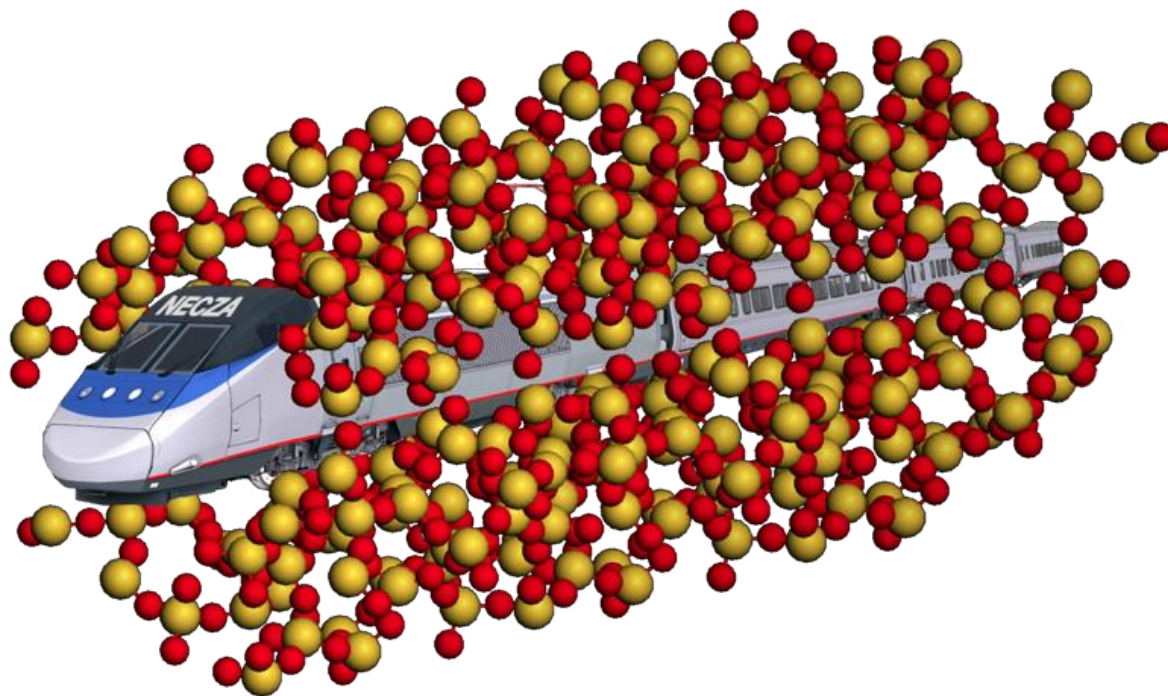


# **NECZA 2024**

## **The 28<sup>th</sup> Meeting of the North-East Corridor Zeolite Association**



**Friday, December 6, 2024**

**The Villanova Room**

**Connelly Center**

**800 E. Lancaster Ave.**

**Villanova University**

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## 27<sup>th</sup> Annual NECZA Meeting – Organizing Committee

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*The organizing committee is grateful for the following contributions that help make this meeting possible*



## Scientific Program

<b>8:15 – 8:55</b>	<b><i>Registration, Breakfast, Poster Setup</i></b>
<b>8:55 – 9:00</b>	<b><i>Welcome Remarks</i></b>
<b>9:00 – 9:35</b>	<u>Dongxia Liu</u> (University of Delaware) “Electrochemically Catalyzed Zeolite Synthesis: Where Hydrothermal Crystallization and Electrochemistry Converge”
<b>9:35 – 10:10</b>	<u>Qi Fu</u> (BASF) “Monitoring the Zeolite Crystallization Process”
<b>10:10 – 10:45</b>	<b><i>Coffee Break – Poster Session I</i></b>
<b>10:45 – 10:50</b>	<i>Sponsor presentation – Anton Paar</i>
<b>10:50 – 11:25</b>	Anton Paar sponsored speaker: <u>Alexander Katz</u> (University of California Berkeley) “Understanding small-pore zeolites that selectively adsorb CO <sub>2</sub> over water”
<b>11:25 – 12:05</b>	<b><i>Poster Session II</i></b>
<b>12:05 – 1:15</b>	<b><i>Lunch and Business Meeting</i></b>
<b>1:15 – 1:55</b>	<u>Panel:</u> Future of Zeolite Science Panel Discussion
<b>1:55 – 2:35</b>	<u>Selected Poster Presentations (2 x 15 min each)</u>
<b>2:35 – 2:50</b>	<b><i>Coffee break</i></b>
<b>2:50 – 3:25</b>	<u>Scott Auerbach</u> (University of Massachusetts Amherst) “Using Molecular Simulations and Data Science to Investigate How Zeolites Form and Which Hypothetical Frameworks Seem Feasible”
<b>3:25 – 3:30</b>	<i>Sponsor presentation – Microtrac</i>
<b>3:30 – 4:05</b>	Microtrac sponsored speaker: <u>James W. Harris</u> (The University of Alabama) “Identifying Roles of Distinct Surface Sites for Oxygenate Conversion Over Metal-Containing Zeolites”
<b>4:05 – 4:15</b>	Final remarks and meeting adjournment
<b>5:30 onwards</b>	Dinner (for registered banquet participants) at LaScala’s Fire, Villanova

# **Electrochemically Catalyzed Zeolite Synthesis: Where Hydrothermal Crystallization and Electrochemistry Converge**

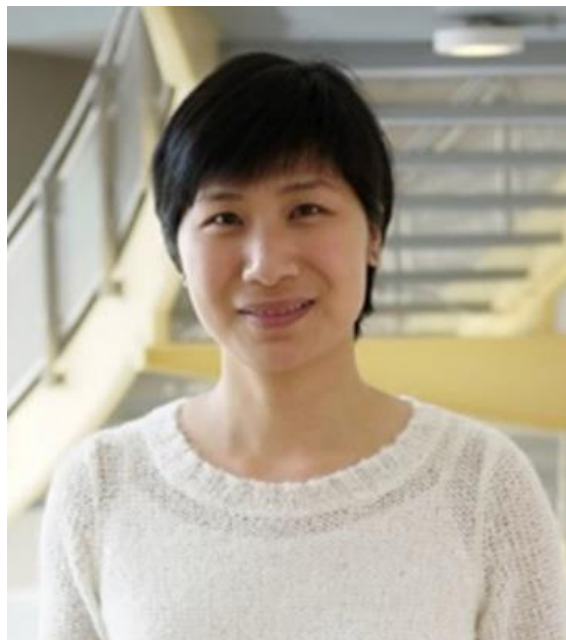
*Dongxia Liu*

Zeolites play a critical role as catalysts, ion exchangers, adsorbents, and membranes in the chemical and petrochemical industries, and their significance is expected to grow in the context of a sustainable future economy. However, zeolite synthesis has seen minimal innovation over the past decades, primarily relying on hydrothermal methods. These traditional processes are energy-intensive and contribute significantly to carbon dioxide emissions, as zeolite crystallization typically requires heating the synthesis gel to temperatures of 100-200 °C over extended periods (20-100 hours). In this presentation, I would like to highlight our recent innovation in zeolite synthesis, catalyzed by an electrochemical approach. We initially applied this method to develop zeolite coatings on metallic substrates, greatly reducing both synthesis time and temperature. The morphology and crystallinity of the zeolite coatings are influenced by factors such as applied current, temperature, time, and precursor composition. We have since extended this approach to zeolite crystallization in solution under hydrothermal conditions. The electrochemically catalyzed zeolite synthesis provides a simple, rapid pathway for producing zeolites, with the potential for developing diverse framework structures, both on substrates and in solution, under milder hydrothermal conditions.

## BIOGRAPHY

Dongxia Liu earned her B.S. in Chemistry from Shandong University in China in 2000, followed by her M.S. degree from the Institute of Chemistry, Chinese Academy of Sciences in 2003. She completed her Ph.D. in chemical engineering at the University of Rochester in 2009. Afterward, she pursued a 2.5-year post-doctoral position at the University of Minnesota. In 2012, she joined the Department of Chemical and Biomolecular Engineering at the University of Maryland (UMD) as an assistant professor and was promoted to an associate professor in 2018 and to a full professor in 2022. In 2023, she joined Department of Chemical and Biomolecular Engineering at the University of Delaware (UD) as a Robert K. Grasselli Professor.

Dongxia is leading the Materials Synthesis and Catalysis Lab at UD, targeting for controlling composition and constitution of nanostructured materials for catalyst, membrane and reactor technologies to address the challenging issues in renewable energy and chemicals production. She has authored more than 100 peer-reviewed journal articles and 12 issued/pending patents on these topics. She serves as an Editor for *Molecular Catalysis* and as an Editorial Advisory Board member for *Catalyst*, *Chem & Bio Engineering*, *ChemCatChem*, *Materials Today Sustainability*, and *The Innovation Materials*. Dongxia has won awards including the UMD's Faculty-Student Research Award (FSRA) awards (2021 and 2013), Junior Faculty Outstanding Research Award in A. James Clark School of Engineering at UMD (2020), and the NSF CAREER award (2013).



