Catalysis Club of Chicago

2025 Spring Symposium

Program Booklet

Monday, May 5th, 2025
8:00 AM – 5:00 PM CDT

Held at GTI Energy

1700 S Mt Prospect Rd, Des Plaines, IL 60018

Symposium Schedule

8:00 **Registration, Breakfast**

8:45 **Welcome and Introduction**

9:00 **Bridging Homogeneous and Heterogeneous Catalysis Using Advanced Quantum Models**
Prof. Alexander V. Mironenko, University of Illinois Urbana-Champaign

9:40 **Detangling Complex Catalytic Systems**
Prof. Ive Hermans, University of Wisconsin–Madison

10:20 Flash Talk: **Assessing the Influence of Acid Site Location in MFI Zeolites on Propene Oligomerization Rates and Selectivity**
Diamarys Salome Rivera, Purdue University

10:40 **Networking Break & Vendor Show**

11:05 **Building the Bioeconomy with Sustainable Pathways to Bio-based Acrylics**
Dr. Christopher Nicholas, Låkril Technologies

11:45 Flash Talk: **Selective Hydrogen Combustion over Silica-Supported Sodium Tungstate Catalysts**
Elijah R. Kipp, University of Minnesota

12:05 **Group Photo**

12:15 **Lunch**

1:15 **Engineering Active Sites and Their Environments to Guide Catalytic and Electrocatalytic Transformations for Sustainable Energy and Chemical and Pharmaceutical Syntheses**
Prof. Matthew Neurock, University of Minnesota (2025 Herman Pines Awardee)

2:05 Flash Talk: **Quantifying the Kinetics of Framework Dealumination during Hydrothermal Aging of Proton-Form CHA Zeolites**
Tania L. Class-Martinez, Purdue University

2:25 **Mapping Decarboxylative Coupling Reactions: Uncovering New Principles that Govern Catalysis**
Prof. Jessica Hoover, University of Minnesota

3:05 **Networking Break & Vendor Show**

3:30 Flash Talk: **Selective Hydrogenation of Biomass-derived Furans Over Cu Catalysts: Experiments and Theory**
Evangelos Smith, University of Wisconsin–Madison

3:50 **Investigating Fundamental Electrocatalytic Processes for Decarbonization and Energy Storage**
Prof. Brian Tackett, Purdue University

4:30 Flash Talk: **Interrogating the Kinetic and Mechanistic Origins of N_2O Formation during NH3 Selective Catalytic Reduction of NO_X on Cu-CHA Zeolites**
Bryan Cruz Delgado, Purdue University

4:50 **Closing Remarks**

Bridging Homogeneous and Heterogeneous Catalysis Using Advanced Quantum Models

Prof. Alexander V. Mironenko

Assistant Professor

Department of Chemical and Biomolecular Engineering

University of Illinois, Urbana-Champaign

Abstract. The majority of industrial catalysts are heterogeneous, allowing easy separation from reaction mixtures and high stability under harsh reaction conditions. Despite these advantages, some chemical technologies still rely on homogeneous catalysts due to the lack of heterogeneous counterparts with comparable activity, selectivity, and stability.

A notable example is the Cativa process for acetic acid production via methanol carbonylation, which uses expensive and hard-to-separate homogeneous complexes $[IrI_2(CO)_2]^-$ and $[RuI_2(CO)_3]$, along with corrosive HI. Recently, a heterogeneous catalyst with atomically dispersed ReO_4 sites on mesoporous SBA-15 was shown to produce high acetic acid yields without a promoter, demonstrating excellent time-on-stream stability (Qi et al. *J. Am. Chem. Soc.* 2020, 142, 14178). The availability of both homo- and heterogeneous catalysts for the same reaction offers a unique opportunity to identify generalities between these catalyst classes, paving the way for heterogenizing remaining homogeneous industrial processes.

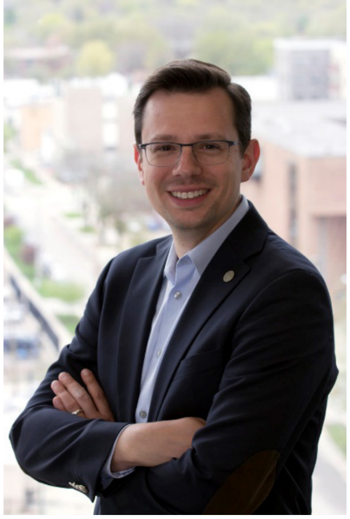
In the first part of my talk, I will describe our efforts to discover the reaction mechanism of methanol carbonylation on ultradispersed ReO_x/SiO_2 using state-of-the-art density functional theory (DFT), natural bond orbital analysis, and first-principles kinetic modeling. Contrary to the consensus that SiO_2-supported catalytic ReO_4 sites exist only in the monopodal $ORe(=O)_3$ form, we find these sites cannot catalyze all elementary steps. While C-C coupling of CH_3 and CO ligands to form CH_3CO on dispersed Re(V) sites is consistent with experimental kinetics, C-O scission in CH_3OH occurs more easily on transient oxidized Re dimers that interconvert with mono Re sites.

