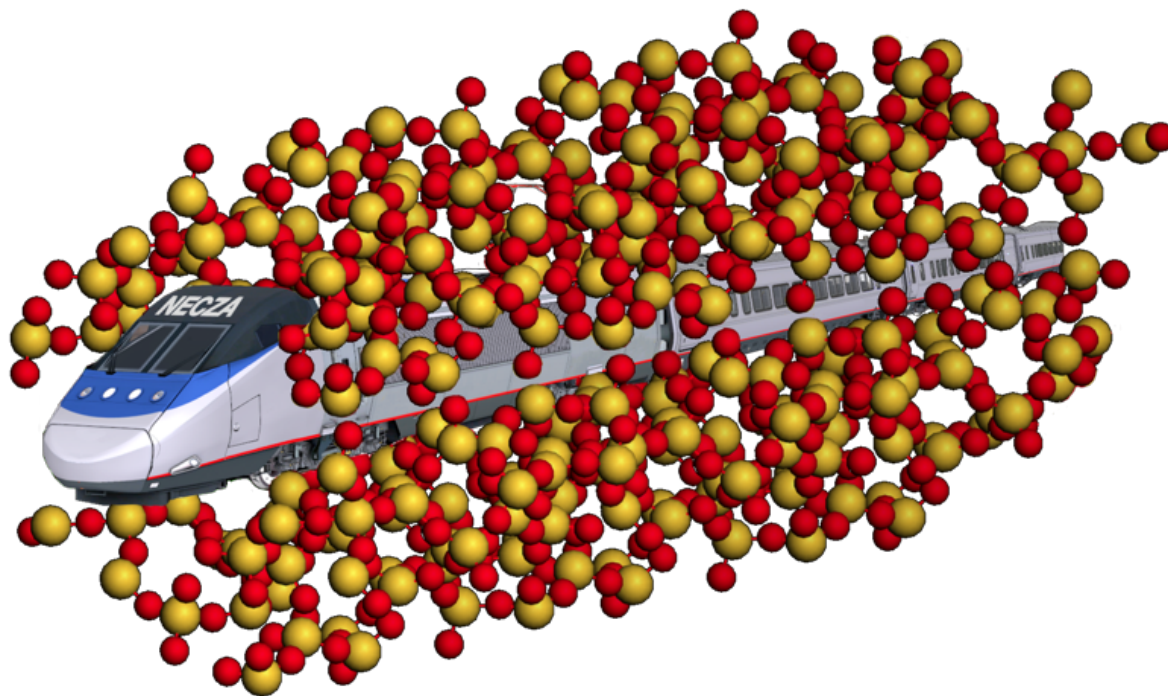


# **NECZA 2023**

## **The 27<sup>th</sup> Meeting of the North-East Corridor Zeolite Association**



**Friday, December 8, 2023**

**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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## 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 – 9:40</b>	<u>David Shepard</u> (Pacific Industrial Development Corporation) “Nano-Oxide Surface Coatings on Cu-SSZ-13 for High Temperature Selectivity SCR Applications”
<b>9:40 – 10:20</b>	<u>Todd Toops</u> (Oak Ridge National Laboratory) “Biofuel Impacts on Cu-Zeolite Emissions Control Catalysis”
<b>10:20 – 11:00</b>	<b><i>Coffee Break – Poster Session I</i></b>
<b>11:00 – 11:40</b>	<u>Raul F. Lobo</u> (University of Delaware) “Light Alkane Dehydrogenation over Zeolite Catalysts”
<b>11:40 – 12:20</b>	<b><i>Poster Session II</i></b>
<b>12:20 – 1:20</b>	<b><i>Lunch and Business Meeting</i></b>
<b>1:20 – 2:00</b>	<u>Jeffrey D. Rimer</u> (University of Houston) “Tuning the Activity of Zeolite Catalysts: From Defect Engineering to the Design of Bifunctionality”
<b>2:00 – 2:40</b>	<u>Selected Poster Presentations (2 x 15 min each)</u>
<b>2:40 – 3:00</b>	<b><i>Coffee break</i></b>
<b>3:00 – 3:40</b>	<u>Sean Wilson</u> (TerraFixing Inc.) “The Challenges of Direct Air Capture: Potential for Zeolites”
<b>3:40 – 4:20</b>	<u>Charles Kanyi</u> (Johnson Matthey) “Synthesis and Characterization of Framework Fe-Al/MFI Zeolite”
<b>4:20</b>	Final remarks and meeting adjournment

# Nano-Oxide Surface Coatings on Cu-SSZ-13 for High Temperature Selectivity SCR Applications

*David Shepard, Jeremy Madynski, Ashwin Sankaran Ph.D., Geng Zhang Ph.D.*

Pacific Industrial Development Corporation, Ann Arbor, Mi 48108 USA  
dshepard@pidc.com

## ABSTRACT

Cu-SSZ-13 has been one of the dominant zeolites utilized in  $\text{NH}_3$  SCR applications in the past decade. The material is utilized in both mobile and stationary applications across a broad temperature range. The performance of Cu-SSZ-13 has been heavily investigated regarding SCR activity versus Cu content. The literature has shown a compromise between low temperature and high temperature selectivity towards  $\text{NO}_x$  reduction as Cu levels increase, we see an increase in low temperature activity but a decrease in high temperature selectivity and vice versa for lower Cu levels.

The goal of this research was to investigate if different nano-oxide surface coatings can maintain low temperature activity while also maintaining selectivity of  $\text{NO}_x$  reduction above  $550^\circ\text{C}$ . The investigation was conducted on low and high Cu-exchanged SSZ-13 material that had been loaded with different oxides (Al and Ce), varied weight loadings, and crystallite sizes of the nano-oxide. The zeolites were then prepared into catalysts and evaluated for SCR activity both fresh and after hydrothermal aging.

A slurry containing water and Cu-exchanged SSZ-13 material at 20% solids was placed under high-shear mixing while boehmite was dispersed in a separate container with water. Upon dispersion the boehmite was added to the zeolite slurry which was then high-shear mixed for 20 minutes. The slurry was then dried in an oven at  $120^\circ\text{C}$  for 12 hours and passed through a  $300\text{ }\mu\text{m}$  sieve.