# Monitoring the Zeolite Crystallization Process

*Qi Fu*

BASF Corporation, Beachwood, OH, USA.

BASF provides a comprehensive portfolio of state-of-the-art zeolite-based catalysts, including refinery fluid catalytic cracking catalysts, emissions catalysts for both mobile and stationary applications, petrochemical catalysts for alkylation and isomerization reactions, and specialty catalysts applied to reactions such as oxidation, amination, and ammoximation. Additionally, we offer zeolite-containing adsorbents for the removal of water, CO<sub>2</sub>, NH<sub>3</sub>, alcohols, H<sub>2</sub>S, and other substances. We also collaborate with customers to optimize, scale up, and toll zeolites, leveraging our expertise in shaping zeolite catalysts.

We closely monitor the zeolite crystallization process during development and manufacturing to rationally design zeolites and improve production efficiency. In this presentation, I will share various in-situ and ex-situ methods to monitor the crystallization of zeolites and how we utilize these methods to develop chabazite zeolites through an intermediate mordenite (MOR) phase, achieving enhanced hydrothermal stability and improved selective catalytic reduction (SCR) performance.

## BIOGRAPHY

Qi Fu is a Senior Engineer in Group Research at BASF Corporation. Her expertise is in catalyst and adsorbent synthesis, scale up and tech transfer and manufacturing support. She led several projects on zeolite and zeolite-based additives for use in Fluid Catalytic Cracking (FCC) and then transitioned to Process Catalysts & Adsorbents Scale-up North America, focusing on Chabazite for emission control and most recently, development of Hydroisomerization Catalysts for Renewable Diesel and Catalysts for Methanol to Sustainable Aviation Fuel. She has commercialized 9 products and is a co-inventor for 12 patents and 4 publications. Qi holds a Ph.D. in chemical engineering from Tufts University.



## Understanding small-pore zeolites that selectively adsorb CO<sub>2</sub> over water

*Hwangho Lee<sup>1</sup>, Kun-Lin Wu<sup>3</sup>, Shu Hikima<sup>4</sup>, Le Xu<sup>1</sup>, Alexander Okrut<sup>1</sup>, Dan Xie,<sup>2</sup> Ambar Kulkarni<sup>3</sup>, Ryouji Onishi<sup>4</sup>, Takahiko Takewaki<sup>4</sup>, Stacey I. Zones<sup>2</sup>, Alexander Katz<sup>1,\*</sup>*

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Zeolites are promising adsorbents for CO<sub>2</sub> adsorption both for DAC as well as point sources due to their high volumetric capacity, as well as the tunability afforded by their exchangeable cations and microporous framework structure. However, the presence of water (unavoidable for a postcombustion gas mixtures as well as DAC where water is typically a thousand-fold higher in concentration compared to CO<sub>2</sub>) causes competitive adsorption that significantly diminishes CO<sub>2</sub> adsorption capacity of zeolites. Our research addresses the rational design of selective CO<sub>2</sub> binding sites in zeolites. This is an uphill battle (water adsorbs to zeolites with 7.5 kcal/mol higher bonding energy compared to CO<sub>2</sub>), and one that is underrepresented in the literature (about 1.5% of published manuscripts dealing with CO<sub>2</sub> adsorption in zeolites make mention of water as a multicomponent adsorbate), but one that promises large possible benefits in terms of decreasing the capital and energy costs associated with predrying gas mixtures prior to adsorption. In this presentation, focusing on examples from three small-pore zeolite frameworks possessing double 8 membered rings (D8Rs), consisting of RHO, MER, and PAU, we demonstrate the D8R as a highly proficient CO<sub>2</sub> adsorption site, which can favor the adsorption of CO<sub>2</sub> over water (at up to 10% relative humidity) under thermodynamic control. This is enabled by cooperativity between CO<sub>2</sub> and water, which is manifested in CO<sub>2</sub> thermodynamic adsorption amounts that are higher under wet compared to dry conditions. We discuss this cooperativity from the standpoint of a structure derived from Reitveld refinement of PXRD data. Combining gravimetric analysis with IR spectroscopy, our data highlight this cooperativity in terms of water being able to facilitate stronger interactions between CO<sub>2</sub> and cations in the D8R, while also unequivocally demonstrating sites in which CO<sub>2</sub> adsorption causes the desorption of water. These results motivate work in the ultimate quest of a selective zeolitic CO<sub>2</sub> adsorbent, which treats water as just another light gas, obviating the need for drying pretreatment.



## BIOGRAPHY

Alex Katz received his B.S. and M.S. in Chemical Engineering from University of Minnesota, working with Prof. Michael D. Ward at the interface of chemistry & chemical engineering. Four years later, as a Fannie & John Hertz Foundation Fellow, he completed his Ph.D. with Mark Davis at Caltech. He pursued an NSF International Awards Postdoctoral Fellowship in Strasbourg, France at the Institut of Supramolecular Chemistry (Institut Le Bel) at the University of Louis Pasteur. Since 2000, he has been the principal investigator of a multidisciplinary research group in the Department of Chemical & Biomolecular Engineering at UC Berkeley, exploring the molecular design, synthesis, and characterization of functional materials consisting of organic-inorganic active-site assemblies, and the application of these materials in catalysis and selective adsorption. He is a leader in the understanding of functional sites on the molecular level, as an enabler of rational materials-design approaches. Much of his research group's approach consists of synthesizing controlled organic-inorganic interfaces, in order to elucidate synthesis – function relationships. He has been awarded a Fulbright Fellowship, the Catalysis Society of Metropolitan New York Award for Excellence in Catalysis, as well as the Newman Entrepreneurial Initiative Award.



# Using Molecular Simulations and Data Science to Investigate How Zeolites Form and Which Hypothetical Frameworks Seem Feasible

*Scott Auerbach*

Department of Chemistry, University of Massachusetts Amherst  
Department of Chemical Engineering, University of Massachusetts Amherst

Even though millions of siliceous zeolite structures have been generated by computer-aided searches, no new hypothetical framework has yet to be synthesized. This inability frustrates efforts to fabricate promising zeolites for new technologies in areas such as carbon mitigation, and raises the fascinating question: what if anything makes real and hypothetical zeolites systematically different? This question has intrigued zeolite scientists for decades; yet, most work to date on the zeolite problem has been limited to assessing intuitive structural descriptors. Here, we tackle this problem through a rigorous data science scheme called the “zeolite sorting hat.” The zeolite sorting hat blends principal component analysis, a linear support vector machine (SVM), and a data-driven thermodynamic stability filter. This approach yields three hypothetical frameworks as promising targets for synthesis, each with a composition suggested by the zeolite sorting hat. The zeolite sorting hat points to 2nd neighbor Si-O distances as the key factor that distinguishes real and hypothetical structures. We emphasize that this finding is an outcome of our study – not an assumed working hypothesis.

The sorting hat workflow was extended to analyze a large dataset of Monte Carlo trajectories that simulate zeolite LTA crystal formation. The Monte Carlo simulations predict (and experiments confirm) that LTA forms faster with two organic structure-directing agents (OSDAs) that match the sizes of the small and large LTA pores (“2OSDA” synthesis), than it does when only using one large OSDA type (“1OSDA” synthesis). A linear SVM was trained to segregate structural microstates from 1OSDA and 2OSDA datasets, suggesting that the 2OSDA dataset is much more structurally homogeneous. Inspired by this finding, we computed the pair entropy for each microstate in the 1OSDA and 2OSDA datasets, finding that the difference in Si-Si pair entropy semi-quantitatively accounts for the speedup in zeolite formation seen in Monte Carlo simulations. Experimental implications for this entropic speedup in terms of high-pressure syntheses are discussed.

## BIOGRAPHY

### **Scott M. Auerbach, Ph.D.**

*Full Professor of Chemistry*

*Adjunct Full Professor of Chemical Engineering*

*Founder & Mahoney Family Sponsored Executive Director,*

*Integrated Concentration in STEM (iCons) Program*

*University of Massachusetts Amherst*

auerbach@umass.edu

Scott Auerbach is professor of chemistry at UMass Amherst. Auerbach's research focuses on simulating nanostructured materials important to technologies promoting sustainability including biofuels and fuel cells – leading to 2 books and 130 articles. Auerbach earned a BS in Chemistry from Georgetown in 1988 and a PhD in theoretical chemistry from UC Berkeley in 1993. After an NSF postdoc at UC Santa Barbara, Auerbach began his career in 1995 at UMass Chemistry and was promoted to full professor in 2004. Auerbach won an NSF Career Award in 1998, a Sloan Fellowship in 1999, and a Dreyfus Teacher-Scholar Award in 1999. Auerbach is the founder and the Mahoney Family Sponsored executive director of the Integrated Concentration in STEM (iCons) Program, which challenges STEM and Business students to design solutions for societal problems in clean energy and biomedicine. In 2016, Auerbach won the inaugural Manning Prize for Teaching Excellence; and in 2017 Auerbach won the UMass Distinguished Teaching Award. Auerbach enjoys music, fitness, and all forms of skiing.



