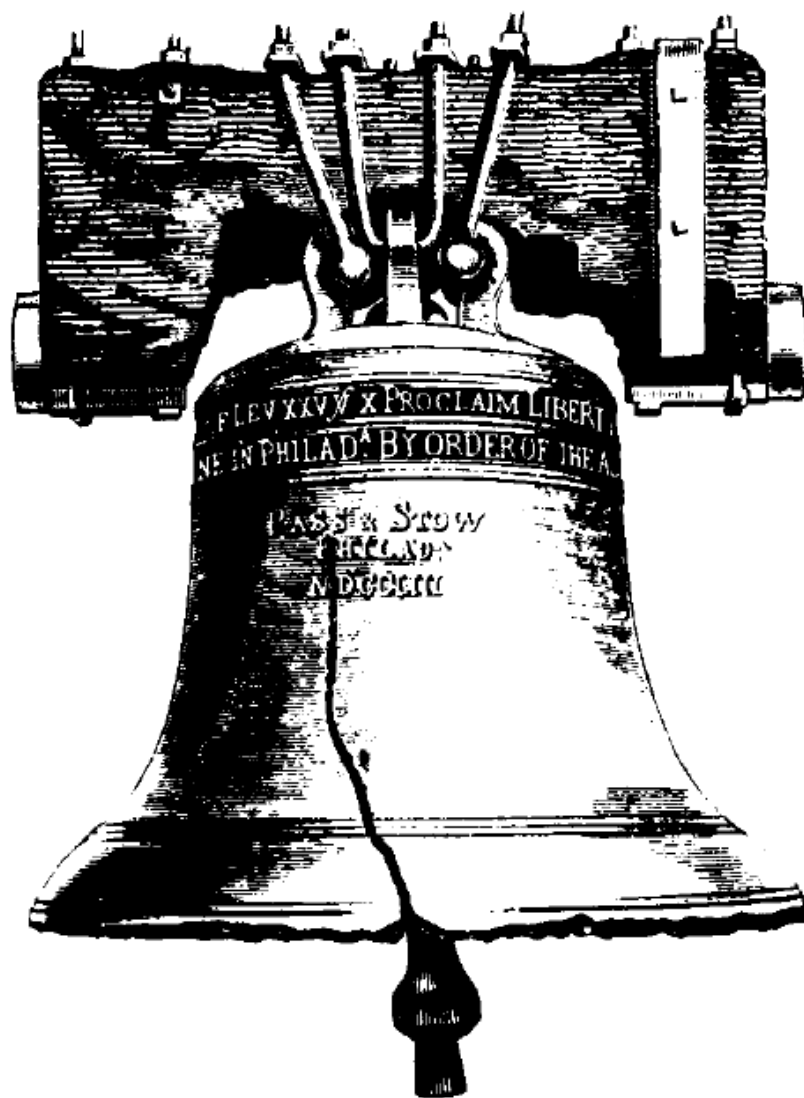


Catalysis Club of Philadelphia
2024 Spring Symposium Program



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Thursday, April 18, 2024

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2024 Catalysis Club of Philadelphia (CCP) Annual Symposium-Student Poster Joint Conference

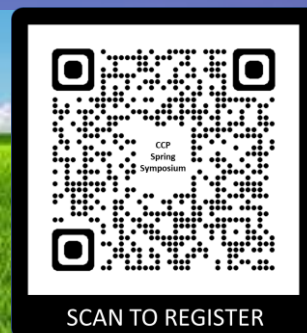
Catalysis for a greener future

Thursday, April 18, 2024 @ Brandywine Plaza Hotel

630 Naamans Road, Claymont, DE, 19730, USA



Symposium chair: Dr. Zhuonan (Nick) Song (WL Gore & Associates)
Student poster chair: Dr. Donghua Zuo (Covation Biomaterials)



Symposium Program at a Glance

Keynote speakers



Dr. Daniel A. Hickman
Senior R&D Fellow,
*Engineering & Process
Science, Core Research &
Development, The Dow
Chemical Company*



Prof. Raul F. Lobo
Claire D. LeClaire Professor of
Chemical & Biomolecular
Engineering, Associate Chair,
University of Delaware

Seminar speakers



Prof. Fanglin Che
UMass Lowell



Dr. Robert M. Palomino
Senior Chemist II, BASF



Dr. Vladimiro Nikolakis
Catalyst Scientist, WL Gore



Esun Selvam
PhD candidate, UD

Seminar topics: reaction engineering, biomass conversion and techno-economic analysis, CO₂ capture and conversion, continuous flow reactor, 3D imaging with Artificial Intelligence (AI), microwave and Joule heating

Event highlights:

- Seminars Covering Cutting-Edge Catalysis Topics
- Q&A Sessions with Esteemed Speakers
- Networking Opportunities with Industry Professionals
- Engaging Student Poster Presentations

Early Registration: April 4th, 2024

<http://catalysisclubphilly.org/2024-spring-symposium-and-poster-session/>

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Spring Symposium 2024 Schedule of Events