The resulting powder was re-slurried and applied as a wash coat to a 13 cc cordierite honeycomb core, with a target catalyst loading of 180 g/L. The wash coated cores were dried at  $120^\circ\text{C}$  for two hours and calcined at  $600^\circ\text{C}$  for two hours. Evaluation took place on a synthetic gas bench including a Parr Instruments furnace, MKS mass flow controllers, and an MKS MultiGas 2000 FTIR under the following conditions: 40,000  $\text{SV}^1$  including 450 ppm  $\text{NO}$ , 550 ppm  $\text{NH}_3$ , 8~10% each of  $\text{CO}_2$ ,  $\text{O}_2$ , and steam with nitrogen balance. The SCR measurements were taken via steady state and specific temperature points from  $175^\circ\text{C}$  to  $650^\circ\text{C}$ , and the ammonia storage protocol was done at  $200^\circ\text{C}$ .

The addition of nano- $\text{Al}_2\text{O}_3$  to the surface of the Cu-SSZ-13 provided an improvement in high temperature  $\text{NO}$  reduction, while the low temperature performance was negatively impacted by higher weight % loadings. The  $\text{NH}_3$  break-through time also an improvement with over 75 seconds longer time to saturation.

The findings here can potentially lead to broader usage of Cu-SSZ-13 in applications which require selectivity at both low and high temperature windows. This could potentially be done now with a single modified zeolite versus a combination of Cu/Fe zeolites.



## **BIOGRAPHY**

David Shepard is the Global Applications Manager at Pacific Industrial Development Corporation, supporting all of PIDC's business units. David began his career with PIDC in 2011 working in research and development on rare earth modified aluminas, ceria doped zirconia, and small pore zeolite synthesis. He then transitioned to product scale-up to assist in the growth of R&D programs to commercial scale. In 2015, David began leading applications support for PIDC, providing technical support to both customers and the sales team, overseeing applications testing development for the catalyst focused business units, and acting as a liaison between the customer and R&D teams. David is the co-inventor of 10 patent grants and an additional 15 patents pending. David holds a BA in chemistry from the University of Detroit Mercy.



# Biofuel Impacts on Cu-Zeolite Emissions Control Catalysis

*Todd J. Toops*

Oak Ridge National Laboratory, Oak Ridge, TN, 37831 USA  
toopstj@ornl.gov

## ABSTRACT

One way to decarbonize the transportation industry is to adopt renewable low-lifecycle carbon fuels (LLCF), especially relevant for hard to electrify sectors – heavy duty (HD) trucks, marine, rail, and off-road. The most promising LLCF candidates are typically derived from plant-based sources which all contain phosphorous (P) and is known to impact emissions control devices from earlier P-containing lubricant studies [1]. Biodiesel is one such fuel that has a specified P limitation of 10 ppm [2] and it also has a newly defined combined limit of 4 ppm for total metals on Ca, Mg, Na, and K metals. Although some studies have been performed on these metals [3], an improved understanding of their interactions with zeolites is needed. Additionally, understanding how biofuel-based P differs from lubricant sources is important. The emissions control systems and regulations can vary significantly for these lean combustion engines, especially as emissions regulations get more stringent [4], but generally diesel oxidation catalysts (DOCs), Cu-zeolite based selective NO<sub>x</sub> reduction catalysts (SCR), and diesel particulate filters (DPFs) will be required either in current or future systems. With these considerations in mind two systematic studies were initiated to expose emissions control systems to either fuel-borne P or Na/Ca/K metals using a diesel genset followed by flow reactor evaluations to investigate the impact.

A range of emissions control configurations were deployed in these studies. The first is relevant to the light duty (LD) with the DOC first, followed by two SCR monoliths, and finally the DPF: DOC→SCR→DPF. The second is relevant to current HD configurations with the SCR last: DOC→DPF→SCR. A third configuration was introduced for future HD configurations considerations where an upstream light-off SCR (LO-SCR) catalyst is expected to be needed to aid in low temperature NO<sub>x</sub> conversion: LO-SCR→DOC→DPF→SCR. Accelerated aging was performed with 7-28x acceleration factors.

A range of behaviors were observed in the results with some very unexpected behavior and some critical material transformations. For the metal-exposed SCR in the LD-configuration, DOC→SCR→DPF, the Na and K showed deactivation in the front portion of the SCR and resulted in substitution for the Cu in the zeolite framework.

## BIOGRAPHY

Dr. Todd J. Toops has been at Oak Ridge National Laboratory (ORNL) since 2001 where he is a Distinguished R&D Scientist in the Applied Catalysis and Emissions Research Group. He also has an appointment as Adjunct Faculty at the University of Tennessee. After receiving his B.S. in Chemical Engineering in 1996 from the University of New Mexico, Dr. Toops pursued his Ph.D. in Chemical Engineering from the Pennsylvania State University under Prof. Albert Vannice where he studied catalysis and emissions control with an emphasis on improving fundamental understanding of systems under realistic conditions. His research at ORNL has covered a wide range of clean energy topics including emissions control, biofuels, fuel cells, electrolysis, and neutron imaging of transportation devices. He has published over 135 journal articles and book chapters, 65 DOE reports, 4 patents/patent applications, and delivered over 80 invited/keynote/plenary lectures. He is a two-time winner of the Biodiesel Researcher of the Year (2012 and 2015) award and has an R&D 100 award (2014). He is a member of the Society of Automotive Engineers, North American Catalysis Society, American Institute of Chemical Engineers, and American Chemical Society. He is the Chair of the 29<sup>th</sup> North American Catalysis Society Meeting (NAM29) to be held in 2025 in Atlanta, served as the Chair of the 8th International Conference on Environmental Catalysis (2014), and is on the Editorial Board of the scientific journal: Emissions Control Science and Technology. Additionally, he has either mentored or advised 20+ post-graduate fellows/graduate students.