## Identifying Roles of Distinct Surface Sites for Oxygenate Conversion Over Metal-Containing Zeolites

James W. Harris

The University of Alabama, Chemical and Biological Engineering

Quantifying active sites under reaction conditions is paramount to quantification of per-site turnover frequencies and consequently to direct comparisons of the reactivity of heterogeneous catalysts. In this talk, I will give discuss our efforts to determine the functions of, and quantify, multiple types of active sites present on metal-containing dealuminated Beta (deAlBeta) catalysts. These materials are useful for production of C<sub>3+</sub> olefins from ethanol in a single reactor en route to production of sustainable aviation fuel, in a distinct pathway from commercial processes that first dehydrate ethanol to ethylene, then dimerize ethylene to butene in a second reactor. This reaction occurs over multifunctional copper-, zinc-, and yttrium-containing deAlBeta zeolites, via a series pathway requiring dehydrogenation, aldol condensation, hydrogenation, and dehydrations in a precise sequence. Product formation rates in these trimetallic catalysts are proportional to the density of Lewis acidic yttrium sites, motivating studies of monometallic Y/deAlBeta catalysts. We have quantified the number of Lewis acidic active sites in these materials via *ex situ* and *in situ* chemical titrations, and determined that there is evidence for at least two types of yttrium sites that collectively catalyze dehydration, aldol condensation, and Meerwein-Ponndorf-Verley (MPV) reduction. Y-containing sites that form crotonaldehyde and crotyl alcohol are distinct from those that catalyze crotyl alcohol dehydration, based on *in situ* titration experiments and the deactivation profiles for each product with time on stream. By varying residence time, we evince that crotonaldehyde and crotyl alcohol are intermediates enroute to butadiene formation. Isotopic tracer studies on Y/deAlBeta and La/deAlBeta suggest ethanol to acetaldehyde conversion via coupled MPV reduction and Oppenauer oxidation (MPVO) reactions occur in addition to crotonaldehyde to crotyl alcohol MPV reduction, and that ethanol-acetaldehyde interconversion is quasi-equilibrated. The kinetics and product selectivities during reaction of ethanol-acetaldehyde mixtures over monometallic yttrium- or lanthanum-containing deAlBeta zeolite catalysts are disparate, suggesting predictable differences in these metals as primary binding sites for adsorption and conversion of small oxygenates. These findings aid in our ongoing efforts to reduce the cost and carbon footprint of SAF production.

## BIOGRAPHY

James W. Harris received a B.S. in Chemical Engineering from the University of Virginia in 2012 and a Ph.D. in Chemical Engineering from Purdue University in 2017. Harris joined the Department of Chemical and Biological Engineering at The University of Alabama as an Assistant Professor in Fall 2019. His research group is involved in projects related to the responsible use of energy carriers for production of fuels and chemicals. Professor Harris is particularly interested in catalysis occurring over metal surfaces whose properties evolve as a function of their environment, and over sites confined within the pores of zeolites. Professor Harris has been awarded the Oak Ridge Affiliated Universities Ralph E. Powe Award, the University of Alabama Undergraduate Research and Creative Activity Conference's "Top Faculty Mentor" award, the American Chemical Society's Petroleum Research Fund (PRF) Doctoral New Investigator Award, and was named a "Pioneer of Catalysis and Reaction Engineering" by the AIChE CRE Division in 2024. Harris was selected to the inaugural class of "Hewson Engineering faculty Fellows" by The University of Alabama in 2024. His group's research is supported by the National Science Foundation, the U.S. Department of Defense, and the U.S. Department of Energy. Harris serves as the programming co-chair for the AIChE CRE Division, as an alternate councilor for the ACS CATL division, and as the President of the Southeastern Catalysis Society (SECS). In his spare time, Dr. Harris enjoys cycling and playing tennis.



**POSTER  
ABSTRACTS**

2024-NECZA Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

## **Electrochemical Synthesis of Zeolite Coatings with Controlled Crystal Polymorphism and Self-Regulating Growth**

Warty, A.<sup>1</sup>, Chen, A.<sup>2,3</sup>, Tran, D.T.<sup>3</sup>, Kraus, H.<sup>4</sup>, Woehl, T. J.<sup>4</sup>, Liu, D.<sup>1\*</sup>

<sup>1</sup> *Department of Chemical and Biomolecular Engineering, University of Delaware, Delaware, DE 19716, USA*

<sup>2</sup> *Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA*

<sup>3</sup> *DEVCOM Army Research Laboratory, FCDD-RLA-GD, 2800 Powder Mill Road, Adelphi, MD 20783, USA*

<sup>4</sup> *Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, USA*

Zeolite coatings are studied as molecular sieves for membrane separation, membrane reactors, and chemical sensor applications. They are also studied as anti-corrosive films for metals and alloys, antimicrobial and hydrophobic films for heating, ventilation, and air conditioning, and dielectrics for semiconductor applications. Zeolite coatings are synthesized by hydrothermal, ionothermal, and dry-gel conversion approaches, which require high process temperatures and lengthy times (ranging from hours to days). Here we report the first zeolite coatings synthesized via electrochemical deposition on cathodic electrode, with controlled crystal polymorphism achieved within a sub-hourly duration. We demonstrate this approach by developing sodium zeolite (e.g., sodalite (SOD), NaA (LTA), and Linde Type N (LTN)) coatings on a titanium electrode and extending the synthesis method to porous stainless steel. The coating morphology and crystallinity depend on temperature, time, and applied current. The coating thickness is independent of the applied current, showing the presence of a self-regulating mechanism to ensure uniform coating thickness across the metal surface. The electrochemical zeolite growth mechanism was elucidated with high-resolution transmission electron microscopy and applications of the resultant zeolite coatings for oil/water separation and ethanol/water pervaporation were exploited. Electrochemical synthesis represents a novel, simple, fast, and environmentally friendly approach to preparing zeolite coatings. It can potentially be generalized for developing zeolite materials with diverse framework structures, morphologies, and orientations for substrates with complicated geometries.

2024-NECZA Poster Abstract

Type: (Graduate)

Consideration in poster competition: (Yes)

## Spectro-Kinetics of Carbocation Transformations in Zeolite Pores

Bhave, D. Jentoft, F.C. \*

Department of Chemical Engineering, University of Massachusetts Amherst, 686 North Pleasant Street, Amherst, Massachusetts 01003, USA

\*email: fcjentoft@umass.edu

Small olefins like ethylene and propylene are precursors for important chemicals including ethylene oxide, ethylene glycol, and propylene oxide, and they serve as the monomers for key polymers (PE, PP). Methanol-to-olefins (MTO) conversion<sup>1</sup> catalyzed by zeolites or zeotypes is an alternative, potentially sustainable route to produce olefins, if methanol is synthesized from biomass or CO<sub>2</sub> rather than fossil resources. A characteristic of the reaction mechanism is the presence of long-lived surface intermediates (“hydrocarbon pool”) in the pores of the zeolite, which are believed to be essential for olefin formation.<sup>2</sup> Cyclic species, identified as alkylcyclopentenylum and alkylbenzenium ions, constitute a large fraction of the species in the pores and are among the proposed intermediates in the catalytic cycle.<sup>3,4</sup> However, the pathways for the formation and transformation of these intermediates and their relevance are still debated. Especially, knowledge of true activation energies for the individual reaction steps occurring in the hydrocarbon pool, such as ring contraction, cyclization, isomerization, alkylation, and cleavage is lacking.

The goal of this work is the determination of true activation energies of MTO-relevant cation transformations by avoiding obfuscation through transport and adsorption/desorption steps in zeolite pores. The reactions investigated are ring contraction and cyclization within the zeolite frameworks of MFI, MOR, BEA, and FAU. Zeolites were obtained from Zeolyst. IR and UV-vis spectroscopy were applied to monitor the reaction kinetics under isothermal conditions. As model reactants, 1,3,5,5-tetramethylcyclohexadiene (TMCH) or 2,6-dimethyl-2,4,6-octatriene (OCT) were used, as illustrated in Figure 1. Protonation of TMCH molecules gave cyclohexenyl cations (C=C-C<sup>+</sup> stretching vibration at 1549 cm<sup>-1</sup>), which contracted to a mixture of cyclopentenyl cations (1506 cm<sup>-1</sup> and 1489 cm<sup>-1</sup>). OCT was protonated in the pores to octadienyl cations (1567 cm<sup>-1</sup>), which cyclized to cyclopentenyl cations (1491 cm<sup>-1</sup>).