Screening reaction pathways and finding transition states on the ReO_x sites with DFT is computationally costly. In the second part of my talk, I will discuss a lower-cost theoretical framework that can make such calculations more affordable. I will introduce the independent atom ansatz within DFT as an alternative to the common Kohn-Sham DFT ansatz. Tested on H_2, He_2, period-2 diatomics, and H_2/Al, the ansatz demonstrates low cost and superior accuracy compared to standard DFT using at most two parameters: the 2s and 2p exponents of the minimal basis set. Besides accuracy, it provides charge and energy decomposition analyses at no additional cost, facilitating identification of factors responsible for chemical and catalytic activity. We anticipate that the independent atom ansatz will enable rapid computational characterization of diverse structures in homo- and heterogeneous catalysis, particularly for methanol carbonylation, which will help bridge both fields.

Presentation Abstract: Mironenko

Bio. Dr. Alex Mironenko is an Assistant Professor at the Department of Chemical and Biomolecular Engineering at the University of Illinois, Urbana-Champaign. His research lies on the boundary between computational heterogeneous catalysis, fundamental quantum mechanics, and molecular simulations and focuses on developing new methods to understand the workings of real catalysts for renewable energy applications. Before joining the University of Illinois in 2020, he was the Kadanoff-Rice Postdoctoral Fellow in Physical Chemistry at the University of Chicago. Alex Mironenko earned his Ph.D. in chemical engineering from the University of Delaware in 2018. He received a number of awards, including the ACS Petroleum Research Fund Doctoral New Investigator Award (2021), Allan P. Colburn Outstanding Dissertation Prize (2019), J. William Fulbright Fellowship (2010-2012), Department of Energy EFRC Achievement Award (2016), Theodore A. Koch Award from the Catalysis Club of Philadelphia (2016), and Richard J. Kokes Award for the 24th North American Catalysis Society Meeting (2015).

Detangling Complex Catalytic Systems



Prof. Ive Hermans

John and Dorothy Vozza Professor

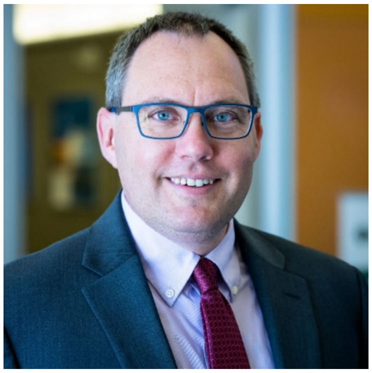
Department of Chemistry & Department of Chemical and Biological Engineering

University of Wisconsin–Madison

Abstract. In this talk I will elaborate on our convergence research approach, combining materials synthesis and characterization, kinetics and reaction engineering, *in situ* spectroscopy and computational description and prediction as applied to CO_2 hydrogenation. One powerful tool that I will highlight is Modulation Excitation Spectroscopy, a dynamic technique where the concentration of one of the reagents is periodically altered. By studying the response of the system to this perturbation we can filter out noise and signals stemming from spectator species and obtain kinetic insights in the activation and transformation of reagents over participating sites at the fluid-solid interface.

Bio. Ive Hermans obtained his PhD under the supervision of Profs. Pierre Jacobs and Jozef Peeters (2006; KU Leuven, Belgium). In addition to his scientific education, Ive Hermans also holds a postgraduate degree in Business Administration (KU Leuven, 2006). After post-doctoral research on *in situ* spectroscopy and reaction engineering with Prof. Alfons Baiker, he became assistant professor (spring 2008) at the Institute for Chemical and Bioengineering of ETH Zurich in Switzerland. In January 2014, Prof. Hermans joined the University of Wisconsin-Madison, holding a dual appointment in the Department of Chemistry and the Department of Chemical and Biological Engineering. He was co-founding editor-in-chief of ChemistryEurope (Wiley) and currently serves as editor for ACS Sustainable Chemistry and Engineering. A selection of recent awards includes the 2017 inaugural Robert Augustine award by the Organic Reaction Catalysis Society and the 2019 Ipatieff Price by the American Chemical Society. He was selected as a 2021 Alexander von Humboldt Professor but declined the offer to remain in the US. Dr. Hermans is a Fellow of the American Chemical Society, the Royal Society of Chemistry and AAAS.