# Zeolite Catalysts for Light Alkane Dehydrogenation

*Raul F. Lobo*

Center for Catalytic Science and Technology, Department of Chemical and Biomolecular  
Engineering, University of Delaware, Newark, DE 19716  
lobo@udel.edu

## ABSTRACT

The chemical industry is an important contributor of greenhouse gas emissions to the atmosphere and one of the goals of my research program is to develop process alternatives that can deliver the chemical products our modern society needs while minimizing CO<sub>2</sub> emissions. In this talk I will describe recent research on three classes of zeolite catalysts for light alkane dehydrogenation:

1. *Gallium- and zinc-containing zeolites*: We have conducted an investigation of this class of materials spanning several zeolite structures (MFI, CHA and SZR), Si/Al ratios, and metal loadings and characterization techniques. This talk will summarize the salient findings of these investigations, in particular, the speciation of these metals in the zeolite pores, and the relation of these sites with catalytic rates of dehydrogenation.
2. *Mn-oxide supported on zeolite crystals*: We discovered that Mn-containing zeolites prepared by incipient wetness impregnation (IWI) catalyze the ethane dehydrogenation reaction with high selectivity. Preparation by IWI leads to the formation of Mn<sub>2</sub>O<sub>3</sub> nanoparticles on the external surface of the zeolite crystals and these are the location of the active sites for both ethane and propane dehydrogenation. We will compare the effect of zeolite structure and composition on catalytic activity and stability.
3. *Oxidative Ethane Dehydrogenation over Zeolites*: B-chabazites (B-CHA) are excellent catalysts for the ODHE reaction, showing fast catalytic rates, with high selectivity towards ethylene from 500 to 600 °C. The zeolite pores stabilize surface B species leading to a negligible decrease of boron content in the spent B-CHA catalyst. A reaction network and a model for the active sites based on <sup>11</sup>B NMR spectroscopy are proposed.

## BIOGRAPHY

Raul F. Lobo obtained his undergraduate degree in Chemical Engineering at the University of Costa Rica in 1989 and later moved to California to pursue graduate studies in Chemical Engineering at Caltech. He worked for one year at Los Alamos National Laboratory, New Mexico as a postdoctoral fellow and started his academic career at the University of Delaware in 1995 where he is currently Claire D. LeClaire Professor of Chemical and Biomolecular Engineering and Associate Chair.

His interests span the development of novel porous materials for catalysis and separations, the chemistry of zeolites, catalysis for energy and the environment, and the scientific aspects of catalyst synthesis. He has published over one two hundred refereed reports and he is co-inventor in eleven US patents.



# Tuning the Activity of Zeolite Catalysts: From Defect Engineering to the Design of Bifunctionality

*Jeffrey D. Rimer*

Department of Chemical and Biomolecular Engineering, University of Houston

## ABSTRACT

Zeolites are commonly used catalysts in both traditional and emerging (petro)chemical processes owing in large part to their tunable acidity, which can be engineered through the incorporation of various framework and extra-framework Brønsted and Lewis acid sites. This talk will describe recent efforts by our group to understand the nature of Al incorporation as well as its substitution with heteroatoms (e.g., Ga, B, Ti, etc.). The first part of the talk will focus on zeolite ZSM-5, which is highly prone to contain defects in the form of residual amorphous material, crystallographic dislocations, and non-framework or extra-framework Al species. Minimizing these defects is a subject of interest owing to their correlation with the onset of catalyst deactivation. Here, we will discuss how defects are more prevalent in hierarchical ZSM-5 materials than previously reported in literature, focusing on five classes of nanosized/hierarchical zeolites: nanosheets (ca. 3 nm thickness), self-pillared pentasils (ca. 3 nm thickness), nanoparticles (ca. 20 nm), finned zeolites (ca. 30 nm fins), and coresheils (ca. 10 nm shell thickness). Using methanol to hydrocarbons (MTH) as a benchmark reaction, we have shown that as-synthesized materials are universally less active than either commercial or conventional ZSM-5; however, our studies reveal that catalyst performance can be dramatically improved via post-synthesis treatments to reduce defects, which include hydrothermal annealing wherein crystals are subjected to a saturated siliceous solution at high-temperature. Our findings reveal that the removal of defects from ZSM-5 catalysts result in as low as 3-fold to as high as 10-fold increases in turnover number compared to their as-synthesized counterparts. In the second part of the talk, we will show how Al can be substituted with other heteroatoms that either reduce the overall acidity or add Lewis acids as bifunctional catalysts. Examples span Ti-zeolites for epoxidation reactions to Ga-zeolites for dehydration reactions. We have also been exploring the use of metal-substituted zeolites for oxygen-assisted oxidative dehydrogenation of propane (ODHP) to produce propylene as well as the upgrading of model biomass compounds to aromatics. Here, we will discuss methods of synthesizing zeolites catalysts with different active site speciation as a means of developing structure-performance relationships. Our collective findings aim to better understand the impact of active site identity (speciation) on the performance of zeolite catalysts for diverse applications.



## BIOGRAPHY

Jeff Rimer is the Abraham E. Dukler Endowed Chair and Professor of Chemical Engineering at the University of Houston. Jeff received B.S. degrees in Chemical Engineering and Chemistry from Washington University in St. Louis and Allegheny College, respectively. He received his Ph.D. in Chemical Engineering from the University of Delaware and spent two years as a postdoctoral fellow at New York University prior to joining Houston in 2009. Jeff's research in the area of crystal engineering focuses on the rational design of materials with specific applications in the synthesis of microporous catalysts and adsorbents, and the development of therapeutics to inhibit crystal formation in pathological diseases. Jeff is a Senior Member of the National Academy of Inventors and has received numerous awards that include the NSF CAREER Award, the 2016 Owens Corning Early Career Award and 2017 FRI/John G. Kunesh Award from AIChE, and the inaugural 2016 Mellichamp Emerging Leader Lecturer at the University of California at Santa Barbara. In 2018 he received the Norman Hackerman Award in Chemical Research from The Welch Foundation, and in 2020 the Edith and Peter O'Donnell Award in Engineering from TAMEST. He has also received several research, teaching, and mentoring awards at both the University and College levels. He is a former chair of the Southwest Catalysis Society, an executive committee member (Treasurer) and co-chair of the structure commission for the International Zeolite Association, and has chaired two Gordon Research Conferences on Crystal Growth & Assembly and Nanoporous Materials & Their Applications. He currently serves as the Director of Graduate Studies and as the Program Director for the Welch Center for Advanced Bioactive Materials Crystallization. Jeff is also an Associate Editor of *Crystal Growth & Design* and serves on the advisory boards for the *AIChE Journal*, *Molecular Systems Design & Engineering*, *Reaction Chemistry & Engineering*, and *Green Carbon*.



# The Challenges of Direct Air Capture: Potential for Zeolites

*Sean M.W. Wilson*

TerraFixing Inc., Ottawa ON, Canada

## ABSTRACT

Global warming is being driven by increasing levels of CO<sub>2</sub> in the atmosphere which increases global surface temperatures. The effects of global warming are particularly worrisome for polar ice-capped regions, like Greenland and Antarctica which experience more significant warming than the rest of the planet; as their ice caps melt and the sea levels rise, many coastal populations will have to be displaced. To mitigate the consequences of global warming, researchers, companies, and governments are investing time and effort into finding ways to effectively reduce the amount of CO<sub>2</sub> entering the atmosphere or to capture CO<sub>2</sub> directly from the air. The latter, direct air capture (DAC), is a technology that captures CO<sub>2</sub> directly from the air and concentrates it. When coupled with geological storage, DAC can be used to sequester CO<sub>2</sub> permanently into the earth, enabling us to reach net-zero commitments as well as going beyond to clean up emissions of the past.