The kinetics of ring contraction were found to be complex, with parallel formation of two differently substituted cyclopentenyl cations below ~ 100 °C and interconversion of these two products at higher temperature. The reaction progress could be captured by a first-order kinetics model reflecting this network of parallel and sequential reactions, and Arrhenius plots delivered activation energies between 62 ± 3 (A to B in Figure 1) and 87 ± 5 kJ/mol (A to C). The kinetics of cyclization presented a simpler case. The activation energy for the cyclization reaction in H-MOR and H-ZSM-5 was similar with 54 ± 5 kJ/mol, suggesting a minor influence of the framework.

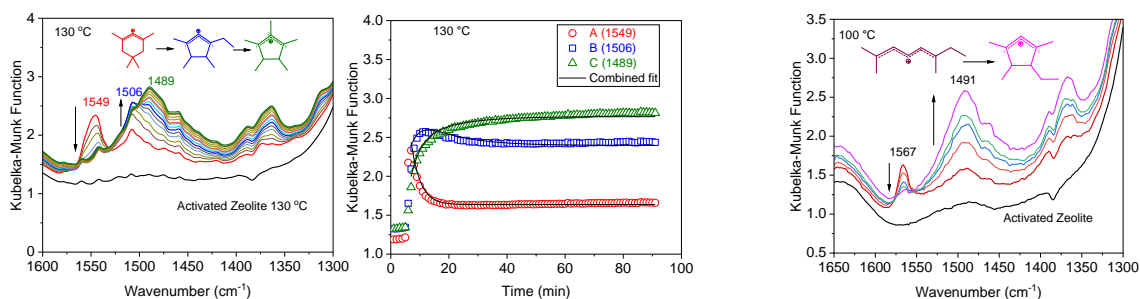


Figure 1: Spectro-kinetics for ring contraction of the tetramethylcyclohexenyl cation (left) and time-resolved IR spectra of the cyclization of the dimethyloctadienyl cation in H-MOR (right)

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- [3] E. D. Hernandez; F. C. Jentoft, *ACS Catalysis*, **10** (2020) 5764.
- [4] J. F. Haw; W. Song; D. M. Marcus; J. B. Nicholas, *Acc. Chem. Res.*, **3** (2003) 317.



2024-NECZA Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

## Reaction-Based Techniques for Identification of Acid and Metal Sites in (Bifunctional) Zeolites

**Cole W. Hullfish,<sup>1</sup> Jun Zhi Tan, and Michele L. Sarazen<sup>1,\*</sup>**

<sup>1</sup>*Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544*

Acid site distributions in zeolitic micropores and on external surfaces have been shown to yield differences in rates and selectivities due to site accessibility and shape-selective transition state stabilization. In such systems, product distributions often depend on zeolite pore size, connectivity, and intracrystalline residence times, and these effects are accentuated for reactions involving diffusion-limited molecules.<sup>1</sup> Such ramifications are not limited to monofunctional Brønsted acidic zeolites, as metal siting in bifunctional zeolite-metal nanoparticle catalysts yield similar catalytic consequences due to reactant and product diffusion to and between functions.<sup>2</sup> While these effects are well-documented in select reactions, extension to other systems is limited by the ability to determine active site distributions, which can be difficult to obtain. Herein, we examine reaction-based methods to quantify Brønsted acid and metal nanoparticle site distributions in (metal-loaded) zeolite catalysts. External acid site densities in metal-free MFI zeolites are evaluated by trimethylbenzene (TMB)-dibenzyl ether (DBE) alkylation reactions which occur exclusively on crystallite surfaces. Measured zero-order alkylation rate constants trended with Al-normalized surface BAS densities utilizing a published linear correlation,<sup>3</sup> though surface BAS notably did not trend with total Al content. Similar size-exclusion principles are utilized to evaluate external metal nanoparticle densities in metal-loaded zeolites in which 1-pyrenemethanol partial oxidation turnovers are comparatively few relative to a reference Pd/SiO<sub>2</sub> catalyst, thus suggesting near-complete nanoparticle encapsulation in BEA. This study demonstrates how reaction-based frameworks can assess metal and acid siting in zeolites and the subsequent catalytic consequences of internal vs. external sites and metal-acid proximity. Further, this work informs tailored catalyst synthesis for global challenges such as polyolefin upcycling and natural gas to liquids for which siting phenomena observed herein are relevant.

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- [3] Ezenwa, S., Hopping, G.M., Sauer, E.D., *et al.* *React. Chem. Eng.* **9** (2024) 1096.

2024-NECZA Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

## Development of a Joule-Heated Reactor with Porcupine Coil Heating Element for Endothermic Reactions

Enerelt Burentugs,<sup>1</sup> Raul F. Lobo<sup>1</sup>

<sup>1</sup> *Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716,*

Over the past decade, greenhouse gas emissions have reached the highest levels in human history, requiring urgent action. The chemical industry was responsible for around two percent of total CO<sub>2</sub> emissions in 2021<sup>1</sup>, and it is important that chemical manufacturing processes are electrified. Compared to conventional thermochemical reactors, joule-heated reactors (JHR) provide local uniform heating, maximizing catalyst utilization while limiting unwanted byproducts. Additionally, this reactor configuration allows for a quicker start-up time and can achieve higher temperatures at a higher energy efficiency<sup>2</sup>. While JHR has demonstrated improved reaction yields and efficiencies, many technical aspects remain challenging, including scalability, temperature control, and mass and heat transfer.

In this study, we develop a JHR that uses a porcupine coil to electrify highly endothermic, high-temperature chemical reactions. The reactor's performance was tested by carrying out a catalytic ethane dehydrogenation reaction (EDH) using a highly active Mn-containing ZSM-5 catalyst<sup>3</sup>. With conditions comparable to conventional reactors, the proposed reactor system exhibited excellent catalytic performance at low power inputs. The effects of different operating parameters on the performance of EDH reaction are evaluated experimentally and numerically using Computational Fluid Dynamics (CFD) simulation. Preliminary experimental and modeling results indicate that increasing washcoat thickness increases the catalytic rate while increasing the input power leads to coke formation on the catalyst due to thermal cracking. Moreover, CFD results revealed that porcupine coil geometry produces turbulent-like flow conditions, alleviating mass-transfer limitations. Future work will include quantifying the energy efficiency of the current setup and optimizing both the model and the JHR.

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- [2] Xinying Li, Ding Yuan, Tian Xie, Quancong Zhang, Wenjun Xu, Ting Fu, Xuyang Chu, Tao Luo, Linjing Wu, and Wei Zhou. UV-Laser ablation enhanced Joule-heating catalyst support for electrified MSR in microreactor. *Chemical Engineering Journal*, 459:141571, March 2023. ISSN 1385-8947.
- [3] Pan, J.; Lobo, R. F. Ethane Dehydrogenation over Manganese Oxides Supported on ZSM-5 Zeolites. *Catal. Sci. Technol.* 2023, 13 (9), 2794–2801.

2024-NECZA Poster Abstract

Type: (Graduate)

Consideration in poster competition: (Yes)

## High Temperature and Pressure Pure-Silica Zeolite Ammonia Adsorbents and Their Use in Adsorption-Enhanced Catalytic Reactors

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Improving the efficiency of ammonia synthesis processes by integrating reaction with separation is a topic of long-standing interest. One approach is the use of sorption-enhanced catalytic reactors<sup>1</sup>, where *in situ* ammonia sorption removes it from the vapor phase and allows reaction to proceed with ammonia yields beyond those dictated by thermodynamic equilibrium in the absence of sorption. While many sorbents have been used for this purpose, challenges remain with full regeneration at practical ammonia pressures limiting the potential benefits of sorption-enhanced reactors<sup>2,3,4</sup>. In this work, we introduce pure-silica zeolites for this application. First, we determine high-pressure high-temperature adsorption data using a specially designed adsorption equipment. Our findings indicate that pure-silica zeolites, especially the ones with high concentration of SiOH, exhibit high ammonia working adsorption capacity compared to previously reported commercial adsorbents. Gibbs ensemble Monte Carlo simulations allow to extend the data range to higher temperatures and pressures, provide information on adsorbate distribution, and explain observed trends in adsorbed amounts and enthalpies. A proof of concept is demonstrated using a batch sorption-enhanced catalytic reactor.