Building the Bioeconomy with Sustainable Pathways to Bio-based Acrylics



Dr. Christopher Nicholas

President and Co-Founder

Låkril Technologies

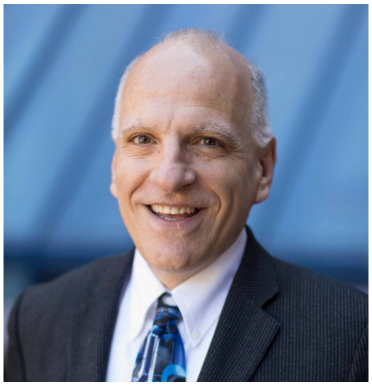
Abstract. Acrylic acid and the four primary acrylate derivatives are the cornerstone of a $11B market with broad application across coatings, adhesives, and the super-absorbent polymers industries. AA and acrylate derivatives are currently produced through a petroleum-derived value chain from propylene creating significant CO2 emissions; about 3.5 kg CO2 / kg AA. While AA-derived products are an integral part of modern society, more sustainable and eco-friendly production methods are necessary. Consumers increasingly seek sustainable, non-petroleum-based products in a variety of market segments. We focus on the use of feeds derived from lactic acid, a product sustainably fermented from a range of bio-derived sugar sources.

Our novel bifunctional catalytic process converts biomass-derived lactic acid to acrylates and acrylic acid at >90% yield. The FAU zeolite is modified with engineered bases such as amines to achieve these high yields. The catalytic dehydration of lactates to acrylic acid brings a number of challenges we discuss. Among them are A) control of competing reaction mechanisms, with dehydration and decarbonylation favored under certain reaction conditions, B) characterization of oxygenated products produced during reaction, and C) impacts of water on catalysis and hydrolysis of alkyl lactates.

Bio. Chris is the Co-Founder and President of Låkril Technologies, the startup he created in mid-2021 to commercialize a catalytic process for bio-based acrylic production. Prior to founding businesses based on sustainable catalysis, he worked 15 years at Honeywell UOP in technical and managerial roles. While his primary roles have focused on inventing and catalytically testing new materials and processes, his experience spans the process of commercialization, with experience scaling technology and working on manufacturing lines. His work crosses chemistry and chemical engineering with diverse areas including heterogeneous catalytic processes such as olefin oligomerization and alkylation, synthesis of inorganic materials (primarily metal oxides and zeolites), process engineering, molecular adsorption, and olefin metathesis. For this work he has received the 2020 Herman Pines Award in Catalysis from the Chicago Catalysis Club and the 2022 Award for Excellence in Catalysis from the Southwest Catalysis Society.

Chris earned his Bachelor of Arts from Kalamazoo College and a PhD at Northwestern University. Chris is a 25-year ACS Member and an AIChE Fellow who is an inventor on more than 120 issued US and foreign patents and coauthor of over 30 peer-reviewed journal articles and a book chapter. Along with responsibilities as a member of the Editorial Advisory Boards of *ACS Catalysis* and *Industrial & Engineering Chemistry Research*, he has been involved with the Chicago Catalysis Club since graduate student days and has served as Director, Program Chair and President.

Engineering Active Sites and Their Environments to Guide Catalytic and Electrocatalytic Transformations for Sustainable Energy and Chemical and Pharmaceutical Syntheses