As promising as DAC can be, there are many challenges for a well-designed process to capture CO<sub>2</sub> from the air. A significant challenge for DAC is that CO<sub>2</sub> in the air is dilute and capturing 1 tonne of CO<sub>2</sub> would require approximately 1,400,000 m<sup>3</sup> of air. Because the concentration of CO<sub>2</sub> in air is so low, it is uneconomical to significantly change the input air conditions (e.g., temperature, pressure, humidity) during the capture step of a DAC process. Initial studies ruled out physisorption separations for DAC because H<sub>2</sub>O would competitively adsorb over CO<sub>2</sub>. Instead, they explored chemisorption separations which favour capturing CO<sub>2</sub> from H<sub>2</sub>O in the air, and accepted the high regeneration energy required for the process. This did not remove water as a problem however, and estimated costs for such technologies are typically greater than \$300/tCO<sub>2</sub>.

Being from Canada and suffering from dry and cracking lips each winter, we can testify that not all air contains significant amounts of H<sub>2</sub>O. For physisorption separations using zeolites, cold air can be economically dried prior to capturing the CO<sub>2</sub>. Coincidentally, physisorption DAC technologies in cold climates have other advantages including the thermodynamic efficiencies and synergies of cold temperature gas separations, and that adsorption capacity loadings are substantially larger as temperature drops.

Knowing that 1) cold climates enable more thermodynamically favorable separations; 2) adsorbents (physisorbents) can adsorb significantly more CO<sub>2</sub> in colder conditions; and 3) naturally drier air and less water to separate prior to separating the CO<sub>2</sub>, could locating an adsorbent-based DAC process in the cold dry regions of the planet be an instrument in solving global warming? In this talk, we will explore the opportunity of using affordable and industrially available zeolites in a DAC process located in cold locations such as Canada, Alaska, Greenland, and Antarctica, as a means to reach net-zero and go beyond. This talk will discuss the interplay between DAC processes and their materials, the larger carbon capture system in play, and an economical path forward for DAC.



## BIOGRAPHY

Dr. Sean M.W. Wilson, Founder and CEO of TerraFixing, is a leading global expert in adsorption-based gas separations with a speciality in carbon capture. With over a decade of experience in atmospheric carbon removal, he has pioneered the development of the first ever direct air capture (DAC) technology that is geared towards cold climates, enabling DAC for Alaska, Canada, Greenland and other cold climate locations. He obtained his PhD in chemical engineering from the University of Ottawa and is at the forefront of the DAC field. Passionate about the environment, Dr Wilson is a proponent for knowledge sharing (both industrially and socially) and community engagement to enable the world to reach its 2050 net zero commitment.

TerraFixing is a Canadian Direct Air Carbon Capture (DAC) start-up with an unfair technological advantage: it leverages cold climates to remove CO<sub>2</sub> from the atmosphere at the lowest \$/tCO<sub>2</sub>. Their IP protected technology has the highest efficiency and scalability in the DAC space. Coupled with an aggressive business model, scaling this next generation technology will enable the reversal of global warming and rescue humanity from the pending climate crisis.



# Synthesis, Characterization, and Formulation of Framework Fe-Al-MFI to FCC Additive

*Kanyi, C.W.*

Johnson Matthey, 115 Eli Whitney Blvd, Savannah, 31408

## ABSTRACT

Demand for propylene continues to increase with refineries using different approaches to increase propylene: increasing riser temperature, using base catalyst with lower REO, and higher usage of ZSM-5 additive. The above approaches result in, higher coke yield, lower stabilized base catalyst, and dilution of inventory, respectively. Of the three, use of ZSM-5 is most preferred as it offers flexibility; ability to use on as need basis.

To circumvent inventory dilution, more active ZSM-5 additive is required (achieve higher propylene yields at low inventory). Recently there is increased attention in using metals in ZSM-5 additives to increase activity. This talk will initially focus on synthesis and characterization of ZSM-5 containing both iron and aluminum in the framework. The latter part will focus on formulation of the zeolites to additives and testing of the additives for propylene make.

Mixing of the raw materials to make the zeolite gel has great impact on the time iron get incorporated into the framework as well as crystallization time. The zeolite morphology changes with iron and/or alumina content. Above certain aluminum and iron content, presence of iron outside the framework is evident. Formulating Fe-Al-ZSM-5 into additive requires slightly different optimization compared to standard Al-ZSM-5. Significant improvement in performance (propylene) is observed with Fe-Al-ZSM-5 additive compared to standard additive (Al-ZSM-5).

## **BIOGRAPHY**

Charles Kanyi is a Senior Catalyst Development Scientist at Johnson Matthey, Savannah, Georgia. Charles received both his B.S degree (Education Science) and M.S degree (Physical Chemistry) from Moi University, Kenya. Thereafter, Charles relocated to USA pursue further studies. He joined State University of New York at Binghamton for his Ph.D. in Materials Chemistry. Immediately after graduating he got a Postdoctoral position at the same University, Binghamton where he worked for 2 years before joining Rive Technology, NJ (now owned by Grace Davidson). Later, Charles joined Johnson Matthey.

Charles joined Johnson Matthey as Zeolite Scientist, and later got promoted to Senior Catalyst Development Scientist. Charles focuses on zeolite and zeolite-based additives for use in Fluid Catalytic Cracking (FCC). Lately, his role has expanded to hydrotalcites based additives for FCC as well as other products for non-refinery applications. Charles has been a nominee for multiple awards including JM Chief Executive Officer as Outstanding Researcher and Catalyst Technology award for Internal Collaborations.