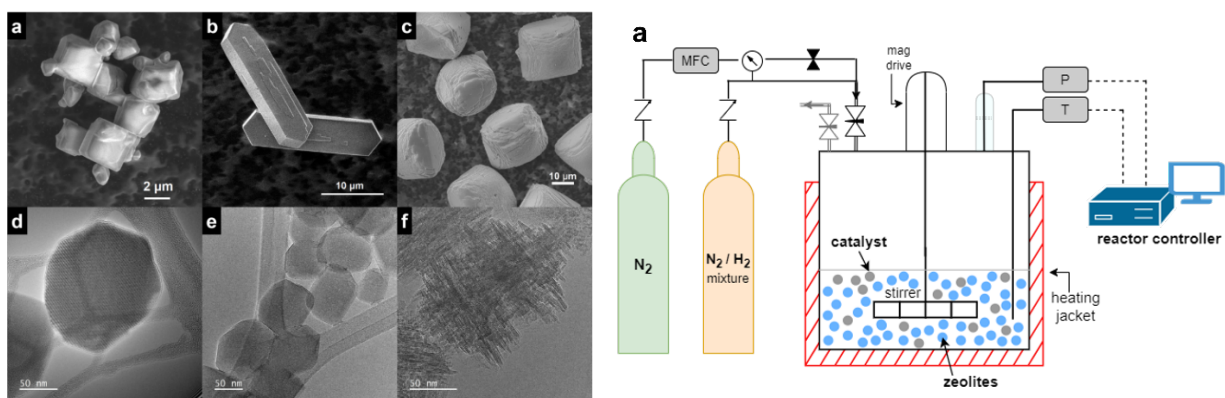


Fig. (Left) Six pure silica zeolite tested in this work. a) F-LTA, b) F-MFI, c) F-BEA, d) deAl-ZSM-5 (Zeolyst), e) OH-MFI, f) SPP. (Right) A schematic diagram of the integrated adsorption-reaction system.

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2024-NECZA Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

## Unveiling Structural Insights of RE/Beta Zeolites for Selective Biomass Valorization

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Rare-earth (RE) metal-incorporated zeolite Beta presents a promising strategy for improving conversion and selectivity specifically in the ethanol-to-olefins (ETO) process for sustainable aviation fuel (SAF) synthesis,<sup>1</sup> while also offering potential applications in other catalytic reactions such as isomerization, hydrogenation, and alkylation.<sup>2-4</sup> In this study, we present a high-throughput computational analysis of yttrium-modified zeolite Beta, examining five proposed Y sites and generating 91 distinct Y/Beta structures. Through systematic screening, we identified 19 stable configurations, closely aligned with experimental data from X-ray spectroscopy and pyridine FTIR, supporting the diversity of observed experimental structures in Y/Beta frameworks. CI-NEB simulations of ethanol dehydration on defect-open and dehydrated defect-open sites reveal Lewis acid catalytic activity, with calculated activation energies closely matching experimental observations. Our findings highlight the potential of Y-modified zeolite Beta for catalyzing reactions requiring Lewis acidity.

Extending this approach, we explored the incorporation of various rare-earth (RE) elements into the Y/Beta framework using hybrid-GGA HSE06-D3 (BJ) simulations. The results consistently showed structural stability, indicating the versatility of the Y/Beta structure for accommodating RE elements. A detailed scaling analysis of M-O bond lengths and M-Si-O bond angles further supported their adaptability across different RE atom sizes. Moreover, pyridine adsorption studies revealed a linear correlation between acid strength and HOMO, LUMO energies, providing predictive insight into the catalytic performance of RE-modified zeolites. Our findings not only provide the essential nature of RE/Beta acid sites but also set stage for their application in a wider range of catalytic processes. These will further contribute to the broader objectives of reducing aviation-related CO<sub>2</sub> emissions and advancing sustainable energy solutions.

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2024-NECZA Poster Abstract

Type: Undergraduate

Consideration in poster competition: Yes

## **Impact of Pt Encapsulation and Macroporosity in MFI on Catalytic Plastic Upcycling**

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Conventional methods of plastic recycling such as mechanical recycling typically require high-purity plastic waste and yield recycled polymers of lower quality. Chemical recycling is a promising supplement to the existing waste-processing repertoire, allowing for the conversion of polyolefin chains into value-added hydrocarbon products that can be used as chemical intermediates or fuels. Among different chemical recycling methods, catalytic cracking on solid acid catalysts (i.e., zeolites) has emerged as a promising method to deconstruct plastics. Previous work has shown that zeolites, with their high thermal stability and well-defined micropore structure, are particularly suited for such cracking reactions. Ongoing efforts seek to probe the impacts of structural modifications within zeolites, such as introducing hierarchical structures and encapsulating metals, on plastic conversion rates and product selectivities. As bulkier feed hydrocarbons (i.e., polyethylene) result in highly mass transfer-limited reaction kinetics, introducing hierarchical porosity is particularly interesting as a strategy to improve diffusion of polymer chains into active sites within microporous voids. Beyond porosity, the incorporation of metal nanoparticles has been shown to significantly impact product selectivity and coke formation, but the nature of this influence is not yet completely understood. Here, we show that introducing a macroporous (> 50 nm) structure to a metal-free, microporous MFI catalyst leads to higher solid conversion rate than microporous MFI. Additionally, we provide insights into the synthesis of metal-encapsulated MFI catalysts, which can provide mechanistic insights into the respective roles of acid and metal sites in bifunctional hydrocracking reactions.

2024-NECZA Poster Abstract

Type: (Undergraduate, Graduate, Postdoc)

Consideration in poster competition: (Yes or no)

## Probing Structural Dynamics and Selectivities during MOF Oxidation Reactions

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Metal-organic frameworks (MOFs) exhibit attractive catalytic properties such as high surface areas, which enable greater utilization of internal metal sites, and tunable environments (pore sizes and local coordination), which can selectively favor certain reaction pathways via preferential stabilization of certain reaction intermediates. This work investigates alkene oxidation on MIL-100(Fe), a MTN zeotype structure that contains  $\mu_3$ -oxo-centered iron (Fe) trimer nodes (with two neutral water ligands and one anionic capping ligand) connected by 1,3,5-benzene tricarboxylic acid (H<sub>3</sub>BTC) linkers.<sup>1,2</sup> Fe-based MOFs have been studied in various oxidation reactions, but fundamental insights on MOF structure and stability during reaction are missing, muddling interpretation of kinetic and mechanistic information. Here, we seek to elucidate rigorous structure-function relationships to inform the design of more stable, selective MOF catalysts. We assess the effects of oxidant (hydrogen peroxide (HP) vs. tert-butyl hydroperoxide (TBHP)) identities on rates, oxygenate product distributions, and MIL-100(Fe) deactivation.

MIL-100(Fe) was solvothermally synthesized,<sup>3</sup> by combining H<sub>3</sub>BTC dissolved in NaOH solution and Fe(II) chloride tetrahydrate dissolved in deionized water. After crystallization at room-temperature for 24 h, the solid was recovered by centrifugation, washed with deionized water and ethanol, and dried at 343 K for 16 h. Catalytic liquid-phase alkene oxidations were performed with 50 mL acetonitrile, 1:3 mmol alkene:oxidant, and 50 mg MIL-100(Fe) at 323 K in a batch reactor under reflux.

MIL-100(Fe)-catalyzed styrene oxidation proceeds via two parallel reaction pathways, one yielding styrene oxide (with further conversion to styrene glycol and phenylacetaldehyde) and the other benzaldehyde (with secondary oxidation to benzoic acid).<sup>4</sup> Initial oxygenate formation rates on as-synthesized MIL-100(Fe) were ~10x higher with HP than TBHP. Lumped styrene oxide and benzaldehyde pathway selectivities were similar for HP vs. TBHP, implying the oxidants activate to form similar fractions of surface-bound hydroxyl vs. hydroperoxyl intermediates, which have been linked to benzaldehyde and styrene oxide formation, respectively.<sup>5</sup> However, within the epoxide pathway, TBHP was more selective toward styrene oxide formation (52% for TBHP vs. 4% for HP), while HP promoted more secondary phenylacetaldehyde and styrene glycol formation. Greater secondary reaction with HP suggested higher MIL-100(Fe) defect densities due to iron and linker leaching during HP-assisted oxidation. MIL-100(Fe) retained long-range order during styrene oxidation with TBHP, with a much lower extent of iron leaching, as evidenced by XRD, TGA, and UV-Vis.

