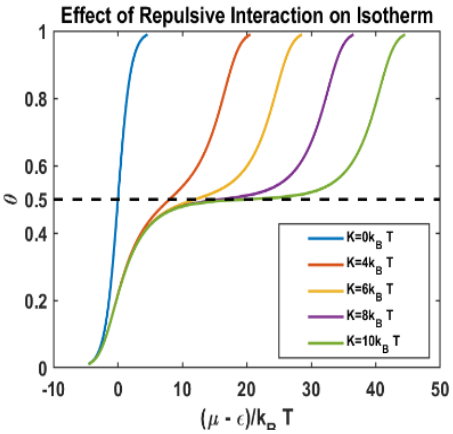

Figure 1: Adsorption isotherms from mean-field (0 k_BT)to highly repulsive interactions using developed formalism

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Poster 15 - Carbon Deposits as Possible Active Sites for Non-Oxidative Methane Coupling Reactions

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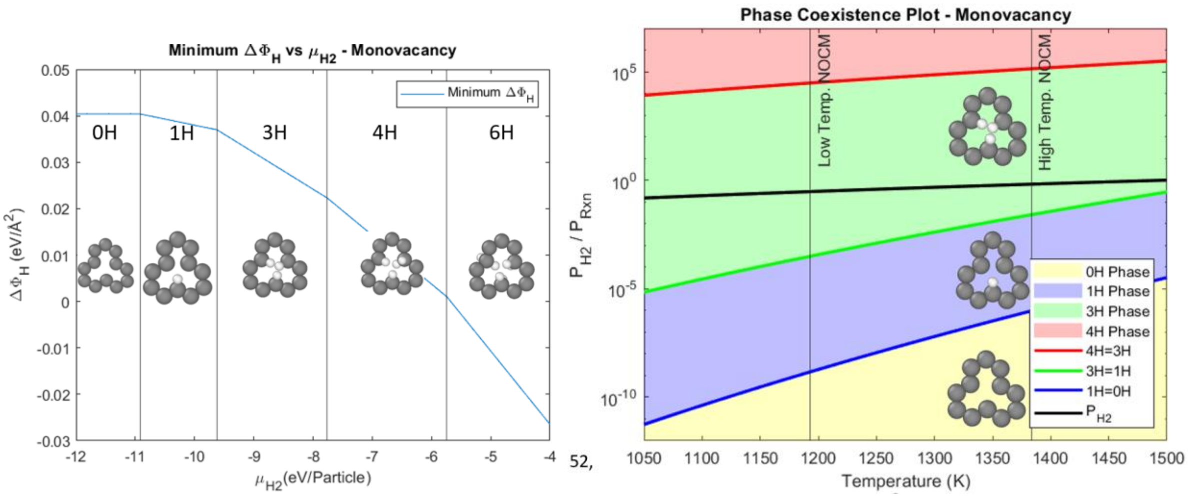
Carbon materials have been studied as potential catalysts for methane conversion reactions.[1] Recently, it was determined that a variety of catalyst materials, after coking to the point of complete coverage, were still able to catalyze the non-oxidative coupling of methane (NOCM) reaction.[2] Previous experimental and computational work has suggested that “defects” within the carbon structure, such as carbon vacancies in the surface or edges that are formed from sheet separation, and resulting in individual carbon atoms with an electron-deficient valence structure, could act as the active sites in these reactions.[1,3] Here, surface free energy and phase coexistence diagrams are employed to determine the stability of model carbon-monolayer defects under NOCM reaction conditions. These diagrams are generated using Density Functional Theory (DFT) calculations to determine the minimum grand free energy of defects with different passivation geometries. Phase coexistence diagrams are then be applied to determine what phase would be most stable under typical reaction pressures and temperatures. The results suggest that all defect models are most stable when fully passivated, where hydrogen binding to carbon atoms adjacent to vacancies fully satisfies their valence structures. Future work will involve studying the activation energy barriers associated with NOCM on these fully passivated defect structures and comparing these energy barriers to those calculated for pristine graphene models.



Left: Minimum grand free energy versus chemical potential of hydrogen gas for a monovacancy model with different degrees of passivation. Right: Phase coexistence plot indicating the most stable surface phase for a given temperature and pressure. The black line indicates the partial pressure of hydrogen gas as a function of temperature during methane conversion.[4]

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Poster 16 - Structural Changes to Molybdenum and Brønsted Acid Sites on Mo-MFI during Methane Dehydroaromatization Reaction-Regeneration Cycles

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Molybdenum supported on MFI zeolites (Mo-MFI) is able to catalyze methane dehydroaromatization (DHA) to equilibrium conversion with high (~80%) aromatics selectivity, but these materials undergo rapid deactivation [1]. Typical high-temperature (>773 K) oxidative regeneration to remove carbon deposits leads to irreversible deactivation and to various structural changes in Mo species and framework Al over successive reaction-regeneration cycles. Here, we develop characterization methods (H_2 TPR, NH_3 TPD) and use DHA kinetic measurements [2] to elucidate changes to the number and structure of Brønsted acid sites and Mo species during DHA reaction-regeneration cycles. Catalysts were prepared by MoO_3 deposition on commercial MFI zeolites (Si/Al ~12), followed by oxidative treatments (823 K) to transform MoO_3 into ion-exchanged (IE) Mo species. We show that H_2 TPR allows distinguishing and quantifying MoO_3 clusters from IE Mo species, and thus monitoring changes in this distribution after each reaction-regeneration cycle. Additionally, residual H^+ sites quantification by NH_3 TPD allows determining the speciation of exchanged Mo ions, which we show is influenced by the presence of proximal Al atoms in the MFI lattice, which were quantified by Co^{2+} titration [3]. Methane DHA reactions were performed using Mo-MFI zeolites, showing that forward rates of benzene formation (950 K, 60 CH_4 kPa) decrease systematically as a function of reaction-regeneration cycles, as the material undergoes structural changes that cause a decrease of IE Mo species and H^+ sites due to hydrothermal degradation during the regeneration step. This work combines information from quantitative characterization techniques and kinetic measurements to identify material properties that influence reactivity and stability, providing guidance for new catalyst synthesis and regeneration strategies for methane DHA.