## **POSTER ABSTRACTS**

## **Mechanical Properties of Gases Adsorbed on Zeolites from the Fluctuation Theory**

**Santiago A. Flores Roman<sup>1</sup>, Alina Emelianova<sup>2</sup>, Gennady Y. Gor<sup>1,3,\*</sup>**

<sup>1</sup> *Dept. of Chemical and Materials Engineering, New Jersey Institute of Technology, Newark, NJ, USA, 07102*

<sup>2</sup> *Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ, USA, 08544*

<sup>3</sup> *Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, USA, 08544*

Fluids present different thermodynamic properties in confinement. Their boiling and melting temperatures shift, their densities are lower than their bulk phase, and their mechanical properties, such as the elastic modulus, enhance depending on the pore size [1]. These results have been analyzed through computational models, such as molecular simulations. However, regarding mechanical properties, this enhancement has especially been studied in mesopores, not micropores. Dobrzanski et al. [2] attempted to analyze the mechanical properties of fluids according to the pore geometry and size. They found that fluids confined in micropores reproduced molecules' distributions far from the normal distribution, preventing the utilization of fluctuation theory to characterize their mechanical properties through molecular simulations. In this work, we use a recent molecular simulation study of gas adsorption in LTA4A and NaX zeolites [3] and further extend it using the fluctuation theory to obtain the mechanical properties of adsorbed nitrogen and carbon dioxide. As a first result, we found that the enhancement of the elastic modulus is observed in micropores, even if the densities are lower than in the bulk phase. This effect is due to reduced fluctuations in the adsorption of the fluid. The same procedure can be extended to any fluid and micropore, and our results bring a deeper insight into the characterization of confined fluids in micropores.

### **References**

- [1] C. D. Dobrzanski; B. Gurevich; G. Y. Gor, *Appl. Phys. Rev.*, **8**(2021) 02137.
- [2] C. D. Dobrzanski; M. A. Maximov; G. Y. Gor, *J. Chem. Phys.*, **148**(2018) 054503.
- [3] A. Emelianova; C. Balzer; G. Reichenauer; G. Y. Gor, *Langmuir*, **39**(2023) 11388-11397.

## Exploring Water Adsorption on Defect Engineered 2-D Single Atom Catalysts

**Yanqi Huang, Brandon C. Bukowski\***

*Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland 21218, United States*

Metal and nitrogen co-doped carbon (M-N-C) catalysts represent a class of single atom catalysts with high atom utilization efficiency. These materials catalyze various fuel generation processes, including oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and carbon dioxide reduction reaction (CO<sub>2</sub>RR)<sup>1</sup>. In liquid phase reactions, such as those described above, reactants must diffuse through the solvent to reach the catalytic sites, with the solvent playing a crucial role in controlling reaction kinetics and influencing catalyst stability through solvent-catalysts interactions.

We focused on a specific type of M-N-C catalysts: 2-D graphene sheets doped with single Fe atoms, each surrounded by four N atoms. Utilizing this model catalyst, we investigated the interactions between solvent molecules and catalytic sites on graphene. To understand the interfacial interactions in catalytic processes, quantum chemistry calculations are necessary to determine the intermolecular potentials between solvents and catalysts. Classical force fields are derived from experimental data, however, they are unable to account for bond breaking and molecular association. We used Density Functional Theory (DFT) calculations to incorporate the electronic structure of Fe cations and their interactions with adsorbed water. Due to the high computational demand and time-intensive nature of DFT, we utilized a Machine Learning Force Field (MLFF) technique to investigate solvent dynamics on graphene sheets enhanced by defect engineering. We trained a machine learning force field and collected a structural dataset using a representative model of 0.063 mmol H<sub>2</sub>O cm<sup>-2</sup> atop isolated catalytic sites on the graphene sheet, incorporating water-water and water-graphene interactions. The force field and structure dataset were subsequently utilized across various water loadings, ranging from 0.010 to 0.085 mmol cm<sup>-2</sup>, above defected graphene sheets. These sheets had varying Fe/C ratios, extending from 0 to 0.083. To understand the behavior of water above single atom sites, we analyzed the time-averaged distribution, adsorption thermodynamics, vibrational density of states, and entropies of water clusters. Our simulations demonstrated that defect sites in graphene significantly enhance hydrogen bonding and lead to a reduction in the height of adsorbed layers. These findings clarify the observed increase in adsorption energies in graphene sheets with a greater number of single atom sites. For low density water cluster adsorption models, there is a sharp rise in adsorption energies when the Fe/C ratio increases from 0 to 0.015. We established a correlation between adsorption energy and defect densities in the graphene sheets and quantified the free energy of these adsorption models by considering adsorption energy and entropy. Intriguingly, we found that the thin layer of water molecules, comprising 0.063 to 0.085 mmol cm<sup>-2</sup>, displayed behaviors similar to bulk liquid water. Overall, our study offers detailed insights into how defect engineering in graphene affects the thermodynamics of water phases. It also pinpoints the specific conditions that lead to the formation of locally stable water clusters above single atom sites in graphene sheets.

### References

- [1] Shi, Z.; Yang, W.; Gu, Y.; Liao, T.; Sun, Z. *Advanced Science* **2020**, 7 (15), 2001069.

## One-Pot Conversion of Acetone to Lactic Acid via Tandem Reactions

**Angyal, N.,<sup>1</sup> Lobo, R. F.,<sup>1</sup> Orazov, M.<sup>2</sup>**

<sup>1</sup> *Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy Street, Newark, DE 19716*

<sup>2</sup> *Richmond Technology Center, Chevron Corporation., 841 Chevron Way, Richmond, CA 94801*

Lactic acid is an important commodity chemical whose market size is projected to continue growing. It has traditional uses in the food, pharmaceutical, and cosmetic industries.<sup>1</sup> Increasingly, lactic acid is used as a building block to produce polylactic acid (PLA) and other polyesters. PLA has received significant attention as an alternative polymer due to its promising physical and chemical properties and its inherent biodegradability and ease of recycling.<sup>1</sup> The use of alcohol esters of lactic acid as green solvents is also appealing. These growing markets drive the demand for lactic acid. Currently, almost all the lactic acid produced industrially is obtained via bacterial fermentation of sugars or starches.<sup>2</sup> While sugars are a renewable carbon feedstock, there are a few challenges with scaling up fermentation to meet the growing demand. To maintain productive cell populations, fermentation requires neutralization of the acid during production (typically with  $\text{Ca}(\text{OH})_2$ ), followed by acidification of the calcium lactate (typically with  $\text{H}_2\text{SO}_4$ ) after the removal of the cells. This stoichiometric use of acids and bases results in additional reagent costs and the production of a waste salt (typically  $\text{CaSO}_4$ ). Even with continuous neutralization, the fermentation process yields relatively low concentrations of lactic acid; as a result, the purification steps needed to concentrate the product are energy intensive.<sup>2</sup> The price of sugars and the intrinsic constraints of fermentation significantly contribute to the final cost of lactic acid. To meet the growing demand and to increase the economic appeal of adopting biodegradable products derived from lactic acid, there is an interest in developing alternative, inexpensive chemical routes to lactic acid from sugars or other feedstocks.