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2024-NECZA Poster Abstract

Type: Graduate

Consideration in poster competition: Y

## Data-driven porosity design in amorphous porous polymer catalysts using molecular simulation and deep reinforcement learning

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Amorphous porous organic polymers (POPs) offer significant design versatility for specific catalytic applications due to their flexible and shape-selective nanopore environments. In particular, POPs functionalized with acid sites can catalyze esterification reactions<sup>1</sup> and selective organic conversions, including the formation of cyclic ester carbonates from CO<sub>2</sub><sup>2</sup>. The intricate and amorphous nature of POPs, however, complicates POP's computational catalysis workflow, resulting in challenges for feature engineering and high computational costs for high-throughput screening. We introduce a strategy comprising two cooperative methodologies to address these limitations. The first part of our strategy is applying a deep reinforcement learning (DRL) algorithm to streamline the discovery and optimization of potential catalysts within POP networks. Our approach leverages DRL to efficiently navigate the design of POPs to generate polymers with desired catalytic properties. The second part of our strategy uses image recognition and clustering tools to identify amorphous active site motifs based on their local environments generate surrogate models that are tractable with Density Functional Theory (DFT). In a simulation environment using porous aromatic frameworks (PAFs) as example initial monomers at different mixing ratios<sup>3</sup>, our model aligns its learning trajectory towards improving desired textural properties. Our DRL environment training results demonstrate the potential and capability to improve the adsorption properties of polymers and to target specific catalytic properties as training objectives.

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Type: Graduate

Consideration in poster competition: Yes

## Molecular Simulation of Zeolite Stiffening by Gas Adsorption

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Zeolites are widely used for applications involving gas adsorption thanks to their crystalline porous structure, high surface area, and mechanical stability. Experiments using magnetoelastic sensors showed that gas adsorption can noticeably alter the elastic moduli of zeolites, making them much stiffer.<sup>1</sup> Here, we utilized a combination of classical molecular dynamics and Monte Carlo simulations to explore this effect at a molecular scale, calculating the elastic moduli of dry zeolites, adsorbed fluids, and zeolite-fluid composites. We considered two gases -- nitrogen and carbon dioxide, in two zeolite structures -- 13X and 4A.<sup>2</sup> The moduli of the composite systems were calculated using two alternative approaches: from the moduli of the constituents (unsaturated zeolite and adsorbed fluid) using the Gassmann equation,<sup>3</sup> and directly, using the Birch-Murnaghan equation of state. Figure 1 shows the resulting moduli after following these two approaches. The direct approach showed better agreement with the experimental observations, showing approximately a two-fold increase in the bulk modulus of zeolites due to gas adsorption. Our results not only raise questions on the applicability of the Gassmann equation for microporous materials but also suggest that the elasticity of fluids adsorbed in micropores is qualitatively different from the elasticity of the same fluids in mesopores.<sup>4</sup>

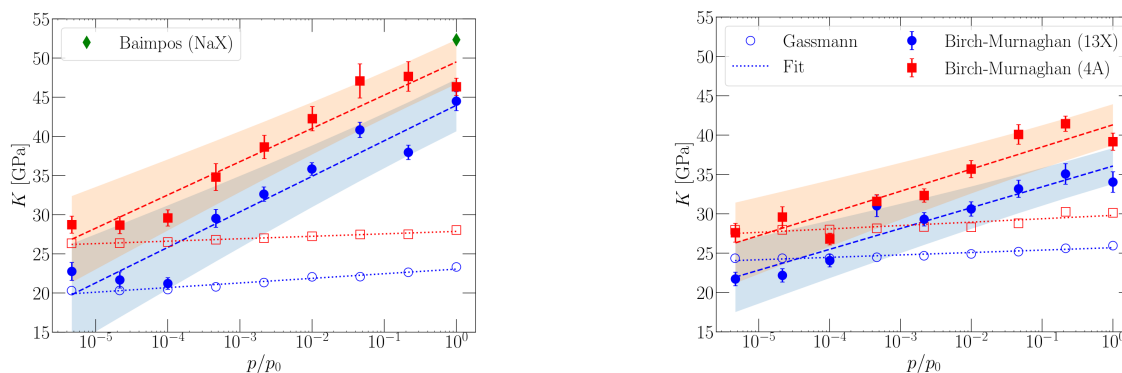


Figure 1: Bulk moduli of the CO<sub>2</sub>-zeolite composites at 273 K (a) and N<sub>2</sub>-zeolite composites at 77 K (b) predicted through the Birch-Murnaghan EOS at loadings dependent on the fluid relative pressure (filled markers) and predictions from the Gassmann theory (empty markers). The experimental point (diamond) is for comparison.<sup>1</sup>

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## Reaction and Deactivation Mechanism of Mo/ZSM-5 Catalysts for Methane Dehydroaromatization

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Methane, the primary constituent of natural gas, is an abundant chemical feedstock but its strong C-H bonds impede valorization to higher value hydrocarbon fuels. Methane dehydroaromatization (MDA) provides one route for direct conversion of methane to liquid hydrocarbons. Zeolite catalysts are typically employed in this reaction due to their shape selectivity and hydrothermal stability, for example Mo/ZSM-5 where  $\text{MoO}_x\text{C}_y$  ion exchange sites are proposed to be active and the ZSM-5 scaffold leads to improved aromatic selectivity with high atom efficiency. Despite this catalyst being active for MDA, numerous challenges including deactivation due to coking are prevalent. To develop stable MDA catalysts, the mechanisms by which carbonaceous deposits form must be understood to prevent deactivation.

In this work, we combined Density Functional Theory (DFT) and molecular dynamics to explore MDA kinetics and the formation of carbonaceous deposits to discover new catalyst formulations with reduced deactivation or facile regeneration. To predict reaction rates, we must obtain accurate predictions for rate constants based on Gibbs free energies sampled with DFT. At MDA reaction temperatures ( $>1000$  K) traditional harmonic oscillator approximations to calculate adsorbate entropy will not be applicable due to adsorbates gaining local translational and rotational degrees of freedom. We performed *ab initio* molecular dynamics (AIMD) simulations at 1000 K to confirm that anharmonic modes were present, and applied mode decomposition methods to calculate adsorbate entropies using classical partition function methods. We found that aromatics react to form hydrocarbon pool species with lower intrinsic activation barriers than reactant methane, providing evidence that at higher conversions, aromatic chain growth may become kinetically dominant. These substituted aromatics adsorb more strongly at active sites than methane, and may play a role in deactivation if they are unable to desorb.

2024-NECZA Poster Abstract

Type: Graduate

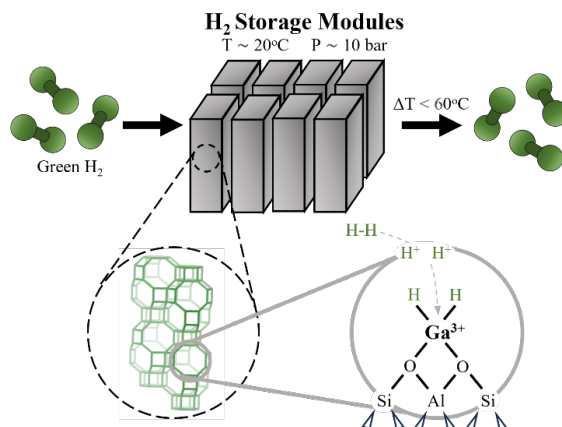
Consideration in poster competition: Yes

## Synthesis and Evaluation of Novel Ga-containing CHA Zeolites for Near-Ambient Hydrogen Storage

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A critical barrier to the widespread deployment of hydrogen as a fuel is its storage. Compared with the physical storage methods of hydrogen, material-based methods for hydrogen storage have the potential to be more safe, cost-effective, transportable, and space-efficient<sup>1-3</sup>. Here, we investigate the fundamental mechanisms and synthesis of a novel Ga-containing CHA zeolite (GaCHA) that can reversibly form Ga hydrides at near-ambient conditions. Reductive solid-state ion exchange (RSSIE) introduces Ga<sup>+</sup> cations into the CHA framework. These cations coordinate to the negatively charged aluminato centers of the zeolite which can form [GaH<sub>2</sub>]<sup>+</sup> in the presence of hydrogen. To maximize hydrogen storage capacity, GaCHA with low Si/Al ratios must be synthesized, but at such low ratios, the zeolite framework is much less stable. Various analytical techniques, including N<sub>2</sub> physisorption and XRD, validate the synthesis of a stable GaCHA with a Si/Al ratio of two, and the formation mechanism is further elucidated with techniques such as H<sub>2</sub>-TPR and MS.