Prof. Matthew Neurock

2025 Herman Pines Awardee

Shell Professor of Chemical Engineering and Materials Science

University of Minnesota

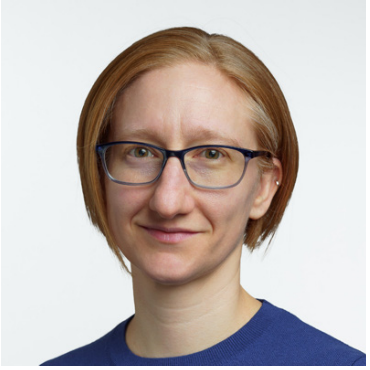
Abstract. Future strategies for sustainable energy, chemicals and pharmaceuticals production will undoubtedly require the design of catalysts that actively and selectively convert natural resources such water and biomass as well as waste streams such as CO_2 into chemicals and fuels. While enzymes elegantly integrate highly active centers together with adaptive nanoscale environments to exquisitely control catalytic transformations, they are limited industrially by their durability and stability. The design of robust heterogeneous catalytic and electrocatalytic materials that can mimic the activity and selectivity of enzymes, however, has been hindered by our understanding of how such transformations proceed over inorganic materials and complex environments. Advances in theory, simulations, spectroscopy and characterization begin to allow us to track the molecular transformations and how they proceed in heterogeneous catalytic systems at specific sites and within particular environments. This information is enabling the design of unique atomic surface ensembles and nanoscale environments that can efficiently catalyze different molecular transformations. Herein we examine the influence of metal catalysts, solvents, and electrochemical environments on heterogeneously catalyzed reactions to carry out selective molecular transformations. More specifically, we discuss the acid-catalyzed dehydration of oxygenates derived from biomass, the electrocatalytic reduction of CO_2 to CO and the electrochemical reduction of organics to valuable chemicals and pharmaceutical intermediates. We draw direct analogies between the elementary processes that govern these seemingly different systems and explore the manipulation of solvents, electrolytes and electrochemical potential to drive the formation of 3D environments that aid in controlling these transformations. In addition, we show the significant promotion by dynamic oscillation of potential to alter the surface coverages and control the local reaction environments.

Bio. Matt Neurock is the Shell Distinguished Professor of Chemical Engineering and Materials Science at the University of Minnesota. He received his B.S. degree in Chemical Engineering from Michigan State University and his Ph.D. from the University of Delaware in 1992. He worked as a Postdoctoral Fellow at the Eindhoven University of Technology in the Netherlands from 1992-1993 and subsequently as Visiting Scientist in the Corporate Catalysis Center at DuPont from 1993-1994. He joined the faculty in Chemical Engineering at the University of Virginia in 1995 where he held joint appointments in Chemical Engineering and Chemistry. In 2014 he moved to the University of Minnesota and is on the faculty in the Department of Chemical Engineering and

Presentation Abstract: Neurock

Materials Science and the Department of Chemistry. He has made seminal advances to development and application of computational methods toward understanding catalytic and electrocatalytic reaction mechanisms, and the sites and environments that carry out reactions under working conditions. He has published over 300 papers, 2 patents and is coauthored the book “Molecular Heterogeneous Catalysis”. He has received numerous awards for his research in catalysis and reaction engineering including the Robert Burwell Lectureship from the North American Catalysis Society, the R.H. Wilhelm Award in Chemical Reaction Engineering from the American Institute of Chemical Engineers and the Paul H. Emmett Award in Fundamental Catalysis from the North American Catalysis Society. He serves on various editorial and advisory boards, is a consultant with numerous chemical companies, and served as an editor for the Journal of Catalysis for ten years.

Mapping Decarboxylative Coupling Reactions: Uncovering New Principles that Govern Catalysis



Prof. Jessica Hoover

Merck Professor of Chemistry

Department of Chemistry

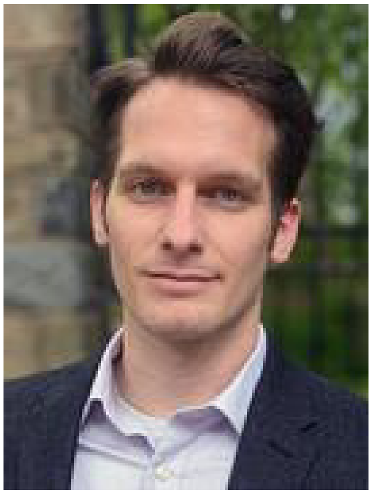
University of Minnesota

Abstract. Oxidative decarboxylative coupling reactions provide an attractive route to generate a diverse array of functionalized arenes from inexpensive and readily available carboxylic acids. These methods, however, are underutilized, in part, due to limitations in the scope of the carboxylic acid coupling partner and the need for stoichiometric silver salt oxidants. Our recent efforts have focused on understanding the mechanisms of these reactions, in particular the origins of these limitations, to enable the design of efficient and universal decarboxylative coupling reactions. In the course of these studies, we have uncovered new fundamental principles that govern catalysis in these systems, and others. This talk will describe our recent work in this area focusing on two newly identified features of catalysis.

Bio. Professor Jessica Hoover earned a B.S. in Chemistry from Harvey Mudd College in Claremont, CA in 2004, and completed her Ph.D. in 2009 at the University of Washington in Seattle under the direction of Professors Jim Mayer and Forrest Michael. She conducted postdoctoral work with Shannon Stahl at the University of Wisconsin-Madison, developing practical copper-catalyzed aerobic alcohol oxidation reactions and studying the corresponding reaction mechanisms. Jessica's independent academic career began at West Virginia University (WVU) in 2012 as Assistant Professor, and she was promoted to Associate Professor in 2018. She moved to the University of Minnesota in 2023 where she is now Merck Professor of Chemistry. Research in the Hoover group aims to elucidate the mechanisms of transition-metal catalyzed organic transformations, in particular those of C-C and C-heteroatom bond forming reactions.