We propose a simple, one-pot chemical synthesis of lactic acid starting from acetone, which is inexpensive and available at large scale. This process involves a tandem oxidation of acetone to methyl glyoxal by  $\text{SeO}_2$  and isomerization of methyl glyoxal to lactic acid by a microporous stannosilicate. The use of Se complexes for ketone oxidation is well known, including the oxidation of acetone to methyl glyoxal.<sup>3</sup> However, high yields of such products are difficult to achieve due to their high reactivity.<sup>4</sup> The mild conditions of the Se-mediated oxidation and its remarkable selectivity at low conversions enable a facile pairing with a Lewis-acid-catalyzed isomerization of methyl glyoxal to produce high yields of stable lactic acid. In this work, we studied a variety of catalysts, solvents, reaction conditions, and system designs to optimize this novel tandem process.

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## A Zeolite-Encapsulated Hydrogenation Catalyst for the Direct Conversion of Glucose to Ethylene Glycol

**Surendhran, R.,<sup>1</sup> Lobo, R. F.,<sup>1,\*</sup> Orazov, M.<sup>2,\*</sup>**

<sup>1</sup> Department of Chemical and Biological Engineering, University of Delaware, Newark, Delaware, 19716

<sup>2</sup> Chevron, Richmond, California, 94801

Ethylene glycol (EG) is a high-volume chemical used primarily in the synthesis of polymers, as a solvent, and as a heat-transfer fluid. The prevalent industrial process for EG production involves epoxidation of ethylene, followed by the hydration of the ethylene oxide intermediate requiring multiple reactors and separation units [1]. Over 95% of the global EG supply is produced through this method utilizing ethylene sourced predominantly from non-renewable natural gas, naphtha, and coal [1]. The overall financial and environmental cost for sourcing the ethylene and converting it to EG incentivizes the development of a technology that can directly convert a renewable feedstock to EG. The direct conversion of cellulose or glucose to EG, then, has been the subject of research in recent years, with a sequential retro-aldol–hydrogenation strategy being particularly appealing [2].

The retro-aldol reaction is equilibrium limited and favors the hexose (glucose) over the smaller fragments (glycolaldehyde and erythrose). This equilibrium limitation can be overcome by utilizing a one-pot tandem strategy that irreversibly transforms the glycolaldehyde to EG via hydrogenation. Previous examples of such systems utilizing W-based retro-aldol catalyst and a Ni or Ru based hydrogenation catalyst were susceptible to indiscriminate reduction of glucose, erythrose and glycolaldehyde and resulted in a mixture of C<sub>2</sub> – C<sub>6</sub> polyols [2]. To improve the hydrogenation selectivity, we investigated encapsulating the active Ni nanoparticles inside zeolites with MFI morphology. The 5.5 Å pores of this zeolite should limit the access of larger molecules, such as hexoses, from accessing the hydrogenation sites [3], improving the selectivity for EG. We have explored the preparation and application of such MFI-encapsulated Ni catalysts for size-selective hydrogenation. A simple, scalable methodology was developed for encapsulation of Ni nanoparticles inside lab-synthesized or commercially available high-silica MFI zeolites. The improved size-selectivity for glycolaldehyde hydrogenation over glucose hydrogenation is demonstrated and insight into Ni nanoparticle distribution is provided through *ex-situ* characterization. We have also combined these size-selective hydrogenation catalysts with W-based retro-aldol catalysts to enable the direct conversion of glucose to ethylene glycol in high yields, with minimized production of sorbitol and mannitol.

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## Mild Temperature Ammonia Synthesis using Metal Nitride Catalysts

**Pranav Roy,<sup>1</sup> Brandon C. Bukowski<sup>1,\*</sup>**

<sup>1</sup>*Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, MD 21218*

Ammonia production stands as a pivotal industrial process with global significance. Despite the historical dominance of the Haber-Bosch process in the 20<sup>th</sup> century, characterized by elevated temperature and pressure conditions, the exploration of alternative methods, particularly catalyst design, has gained prominence. The prospect of catalysts capable of achieving substantial ammonia yields at lower temperature and pressure presents an opportunity to revolutionize contemporary industrial practices in ammonia generation <sup>1</sup>. Metal nitrides emerge as promising candidates in this pursuit, as they exhibit unique properties that make them attractive for catalytic applications, including their diverse surface facets and the potential for manipulating their layers and surface repetitions <sup>2</sup>. Zeolite membranes, with their intricate porous structure and selective molecular sieving capabilities, have garnered significant attention as versatile materials in various applications. By incorporating a metal nitride into the mesoporous domain of zeolite nanosheets, we aim to replicate a conducive environment characterized by mild temperature and pressure, fostering an effective catalyst for ammonia synthesis.

Recognizing the importance of metal nitrides in catalyzing ammonia production, we employed periodic Density Functional Theory (DFT) to investigate the associative Mars-van Krevlen mechanism. This involved the addition of nitrogen and hydrogen gas to rock-salt structured binary transition metal nitrides, utilizing the PBE-D3 functional. Addressing inherent challenges such as self-interaction errors in standard functionals like LDA and GGA, we adopted the DFT+U functional, with the U-value tailored to the formation energy of metal nitrides calculated using the HSE06 functional. Our study encompassed a comprehensive analysis, including density of states and Bader charge evaluations, which underscored the impact of the U-value correction, aligning its performance with the HSE06 functional. Furthermore, we explored the correlation between ammonia adsorption energy and nitrogen-vacancy formation energy for metal nitrides, establishing a vital link in understanding their catalytic behavior. Additionally, our investigation delved into the influence of a quasi-one-dimensional Ni nanowire supported on an MnN substrate, employing DFT+U to improve surface strain. The application of the nudged elastic band method on this system revealed a simplified ammonia formation mechanism., elucidating the potential of nanowires in enhancing catalytic efficiency. Our research provides pivotal insights into the surface and reaction chemistry of metal nitrides, laying the groundwork for developing catalysts capable of generating ammonia at higher yields, even under mild temperature and pressure conditions. This work holds significant promise for advancing the field of catalysis in industrial ammonia production.