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2024-NECZA Poster Abstract

Type: Undergraduate

Consideration in poster competition: Yes

## Catalytic degradation of dyes using activated MIL-100(Fe) metal-organic framework

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Improperly treated wastewater can be harmful to human health and aquatic ecosystems due to residual presence of recalcitrant pollutants, including some aromatic compounds such as in dye- and pharmaceutical-containing effluent. Many treatment methods are used to mitigate aromatic pollutant presence, including advanced oxidation processes harnessing the use of an oxidant and driving force (light or catalyst) to breakdown the species of concern into less toxic byproducts, such as in the Fenton process involving the reaction between iron (Fe) salts and oxidant (such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)). However, such systems often exhibit pH limitations and are not easily recoverable for reuse, the latter of which motivates the exploration of solid alternative materials.<sup>1</sup> Metal-organic frameworks (MOFs), consisting of networks of organic ligands coordinated to metal-containing nodes, exhibit extensive modularity with several having shown potential in adsorptive and catalytic wastewater treatment applications. Fe-based MOFs are the focus of this work due to their coordination of Fe centers that could allow them to react in Fenton-like processes. MIL-100(Fe) is part of a reportedly water-stable series of MOFs formed from earth-abundant metals that have shown promise in pollutant adsorption and degradation.<sup>2,3</sup> In this work, MIL-100(Fe) is synthesized as a catalyst for the degradation of dyes under excess H<sub>2</sub>O<sub>2</sub>, with a focus on methylene blue (MB). Dyes serve as attractive probes for other more toxic compounds, as they are widely available and can have functional groups that are present in other pollutants. As-synthesized MIL-100(Fe) is compared to MIL-100(Fe) pre-activated at 493 K and 393 K under vacuum, with higher temperature conditions improving both MB absorption and degradation rates, possibly due to pre-activation induced species removal from the metal-oxo nodes present in the structure, alongside the creation of Fe<sup>2+</sup> sites at higher temperatures. Similar degrees of leaching (manifesting in similar filtrate reactivities) are seen across both activation conditions at high H<sub>2</sub>O<sub>2</sub> excess (100:1 H<sub>2</sub>O<sub>2</sub>:MB). However, active leached species are less apparent at lower H<sub>2</sub>O<sub>2</sub> concentrations (5:1 and 7.5:1 H<sub>2</sub>O<sub>2</sub>:MB) for 493 K pre-activated material. Reactivity variations across dyes are also explored to understand the impact of charge and size on pollutant degradation. Neutral red (NR) dye, which is cationic at the pH of reaction, shows the most similar absorptive uptake to MB, likely due to similarities in structure between these moieties, while having lower overall reactivity following H<sub>2</sub>O<sub>2</sub> addition. Methyl orange, an anionic dye, and Rhodamine B, a significantly larger cationic dye, show low levels of reactivity, though methyl orange demonstrates an increased absorptive uptake with fresh MIL-100(Fe), owing to the positive charge of the MIL-100(Fe) surface. This work shows that elevated pre-activation temperatures under vacuum for MIL-100(Fe) effectively increase apparent system MB degradation reactivity similarly across H<sub>2</sub>O<sub>2</sub> oxidant loading conditions. While similar levels of aromatic conversion are achievable with similarly structured dyes, the surface charge and internal pore accessibility of the MIL-100 has a significant impact on its ability to absorb and degrade dye.

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2024-NECZA Poster Abstract

Type: Postdoc

Consideration in poster competition: no

## Adsorption-Induced Deformation Kinetics of Microporous Carbons

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Equilibrium and kinetic behavior of adsorption-induced deformation attracted a lot of attention in the last decades.<sup>1,2</sup> This phenomenon is ubiquitous but challenging to predict quantitatively due to numerous factors (pore size and geometry, adsorbent/adsorbate combination, temperature, etc.) affecting its manifestation. Time may be considered as one of these factors as many industrial and real-world processes occur far from thermodynamic equilibrium. The theoretical and experimental works cover activated carbons, coals, zeolites, glasses, etc. However, the majority of the theoretical works are focused only on the equilibrium part of the deformation process or only on the description of the time evolution of the adsorption process. The present contribution<sup>3</sup> aims to cover the existing gap, using the combination of two thermodynamical frameworks: the diffusion-based description of the time-dependent adsorption process and the osmotic ensemble-based description of adsorption-induced deformation. We obtained self-consistent equations describing equilibrium and out-of-equilibrium adsorption as well as deformation processes. As a next step, we verified the obtained equations on the experimental data<sup>4</sup> of carbon dioxide and methane on activated carbons (AC *Chemviron* and AC *T-3*). Our results demonstrate that the model can describe both equilibrium and kinetic adsorption and adsorption-induced deformation data. Also, we considered the possible influence of slow relaxation processes in the adsorbent on the adsorption process. We showed that at low strain relaxation rates, the diffusion process is hindered by deformation. On the other hand, at high strain relaxation rates, the deformation process is defined by the local adsorbate concentration and "follows" the diffusion. The current work helps to interpret experimental data on time-dependent adsorption-induced deformation.

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2024-NECZA Poster Abstract

Type: Postdoc

Consideration in poster competition: (No)

## Sorption-Ultrasonic Characterization of Zeolites and Carbon Xerogels

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Many studies have proven that elastic properties of fluids confined in nanopores deviate from the values observed in bulk [1]. Interactions between the solids (pore wall) and fluids, and pore geometry are the key factors that determine the deviation in the elasticity of nanoconfined fluids. Therefore, experimental measurements of elastic properties of confined fluids can provide information about the porous solids themselves. In this work, we studied the elasticity of two porous materials, carbon xerogel and 13X zeolite [2], as they were gradually saturated with water through the exposure to water vapor. Here, a novel adsorption-ultrasonic experimental setup [3] was employed to measure the ultrasonic wave speeds through the water-saturated test specimens while measuring their water sorption isotherm. The xerogel sample has a bimodal pore size distribution (micro-meso). The measured water sorption on carbon xerogel followed type V isotherm [4], which describes the mechanisms of fluid adsorption to the nanopores with bimodal pore size distribution. The variations in the measured wave speeds, elastic moduli and ultrasonic attenuation during the water sorption on carbon xerogel exhibited a clear correlation with the water adsorption mechanism described by the sorption isotherm. In this study, zeolite samples were prepared by pelletizing the commercial 13X powder without binder and heat treatment. The water sorption measured for 13X zeolite followed type 1(b) isotherm [4] corresponding to the micropore and narrow mesopore filling. The measured relatively low elastic moduli (< 3 GPa), and their irreversible behavior during water adsorption and desorption can be explained by the effects of loosely bound zeolite particles. This study demonstrates utilization of nondestructive ultrasonic testing in probing the elastic properties and their correlation with the fluid adsorption mechanisms of the nanoporous media.

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2024-NECZA Poster Abstract

Type: Applications Specialist, Ph.D.

Consideration in poster competition: No

## **New Instrumentation Technique for Direct Air Capture Evaluation**

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Carbon sequestration via direct air capture (DAC) is an increasingly prevalent research area for adsorption specialists. Different techniques and experiment designs have emerged with specific advantages and disadvantages for certain material classes. Unfortunately, most of these techniques are custom solutions that may not be viable for other materials and experiment conditions. Currently, there is no standard methodology for evaluating the selective adsorption of carbon dioxide under real atmospheric conditions such as the presence of nitrogen, oxygen, and water vapor. This data is a demonstration of how a commercially available dynamic flow analyzer can be used to evaluate competitive adsorption and desorption under various DAC conditions.

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2024-NECZA Poster Abstract

Type: Postdoc

Consideration in poster competition: No

## Orb and CURIE: Bringing Lightning-Fast, DFT-Accurate Simulations in Your Lab's Toolkit

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Density functional theory (DFT) provides atomic level insights that are invaluable to materials development. However, the high computational costs of these simulations make them impractical in the day-to-day workflow of chemists. As an answer to these challenges, we present Orb<sup>1</sup>, the world's fastest and most accurate family of models for simulating advanced materials, offering computation speeds 100 to 1,000 times faster than DFT, depending on system size, while maintaining comparable accuracy.

Orb's versatility allows researchers to conduct large-scale simulations of chemical species previously intractable for DFT. Applications include highly accurate geometry optimizations, molecular dynamics (MD), and Monte Carlo (MC) simulations, which can predict structural stability, transformations, and hypothetical structures' feasibility. These simulations are beneficial for exploring the synthesis of new materials and modifying existing structures for specific applications, such as adsorption or catalysis. A notable application of Orb is its ability to assess binding energies in host-guest interactions, essential for predicting organic structure-directing agents (OSDAs) used in zeolite synthesis. Furthermore, Orb facilitates accurate modeling of aluminum and cation positions in aluminosilicate zeolites—a task traditionally hindered by high computational costs and complexity. By providing fast, lower cost calculations, Orb enables researchers to tackle these challenges efficiently.