Presentation Abstract: Tackett

Investigating fundamental electrocatalytic processes for decarbonization and energy storage



Prof. Brian M. Tackett

Robert & Sally Weist Assistant Professor of Chemical Engineering

Department of Chemical Engineering

Purdue University

Abstract. Electrocatalytic processes will play a vital role in energy storage and decarbonized chemical manufacturing, which are necessary components of a sustainable society. Successful development of these technologies will require fundamental understanding of electrode surface reactions under applied potentials. To date, it has been challenging to extract this information, due to many intertwined chemical and physical phenomena occurring near the electrode-electrolyte interface in aqueous electrocatalytic environments. Here, I present examples of surface-sensitive measurement techniques that enable accurate description of catalytic properties under electrochemical operating conditions. This presentation will focus mainly on the use of a new configuration for electrochemical mass spectrometry and its application for (i) understanding surface restructuring of Cu(111) electrodes, (ii) quantifying adsorption properties for electrochemical activation of light alkanes, and (iii) measuring real-time electrocatalytic hydrogen production to reveal intrinsic kinetics at the aqueous zinc ion battery anode. These examples will demonstrate the versatility of surface sensitive electrocatalytic measurement techniques as enablers for a variety of sustainable technologies.

Bio. Brian Tackett is the Robert & Sally Weist Assistant Professor of Chemical Engineering at Purdue University. He earned a B.S. in chemical engineering from the University of Pittsburgh (2013) and a Ph.D. in chemical engineering from Columbia University (2019), completing a thesis on electrocatalysis under the advisement of Jingguang Chen. Tackett then held a National Research Council Postdoctoral Fellowship at the National Institute of Standards and Technology (NIST, 2019 – 2021), where he studied characterization of electrocatalytic phenomena at the electrode-electrolyte interface, advised by Thomas Moffat. Tackett joined the Davidson School of Chemical Engineering at Purdue in 2021, where he established a lab that investigates electrocatalytic reactions that can help decarbonize industrial chemical processes. His group specializes in applying unique electrocatalytic characterization tools, like mass spectrometry and vibrational spectroscopy, to reveal surface reaction phenomena at the solid-liquid electrocatalyst interface. His group then wields this knowledge to perform reactor analysis for continuous flow electrochemical reactors.

Assessing the Influence of Acid Site Location in MFI Zeolites on Propene Oligomerization Rates and Selectivity

Diamarys Salomé Rivera, Purdue University

Propene oligomerization over Brønsted acid zeolites is a route to upgrade light alkenes into higher molecular weight products useful as transportation fuels. Microporous voids of different size, shape, and interconnectivity govern reactivity and molecular diffusivity. Oligomerization rates and selectivity in medium-pore (10-MR) zeolites are further influenced by strong intrazeolite transport limitations imposed by heavier hydrocarbon products that remain occluded within micropores during catalysis. Previous work measured increasing propene dimerization rate constants (per H^+) with decreasing void size among TON > MFI > BEA > FAU > SiO_2-Al_2O_3, with selectivity to β-scission over oligomerization products that varied with pore dimensionality. Given that rates and selectivity are influenced by void size among different topologies, we surmise they should also depend on the location of H^+ sites in different voids within a given topology, such as MFI channels or intersections. Here, we combine experimental kinetic data and density functional theory (DFT) to interrogate the effect of H^+ site location on propene oligomerization rates and selectivity for MFI zeolites.