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## Simulated high-throughput polymerization and active site motifs screening of potential porous organic polymer catalysts

**Zhou, Xiang<sup>1</sup>, Bukowski, Brandon C.<sup>1,\*</sup>**

<sup>1</sup> Department of Chemical and Biomolecular Engineering, Johns Hopkins University, 3400 North Charles Street, Baltimore, 21218

Amorphous porous organic polymers (POPs) offer greater design versatility for specific catalytic applications compared to zeolites and Metal-Organic Frameworks (MOFs). 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>. They exhibit superior structure flexibility and shape selectivity as catalysts. The intricate and amorphous nature of POPs complicates their experimental and simulation analysis, resulting in high computational costs. Therefore, our objective is to develop an automated approach that efficiently identifies kinetically relevant regions within the POPs network, thereby streamlining and simplifying the study of these materials. This work modifies a molecular dynamics structure generation methodology<sup>3</sup> to a high-throughput polymerization workflow that is object-oriented for creating multiple porous polymers with screening methodology to assess their catalytic capabilities. This work illustrates the generation and modification process of amorphous porous polymer using styrene and divinylbenzene as example initial monomers at different mixing ratios<sup>4</sup>. The screening methodology in this work is achieved via identifying and analyzing active site motifs of simulated porous polymers using DFT calculations and catalytic calculations. To perform computationally efficient Density Functional Theory (DFT) and pore catalytic calculations on large polymer systems, dimensionality reduction, such as Kernel Principal Component Analysis (K-PCA) and Density-Based Spatial Clustering of Applications with Noise (DBSCAN), and Monte Carlo calculations are used to reduce data size and identify kinetically relevant regions within polymer networks. The primary catalytic potential of identified active sites within the simulated polymer are screened by CO<sub>2</sub> adsorption energy, which is calculated via extended tight-binding DFT (XTB DFT). The pore size distribution and other catalytic calculations are also performed using PoreBlazer on the simulated polymer for screening of catalytic capabilities. The result of this work shows the improvement of porous structure and catalytic capabilities of simulated polymers given same type of initial monomers, highlighting the efficacy in improving polymer design for catalysis.

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## Probing the role of acid site distribution on water structure in aluminosilicate zeolites: insights from molecular dynamics

**Mingze Zheng,<sup>1</sup> Brandon C. Bukowski<sup>1,\*</sup>**

<sup>1</sup> Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, MD 21218

Water plays a crucial role in various industrial processes, particularly in the production of fuels and chemicals utilizing ethanol and other bio-based feedstocks. Zeolites are porous catalysts used extensively due to their shape-selective adsorption and confinement interactions. Zeolite effectiveness is significantly impacted by the presence of water, which may reduce product selectivity and reactivity depending on the polarity of transition states<sup>1</sup>. Obtaining a molecular-level understanding of water behavior in zeolites formed during catalysis is essential in designing sustainable and highly efficient industrial catalysts<sup>2</sup>. Using advanced computational techniques including ab initio molecular dynamics (AIMD) and machine learning force fields (MLFF), we examined the stability of various water loadings in zeolite AFI with different Si/Al ratios and Al distributions. This analysis enables us to identify the water distribution in the pore, revealing the formation of water clusters in acid zeolites. This analysis further assists in uncovering the intricate molecular details of complex solvated reactions such as ethanol to olefins for sustainable aviation fuels.

Our analysis reveals that the behavior of water in zeolites is heavily influenced by the Si/Al ratio and the distribution of Al in the framework. We found that the average adsorption energy per water molecule is distinct for each Al distribution both at 0 K and at room temperature as probed by MD. Further, we found that the peaks in the vibrational density of states (vDOS) of water in Al-defected AFI are shifted, particularly at the saturation water loading. Our radial distribution function (RDF) analysis of zeolite AFI unit cell points out that water molecules show a higher order of clustering near the Al site, and the RDFs of zeolite AFI supercell indicate a similar trend of water clustering near the region with higher Al density. Our time-averaged water density heat maps reveal that with increasing water loading and Al-Al distance in zeolite AFI pore, water molecules tend to distribute evenly throughout the entire pore in zeolite AFI. Our results provide crucial insights into the molecular-level behavior of water in zeolites which we are now applying to understand ethanol to olefins kinetics when water is present.

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## **Porous covalent organic framework nanoparticle synthesis and assembly**

**Kainan Feng and Mark A. Snyder**

*Department of Chemical & Biomolecular Engineering, Lehigh University, 27 Memorial Dr. W, Bethlehem, 18015*

Reticulation of covalent organic frameworks (COFs) involves the assembly and covalent attachment of organic building block monomers into extended structures. Imine-linked COFs, particularly desirable for their demonstrated stability, benefit from error correction during reticulation that results from the reversibility of the associated transimination chemistry. Such error correction can enable the formation of bulk crystalline structures with properties of the specific building blocks—like size, geometry, and chemistry—serving as handles for tailoring COF microstructure, pore size/topology, and function. While bottom-up design and control of microstructure is a hallmark of COF synthesis, formulation of COFs into processable nanostructured particles and elucidation of their assembly could enable the tailored synthesis of hierarchically structured and/or hybrid functional porous materials. Yet the ability to nucleate and grow size-tunable COF nanoparticles for use as mesoscale building blocks remains a serious challenge, complicated by the limited current understanding of COF nucleation and growth as well as the lack of generalizable routes to particle stabilization and assembly. The overarching goal of this work aims to unravel some of these challenging questions, beginning with a systematic study aimed at understanding COF nanoparticle synthesis and assembly into long range nanoparticle crystalline structures. Here we demonstrate the role of solvent choice, reagent concentration, and synthesis time as facile handles for realizing COF nanoparticles and tuning particle size in the *ca.* 50-250 nm range. Alternatively, the introduction of monofunctional growth modifiers have limited impact on achievable particle size but can improve crystallinity. In instances when COF nanoparticles have been successfully synthesized, we have demonstrated the ability to convectively assemble these particles into nanoparticle crystalline structures and are exploring strategies for sacrificial templated growth of COFs within amine-functionalized silica nanoparticle crystalline templates.