Despite Orb's transformative potential, its impact relies on effective collaboration between computational and experimental researchers. Bridging the communication gap and ensuring applicability across both domains remains a challenge. To address this, Orbital Materials is developing CURIE (Chemical Understanding & Research Innovation Engine), a suite of tools designed to streamline research workflows. CURIE integrates large-language model (LLM) agents to assist researchers in real-time. Chemists can use these agents to perform calculations with Orb, set up experiments, and analyze results within an intuitive chat interface (Figure 1). CURIE acts as a virtual expert, enabling users to query and modify setup details, dive into outcomes, and initiate new calculations. By bridging computational and experimental chemistry, CURIE enhances collaboration, supporting chemists in hypothesis generation and experimental design. This innovation extends beyond current ML tools, addressing limitations of material-specific<sup>2</sup> or general-purpose LLMs<sup>3</sup> prone to inaccuracies and 'hallucinations'. CURIE's approach marks a significant step forward, empowering researchers to accelerate materials discovery with precision and efficiency.

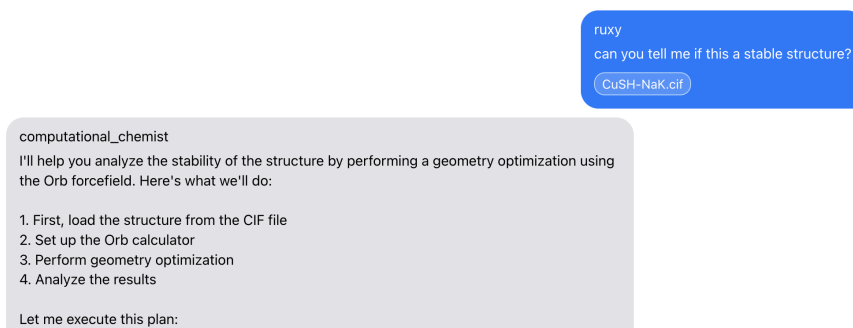


Figure 1. Example of a response using Orb in CURIE to assess stability of a crystal structure.

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2024-NECZA Poster Abstract

Type: Postdoc

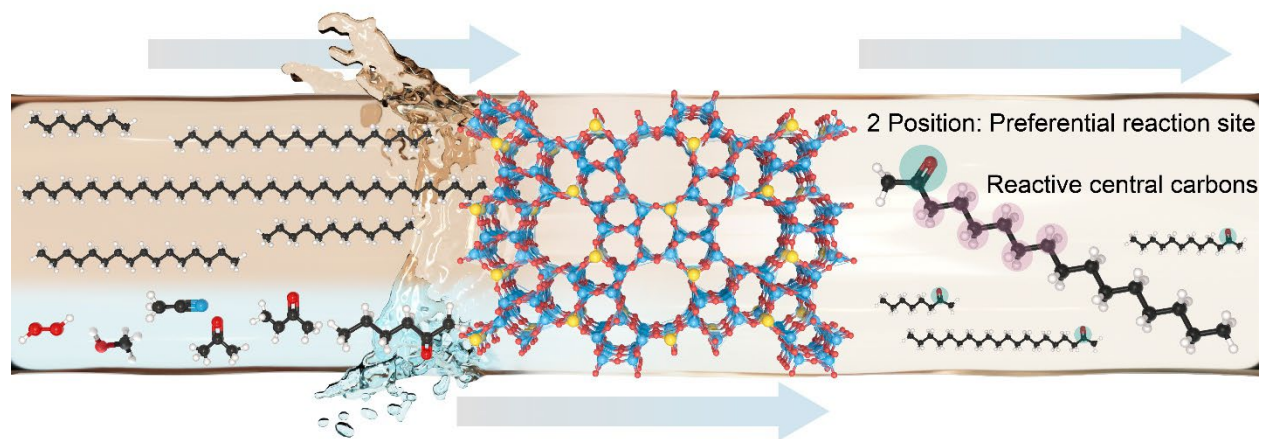
Consideration in poster competition: No

## Oxidation of Linear Alkanes using TS-1 and H<sub>2</sub>O<sub>2</sub> toward Chemical Upcycling of Polyolefins

Park, S.,<sup>1</sup> Lee, D.,<sup>1</sup> Gorte, R. J.,<sup>1</sup> Vohs, J. M.<sup>1,\*</sup>

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The selective oxidation of n-C<sub>8</sub>H<sub>18</sub>, n-C<sub>12</sub>H<sub>26</sub>, n-C<sub>16</sub>H<sub>34</sub>, n-C<sub>20</sub>H<sub>42</sub>, and n-C<sub>36</sub>H<sub>74</sub> was studied with a goal of using these as models to provide insight into how to functionalize polyolefins. Reactions were carried out using a TS-1 catalyst and H<sub>2</sub>O<sub>2</sub> in a batch reactor at 348 K with different solvents, including methanol, acetone, acetonitrile, methyl ethyl ketone, and methyl butyl ketone. Rates decreased with increasing alkane size, apparently due to the reduced solubility of larger alkanes into the water-rich phases. Solvents that promote the partitioning of alkanes in the aqueous phase increased the rates. <sup>1</sup>H NMR spectroscopy demonstrated that ketones were the primary products, with some alcohols also formed. There was preferential reaction at the 2 positions in the alkanes, but reaction at central carbons was also observed. The results of this study suggest strategies for using this catalytic chemistry to functionalize polyolefins, including using hierarchical analogs of TS-1 that provide easier access to the active sites, and solvents that more effectively partition alkanes into an aqueous phase.





2024-NECZA Poster Abstract  
 Type: Postdoc  
 Consideration in poster competition: No

## Mechanistic insights into nitrogen activation at low-nuclearity Ru sites sequestered in self-pillared pentasil using Operando atomistic models and experimental kinetics

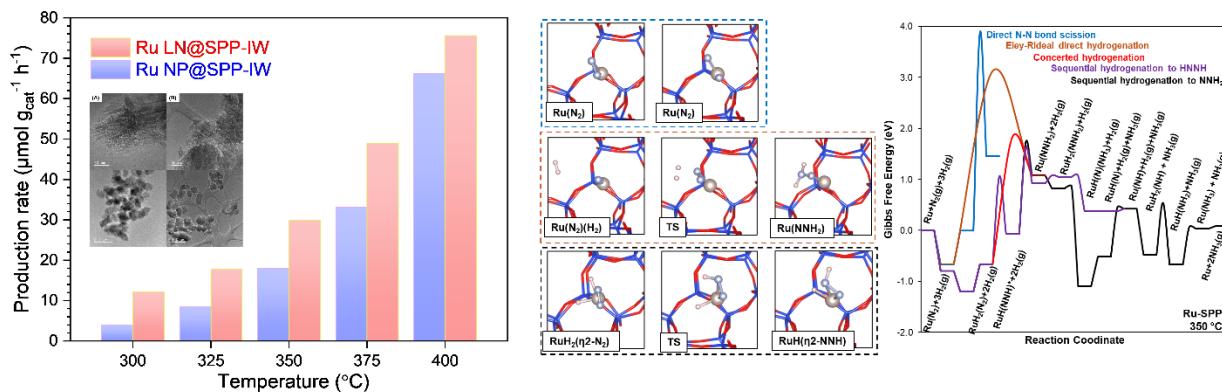
Geet Gupta<sup>1+</sup>, Weiye Qu<sup>1+</sup>, Zihao Rei Gao<sup>1,2+</sup>, Ryan Zhou<sup>1</sup>, Nayeon Kang<sup>1,2</sup>, Paul Haghi Ashtiani<sup>1,2</sup>, Fan Bu<sup>1</sup>, Michael Tsapatsis<sup>1,2,3</sup>, Chao Wang<sup>1\*</sup>, Brandon C. Bukowski<sup>1\*</sup>

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Alternative catalysts to the industrial Haber Bosch process have been of significant interest in the field of heterogeneous catalysis, yet realizing ammonia synthesis under mild conditions (e.g., 300 °C and 10 bar) is challenging due to the low per-pass conversion. One strategy is to disperse low-nuclearity metals and promote the so-called associative ammonia mechanism which eschews N-N bond cleavage.[1-2] Here we use self-pillared pentasil, a self-pillared hierarchical zeolite built by thin MFI zeolite nanosheets, as a support for Ru low-nuclearity clusters for ammonia synthesis. We show that Ru remains well-dispersed during reaction and demonstrate ammonia synthesis rates that are higher than Cs-Ru/MgO. Reaction kinetics show a positive order in  $H_2$  providing evidence for the associative mechanism, which then becomes negative in  $H_2$  if Ru is allowed to aggregate into nanoparticles. Operando Density Functional Theory models for Ru speciation in SPP, free energy diagrams, and microkinetic modeling were then applied to develop a reaction mechanism under relevant reaction conditions that involves sequential hydrogenation of  $N_2$  from a  $RuH_x$  complex. For this hydrogenation to occur, there are site requirements for Ru that in turn inform the improved design of zeolite-supported ammonia synthesis catalysts.



### References

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