Steady-state propene dimerization rates (per H^+) systematically decrease with increasing crystallite size for MFI-DABCO and MFI-EDA samples, indicating rates are transport limited as reported previously for MFI-TPA. The effectiveness factor derived from Thiele Modulus expressions in the limit of strong intrazeolite mass transfer limitations, assuming kinetic rates are intrinsically first-order in propene pressure, predicts that measured rates (per H^+) increase linearly with the inverse of crystallite size, as observed for MFI-DABCO and MFI-EDA samples here, and for MFI-TPA and TON samples reported previously. The slope of the regression is proportional to both the effective kinetic rate constant and the effective diffusivity, $(k_{eff}D_{eff})^{1/2}$. This parameter was ~8x higher for MFI-EDA and MFIDABCO than on MFI-TPA and approach those of TON, consistent with higher fractions of H^+ sites in MFI channels of similar size to the unidirectional straight channels of TON (~0.55 nm). The systematic increase in $(k_{eff}D_{eff})^{1/2}$ values across this series of catalyst families, going from MFI-TPA to MFI-DABCO/EDA to TON suggests that k_{eff} or D_{eff} (or both) increase as confining void size decreases. DFT-predicted effective dimerization free energies barriers were lower at sites in MFI intersections than in straight and sinusoidal channels at all T-sites except T4 , the only T-site without access to the intersection, suggesting that biasing H^+ sites to the channels decreases k_{eff}. To study the effect of H^+ site location on D_{eff}, dimerization rate transients following step changes in C_3H_6 pressure were measured on MFI-DABCO. The number of turnovers required to reach the new steady-state rate was lower than values for MFI-TPA but similar to BEA and FAU zeolites with large pores that alleviate transport limitations. At fixed reaction conditions (X ~0.04%, 503 K, 315 kPa C_3H_6), MFI-DABCO shows higher selectivity to higher molecular weight products, with respect to the primary product (C_6), than MFI-TPA. This suggests that heavier products are able to more easily egress out of MFI micropores on MFI-DABCO than MFI-TPA, implying higher D_{eff} values for the former samples and rationalizing higher measured dimerization rates on MFI-DABCO and MFI-EDA despite DFT-predicted lower k_{eff} values for channel H^+ sites.

Selective Hydrogen Combustion over Silica-Supported Sodium Tungstate Catalysts

Elijah R. Kipp, University of Minnesota

We report that 5 wt. % Na_2WO_4/SiO_2 catalysts preferentially combust H_2 under aerobic conditions in mixtures with several hydrocarbons with >98% selectivity at 883-983 K. Reaction orders and kinetic isotope effect experiments with $D_2/C_mH_n/O_2$ mixtures demonstrate the kinetic relevance of H-H activation, while $16O_2/18O_2$ scrambling experiments demonstrate that O_2 activation is irreversible and kinetically irrelevant at 923 K. N_2O was also found to facilitate H_2 combustion at similar conditions but react with vacant sites two orders of magnitude slower than O_2. H_2 combustion rates at high oxidant pressures plateau at similar values for N_2O and O_2, suggesting that N_2O and O_2 give rise to the same active oxidant on the surface; N_2 formation rates during H_2 combustion in 16 kPa N_2O decrease monotonically with increasing O_2 partial pressure (0-0.6 kPa O_2), evincing a competition between O_2 and N_2O for the same active surface sites. These kinetic data are consistent with a mechanistic sequence involving one of the following as the most abundant surface intermediate: (a) a monoatomic surface species O* that forms from either N_2O or ½ O_2, or (b) a hydroxyl pair HO/OH* derived from H_2 reaction with an adsorbed OO* species that forms from either O_2 or 2 N_2O. Apparent activation energies of H_2 combustion and rates per mol W are similar for Na-WO_x/SiO_2 catalysts with identical Na loadings but different W loadings (0.3-3 wt. %), suggesting that active sites may comprise isolated (Na)-WO_x sites. DFT calculations corroborate the activity of isolated Na-WO_x sites for sequential formation of OO* and HO/OH* pairs during aerobic combustion of H_2.

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

Tania Class-Martinez, Purdue University

Aluminosilicate zeolites are used in their H-forms as Brønsted acid catalysts and in their Cu-exchanged forms for the selective catalytic reduction of nitrogen oxides with NH_3. Oxidative regeneration forms water (~10 kPa H_2O) at high temperatures (>823 K), causing hydrothermal aging (HTA) leading to dealumination, which involves the hydrolysis of Al-(OH)-Si linkages that remove framework Al (Al_f) to form extra-framework Al (Al_{ex}) species that are proposed to migrate through void spaces to react and form alumina agglomerates. Empirical observations indicate that small-pore (eight-membered ring; 8-MR) zeolites such as chabazite (CHA) are more resistant to dealumination than medium- and large-pore zeolites upon HTA. Moreover, total Al content (e.g., Si/Al), Al distribution (e.g., among different T-sites), and structural defects (e.g., silanol groups) have been reported to influence dealumination kinetics (723-873 K, 5-35 kPa H_2O) on MFI zeolites. Here, we study CHA zeolites, a high-symmetry (one T-site) framework, to quantify the kinetics of dealumination and elucidate new mechanistic details about the process.