## Toward synthesis-structure-function relations of hierarchically structured 2D COFs

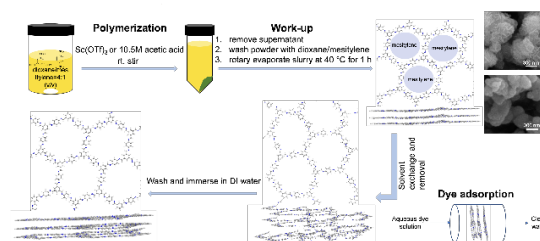
**Hao Guo,<sup>1</sup> Joseph Cline,<sup>2</sup> Christopher J. Kiely,<sup>1,2</sup> Srinivas Rangarajan<sup>1</sup>, and Mark A. Snyder<sup>1,\*</sup>**

<sup>1</sup> Department of Chemical and Biomolecular Engineering, Lehigh University, 124 E. Morton St., Bethlehem, 18015

<sup>2</sup> Department of Material Science & Engineering, Lehigh University, 5 E. Packer Ave., Bethlehem, 18015

The covalent linking of organic building blocks (BBs) into crystalline covalent organic frameworks (COFs) has emerged as an exciting route to materials with tunable porosity. Constructed through the dynamically reversible covalent assembly of organic molecules, COFs benefit from intrinsically tunable pore size, composition, topology, and functionality.<sup>1,2</sup> Yet, designing these materials to meet the demands of specific applications requires knowledge of how synthetic conditions offer control over specific structural hierarchy, spanning molecular and mesoscopic (*i.e.*, pore size, topology) to macroscopic scales (*i.e.*, morphology). Judicious choice of monomeric BBs and control of reaction conditions have been established as tools for controlling pore size and crystallinity.<sup>3</sup> To tailor characteristic diffusion length scales of these materials, recent work has begun to explore how synthesis conditions (*i.e.*, changes of monomers and kinetic factors) can be exploited for controlling COF morphology.<sup>4,5</sup>

Here, we have leveraged COF-LZU1, the first reported 2D imine-based COF, and TAPB-PDA as testbed materials for elucidating synthesis-structure-function relations governing how factors such as catalyst type and composition influence kinetics of assembly, covalent linkage chemistry, crystal growth, and activation. Specifically, we demonstrate how scandium triflate, an efficient catalyst involved in the synthesis of imine-based COFs, can be exploited for controlling COF mesostructure. Through systematic synthesis, comprehensive characterization, and computational insight, we have mapped a compositional pseudo-phase space in which globular COFs with sub-micron diffusion length scales evolve into unique rosette structures simply as a function of the synthetic catalyst content and type. The rosette-shaped COFs, comprised of interconnected, high-aspect-ratio crystalline porous sheets of only several unit cells in thickness, offer orders of magnitude reduction in diffusion length scales and several-fold increase in surface area relative to globular structures. Employing the uptake of bulky molecules of varying kinetic diameter and charge, we elucidate key synthesis-structure-function relations for the application of mesostructured COFs for water purification. More generally, the work establishes early synthesis-structure relations that, combined with building block-based design of microstructure, hold promise for realizing unique control over COF mesostructure, morphology, and function with implications for functional thin film (*e.g.*, membranes, electrodes) and powder (*e.g.*, catalysts, sorbents) processing.



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## Hydrodeoxygenation of *m*-Cresol over WO<sub>x</sub>-Pt/SBA-15 Using Alkanes as Hydrogen Carriers

**Ching-Yu Wang, John M. Vohs\*, Raymond J. Gorte\***

*Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104*

Hydrodeoxygenation (HDO) of *m*-cresol was studied over WO<sub>x</sub>-Pt/SBA-15 using several light alkanes as H<sub>2</sub> carriers. While dehydrogenation of *n*-hexane at 773 K over a Pt/SBA-15 with 9-nm pores was unstable at pressures below 30 bar, the reaction was stable for more than 5 h at pressures greater than 40 bar. The transition from stable to unstable operation depended on the support pore size and structure, occurring at lower pressures on Pt/SBA-15 with 6-nm pores and much higher pressures on conventional Pt/SiO<sub>2</sub>. WO<sub>x</sub>-decorated Pt/SBA-15 was active for both dehydrogenation of *n*-hexane and HDO of *m*-cresol, and both reactions could be carried out in a stable manner at high pressures. HDO of *m*-cresol could also be carried out using H<sub>2</sub> from *n*-pentane and 3-methylpentane over WO<sub>x</sub>-Pt/SBA-15 at high pressures. Possible explanations for the high-pressure stability are given.

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## On the activity and stability of Pt<sub>1</sub> and Pt<sub>2</sub> species in the chabazite framework

Srinivas, S.,<sup>1</sup> Caratzoulas, S.,<sup>2</sup> Vlachos, D.<sup>1,\*</sup>

<sup>1</sup> Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy St., Newark, DE 19716

<sup>2</sup> RAPID Manufacturing Institute, Catalysis Center for Energy Innovation, Delaware Energy Institute, Center for Plastics Innovation, University of Delaware, 221 Academy St., Newark, DE 19716

Supported platinum single atoms (SAs) and sub-nanometer clusters have been garnering attention for the selective, high-temperature alkane dehydrogenation to alkenes<sup>1</sup>. In this particle size regime, these catalysts show high atom efficiency, i.e., high activity per atom<sup>2</sup>, making them a cost-effective alternative to the conventional PtSn/Al<sub>2</sub>O<sub>3</sub> catalyst. Such low-nuclearity Pt-based catalysts present fewer Pt-Pt bonds, which would promote C-C cracking and coking, and thus show high selectivity for alkenes<sup>3</sup>. What hinders the industrial deployment of these catalysts is their stability. The large cohesive energy of bulk platinum provides a strong thermodynamic driving force for sintering.

Indeed, this has been reported in several experimental reports of Pt clusters on the alumina support<sup>4-5</sup>. Encapsulating small Pt clusters in microporous zeolite frameworks has shown great promise for preventing sintering. It has been hypothesized that the zeolite can trap the small Pt clusters within its micropores, creating a physical barrier to sintering<sup>6</sup>. Furthermore, incorporating heteroatoms and engineering silanol defects in the framework has been shown to enhance the stability of the single atoms and sub-nanometer clusters under reaction conditions<sup>7</sup>. However, the role of the heteroatoms and silanol defects in stabilizing single Pt atoms and low nuclearity clusters, as well as the effect of Pt's local environment and nuclearity on activity, are poorly understood.

In this work, we perform electronic structure calculations and *ab initio* molecular dynamics (AIMD) free energy simulations to understand the effect of silanol defects and framework heteroatoms, namely Sn(IV) and Al, on the stability and dynamics of dispersed Pt<sub>1</sub> and Pt<sub>2</sub> species in the CHA framework. Informed by these simulations, we perform DFT optimization to select the stable sites under different conditions and predict their activity via microkinetic modelling. We perform orbital analysis in the natural bonding orbital basis to provide insights into activity-trends across the different local environments and strategies for achieving sintering-resistant atomic Pt dispersion.

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