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Poster 17 - First-Principles Analysis of the Ammonia Decomposition Reaction on High Entropy Alloy Catalysts

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The development of periodic Density Functional Theory (DFT) calculations, combined with advanced synthesis techniques, has accelerated the understanding and development of multimetallic alloy catalysts. Recently, a new class of materials, known as high entropy alloys (HEAs), has opened up additional catalyst design possibilities in the alloy space.[1] HEAs are comprised of many component elements, with completely mixed atomic structures, leading to potentially millions of unique chemical environments around active sites. These materials have attractive properties for catalysis, including enhanced stability due to entropic effects, as well as highly tunable active site structures that could be exploited to optimize catalytic activity and selectivity. Nevertheless, the huge materials space cannot be navigated exhaustively using first-principles methods, and the scaling theories and models proposed for traditional alloys may not be directly translatable to HEAs.[2]

In this study, we develop a simple structural model of disordered alloy catalysts, and we introduce workflows to efficiently sample different binding sites and investigate free energy landscapes for adsorbates on these sampled sites. To illustrate this approach, we choose the ammonia decomposition reaction as a probe reaction and Co-Mo as a model catalyst, based on the promising activity demonstrated experimentally for this chemistry on Co-Mo-based HEA's.[3] We determine the binding energies of various reaction intermediates on many randomly sampled arrangements of the HEA surfaces using DFT. We assess the limitations of linear scaling relationships for these disordered systems, and we complement these scaling relationships with nonlinear machine learning-based strategies to more accurately estimate adsorption energetics. We additionally evaluate thermodynamics and kinetics of elementary steps in ammonia decomposition and deduce that the rate-determining step on disordered CoMo alloys is recombinative nitrogen desorption. The results form a strong basis for further studies and the development of high entropy alloy catalysts for ammonia decomposition and related reactions.

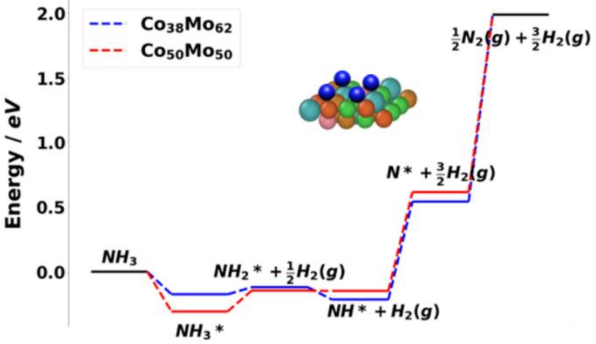

Fig 1. Reaction Free Energy Diagram: Lines represent CoMo-based HEA surface arrangements that give the lowest barrier according to the Sabatier barrier for the predicted rate-determining step (the recombinative nitrogen desorption) for each bulk composition.

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Poster 18 - Sulfated Zirconium Metal–Organic Frameworks as Well-Defined Supports for Enhancing Organometallic Catalysis

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Investigating the mechanism of heterogeneous catalysts is a challenging endeavor due to aspects such as surface site nonuniformity and aperiodicity of conventional materials. One example of this is sulfated metal oxides. These materials can function as highly active catalysts and/or serve as supports for organometallic complexes. These applications (among others) result from attributes such as acidity, weak coordination to metal centers, and ability to promote transformations *via* radical cation intermediates. Research has continued to probe the structure of sulfated metal oxides that imbues the aforementioned properties.

To better understand these materials, metal–organic frameworks (MOFs) have been targeted as structurally defined analogues. MOFs are constructed from inorganic, cluster-based “nodes” and multitopic organic “linkers,” which generates a nanomaterial of high porosity and crystallinity. This makes MOFs appealing for mechanistic studies of heterogeneous catalysts. In this work, we present the sulfated analog of a Zr_6-based MOF NU-1000 that was used to immobilize organoiridium complexes—these anchored organometallic species were rendered catalytically active for H/D exchange of toluene. The generated species were characterized using techniques such as single crystal X-ray diffraction and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The sulfate binding motif is found to change depending on the degree of hydration, as supported by density functional theory (DFT) calculations. Increased Brønsted acidity was also observed upon sulfation of NU-1000, as supported by trimethylphosphine oxide adsorption, ammonia sorption, in situ ammonia DRIFTS, and DFT studies.

With these insights in hand, next steps aim toward applying this methodology to CO_2 functionalization. Specifically, we seek to tune the stereoelectronic environment of supported organometallic active sites using modified MOF supports, whilst attaining key structural information for rational design of next generation decarbonization catalysts. Hypotheses to this end are also presented herein.