On a given CHA sample, the number of Al_f sites decreased with time upon exposure to HTA conditions, reflecting hydrolysis of Al_f-O bonds and removal of Al_f centers to form Al_{ex} species. The temporal decrease in Al_f content was described by an empirical rate to obtain an analytical time derivative, taken as the instantaneous dealumination rate, at different HTA conditions. Dealumination rates (923 K), normalized by H_2O pressure and Al_f content, increase non-linearly with Al_f content at low H_2O pressures (<8.5 kPa), but show a strict linear dependence on Al_f content at high H_2O pressures (>30 kPa) characteristic of a second-order mean-field process, and suggesting a different kinetic regime at low H_2O pressures. If dealumination occurs via a sequential mechanism in which H_2O hydrolyzes four Al_f-O bonds to form Al_{ex} monomers, which then migrate and dimerize to form Al_{ex} agglomerates, then a second-order mean-field dependence on Al_f content is consistent with Al_{ex} agglomeration as the sole kinetically relevant step. Density functional theory calculations are consistent with both, activated Al_{ex} migration and irreversible aggregation. Although dealumination rates (per Al_f and PH_2O) at low water pressures (8.5 kPa H_2O) increase non-linearly with Al_f at low temperatures (<923 K), dealumination rates increase linearly with Al_f content at high temperatures (>973 K), suggesting a shift in kinetic regime controlled by Al_f-O hydrolysis to one controlled by Al_{ex} agglomeration. Thus, both Al_f hydrolysis and Al_{ex} agglomeration are potential kinetically relevant steps in dealumination, but to different extents dependent on HTA conditions (temperature, H_2O pressure). We will also discuss dealumination kinetics for CHA samples of different Al_f density (bulk Si/Al) and local Al arrangement (6-MR paired site content), to test hypotheses suggesting that dealumination rates should remain invariant with Al_f content when measured in a regime controlled by Al_f-O hydrolysis, but not when measured in a regime controlled by Al_{ex} agglomeration.

Selective Hydrogenation of Biomass-derived Furans Over Cu Catalysts: Experiments and Theory

Evangelos Smith, University of Wisconsin–Madison

Increasing dependence on petroleum-based products has renewed interest in biomass-derived feedstocks. 5-hydroxymethylfurfural (HMF) has been identified as a versatile platform molecule that can be synthesized sustainably through the dehydration of simple sugars. An HMF-acetone-HMF (HAH) monomer that displays higher stability than HMF was shown to be obtained in high yields through an aldol condensation. HAH is a highly functionalized platform chemical that opens pathways to produce a wide range of polymers, dyes, and liquid fuels. Recently, we showed that HAH undergoes furan ring hydrogenation over Pd and Ru, while Cu selectively hydrogenated the aliphatic double bonds of HAH. Herein, we combine detailed reaction kinetics experiments with first-principles calculations to identify descriptors that govern HAH hydrogenation over Cu catalysts.

Given the large molecular size of HAH, we employed a furfural acetone (FAc) surrogate molecule to model HAH hydrogenation. To verify that FAc is a suitable surrogate for HAH, we performed batch reaction experiments over a Cu/γ-Al_2O_3 catalyst to compare the hydrogenation behavior of FAc and HAH. From these experiments, FAc underwent two consecutive hydrogenation events. Similar to HAH, FAc first undergoes aliphatic alkene hydrogenation and is converted to PFAc=O, followed by cascade hydrogenation of the carbonyl oxygen to form PFAc-OH, without any furan ring hydrogenation. With FAc identified as a suitable surrogate for modeling HAH hydrogenation, a more detailed reaction kinetics study was conducted using a continuous flow reactor system. Notably, the apparent activation energy barriers for hydrogenation of the aliphatic alkene (0.60 eV) and carbonyl (0.40 eV) groups of FAc are consistent with reported values for HAH hydrogenation. Reaction orders with respect to H_2 and FAc were determined to be nearly one.

Simultaneously, DFT calculations were performed to model the hydrogenation of FAc over a Cu(111) surface. Our predictions showed that the hydrogenation of the aliphatic alkene group (C4) of FAc is more facile than the hydrogenation of the furan ring, which displays weak interactions with the Cu surface. We determined an apparent activation energy barrier for FAc hydrogenation (0.60 eV) that agreed with our DFT predictions (C4 aliphatic alkene hydrogenation barrier of 0.57 eV). Our DFT calculations further show that weak interactions between the furan ring and Cu surface are responsible for the selective hydrogenation behavior.

Interrogating the Kinetic and Mechanistic Origins of N_2O Formation during NH_3 Selective Catalytic Reduction of NO_X on Cu-CHA Zeolites

Bryan Cruz Delgado, Purdue University

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x; x = 1,2) with NH_3 to form N_2 is commercially practiced using copper-chabazite (Cu-CHA) zeolites, but also forms undesired nitrous oxide (N_2O) that possesses a global warming potential 300× that of CO_2. Literature reports propose various pathways to form N_2O, including on Brønsted acid (H^+) sites via ammonium nitrate decomposition or on Cu sites via H_2N_2O-like intermediates. Here, we perform steady-state experiments to quantify N_2 and N_2O formation kinetics with varying reaction conditions that alter the kinetic relevance of Cu(II)/Cu(I) redox SCR half-cycles, transient Cu(II) reduction and Cu(I) oxidation experiments to quantify N_2O formation from different Cu site types and reactions, and combine these data with Density Functional Theory (DFT) and *in-situ* and *operando* X-ray absorption spectra (XAS) to determine the mechanistic origins of N_2O formation on Cu-CHA during low-temperature (<573 K) NO_x SCR.

Low-temperature (<573 K) NO_x SCR with NH_3 involves a Cu(II) reduction half-cycle mediated by a single-site reduction mechanism and a Cu(I) oxidation half-cycle mediated by O_2 via a dual-site oxidation mechanism involving the pairing of two NH_3-solvated Cu(I) ions facilitated by the mobility of these complexes within zeolitic voids. During steady-state SCR catalysis, increasing Cu ion densities or O_2 pressures, increase rates of Cu(I) oxidation relative to Cu(II) reduction, shifting the most abundant reactive intermediates from Cu(I) to Cu(II) complexes. N_2 formation rates show a Langmuirian dependence on O_2 pressure as the kinetically relevant half-cycle shifts from Cu(I) oxidation (first-order in O_2) to Cu(II) reduction (zero-order in O_2). In contrast, N_2O formation rates (per Cu) increase linearly with O_2 pressure, together with commensurate linear increases in the *in-situ* pressures of NO_2 formed via NO oxidation pathways. Indeed, deliberately co-feeding NO_2 (0.003 kPa) resulted in an increase in N_2O selectivity compared to NO_2-free feeds.

Furthermore, increasing the density of nominally isolated Cu ions in a given CHA material (of fixed Si/Al = 26), plotted as the number of Cu per double six-membered rings building units (d6r), led to increases in the first-order rate constant for N_2O formation, consistent with the effects of Cu loading on N_2O formation rates reported previously. The dependence of N_2O formation rates on Cu density suggests that some N_2O formation pathways involve reactions with Cu(II) species, given *operando* XAS data showing that Cu(II) species increase with Cu density given the dual-site nature of Cu(I) oxidation pathways. We used DFT calculations to assess reactions of NO_2 and NO with various Cu(I) and Cu(II) species, including the hypothesis that N_2O forms upon NO_2 reactions with Cu(II) sites. These results propose Cu-based pathways for N_2O formation in Cu-CHA during standard SCR.

Acknowledgments

The Catalysis Club of Chicago would like to thank the following people and organizations for their generous contributions to the success of the 2025 Spring Symposium, including:

- NACS: We acknowledge the North American Catalysis Society for foundational support of the Catalysis Club of Chicago.

- GTI Energy: We are extremely grateful to GTI Energy for their generous support of the CCC Spring Symposium through donation of their event space, and administrative and catering support.

- Honeywell UOP: we thank Honeywell UOP for support of CCC, including via sponsorship of the Herman Pines Award.

- Micromeritics, Inc (Tier 1 sponsor):

micromeritics®

Micromeritics, a global leader, provides high-performance systems for characterizing particles, powders, and porous materials. Our industry-leading portfolio includes equipment for pycnometry, adsorption, dynamic chemisorption, porosimetry, powder rheology, catalyst reactivity and breakthrough studies, and particle size analysis. The company is headquartered in Norcross, Georgia, USA with manufacturing sites in the U.S. and Europe, and direct sales operations throughout North America, Europe, and Asia.

Contact : Kevin Mailloux kevin.mailloux@micromeritics.com

CCC Institutional Representative Committee:

- Ciara Tyler (U. Minnesota) – morning session co-chair
- Bereket Bekele (Purdue) – afternoon session co-chair
- Sara Ahsan (UW-Madison)
- Jose Rebolledo-Oyarce/Steven Yeo (U. Notre Dame)
- Seryeong Lee (Northwestern)
- Minjung Kim (Northwestern)
- Dawson Grimes (Northwestern)
- Carly Byron (Argonne National Lab)

Parking and Entrance