Thursday, April 18, 2024

- 8:00 AM **Breakfast and social hour**
- 9:00 AM **Opening remarks**
- 9:10 AM **Keynote, Dr. Daniel A. Hickman, Dow.**
“Reaction Engineering: An Essential Discipline to Meet Societal Goals”
- 9:55 AM **Prof. Fanglin Che, University of Massachusetts Lowell.**
“Organic-Inorganic Interface Enhanced CO₂ Capture and Conversion”
- 10:30 AM **Tea break**
- 10:45 AM **Dr. Vladimiro Nikolakis, WL Gore & Associates.**
“Scalable Continuous Flow Hydrogenation using Structured Catalyst Reactor”
- 11:20 AM **CCP Award Announcement**
- 11:30 AM **CCP Sponsor Talk, Edward Lim, Microtrac**
- 11:35 AM **CCP Sponsor Talk, Jeff Dixon, Micromeritics**
- 11:40 AM **Lunch (Buffet).**
- 12:50 PM **Afternoon program opening remarks**
- 12:55 PM **Keynote, Prof. Raul F. Lobo, University of Delaware.**
“From Biomass to Recyclable Polymers for A Circularity Economy”
- 13:40 PM **Dr. Robert M. Palomino, BASF.**
“Micro-CT Imaging of Four-Way Catalysts and Quantitative Analysis via Computer Vision”
- 14:10 AM **Tea break**
- 14:25 PM **Student Talk, Esun Selvam, University of Delaware.**
“Catalytic Upcycling and Recycling of Polyolefin Plastic Wastes via Microwave and Joule-Heated Processes”
- 14:50 PM **Symposium closing remarks and Student Poster Session introduction**
- 15:00 PM **Student Poster Session and social hour**
- 17:00 PM **Conference closing**

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Reaction engineering: an essential discipline to meet societal goals

Derived from a collaborative effort with Praveen Bollini, Moiz Diwan, Pankaj Gautam, Ryan Hartman, Marty Johnson, Motoaki Kawase, Matt Neurock, Gregory Patience, Alan Stottlemeyer, Dion Vlachos, and Ben Wilhite

Daniel A. Hickman

Sr. R&D Fellow

Core R&D

Dow

Abstract

In our recent perspective paper,¹ we describe ways in which the field of chemical reaction engineering (CRE) is crucial in achieving societal goals. Key stakeholders, such as policymakers, funding agencies, educators, and corporate stewards, must understand and support its importance. The drive to decarbonize the chemical and process industries and achieve plastics circularity will fail without the guiding principles of CRE. The search for alternative reaction system designs that utilize electricity rather than fossil fuels for energy, including resistive, microwave, inductive, and plasma reactors, must be led by capable CRE experts, with attention given to achieving sufficient energy efficiencies and enabling commercially relevant process capacities at acceptable capital costs. The drive for plastics circularity also provides opportunities for reaction engineers to partner with polymer chemists and materials scientists to design new molecules and better reactor systems to make them, as well as to design reaction process technology to convert waste polymers into raw materials. To achieve these goals, the next generation of process innovation will benefit from continued development of computational chemistry methods for predicting reaction networks and pathways, reaction rate parameters, thermophysical properties, and structure-property relationships. In addition, the application of artificial intelligence and machine learning to the field of reaction engineering shows promise but requires high-quality data laboratory data, which are often influenced by uncontrolled and unmeasured variables. Investment in CRE as a discipline in academic instruction, academic research, and industrial process research and development will yield a high return on investment both by making our new processes cheaper and better with shorter implementation timelines and by avoiding extended development efforts for ideas unfit to meet society's goals.

1. Bollini, P.; Diwan, M.; Gautam, P.; Hartman, R. L.; Hickman, D. A.; Johnson, M.; Kawase, M.; Neurock, M.; Patience, G. S.; Stottlemeyer, A.; Vlachos, D. G.; Wilhite, B., Vision 2050: Reaction Engineering Roadmap. *ACS Engineering Au* **2023**, <https://doi.org/10.1021/acseengineeringau.3c00023>

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Daniel A. Hickman
Senior R&D Fellow

Engineering & Process Science, Core Research & Development
The Dow Chemical Company
Midland, Michigan, 48667
dahickman@dow.com

Dan Hickman is a Senior R&D Fellow in the Engineering and Process Science department of Dow's Core Research & Development. He received his B.S. in chemical engineering from Iowa State University (1988) and his Ph.D. in chemical engineering from the University of Minnesota (1992). In 31 years with Dow, Dan has served as a subject matter expert and technical leader in reaction engineering and process development for numerous reaction systems across many Dow businesses and technologies. His industrial reaction engineering experience includes working with stirred tank reactors, fixed bed reactors, trickle bed reactors, and fluidized bed reactors. His contributions at Dow include the conceptual design of new reactor systems for three commercial processes and the development of training and resources that facilitate efficient and reliable reactor scale-up from the laboratory. Dan holds 25 patents and has authored 32 journal articles and book chapters and more than 200 internal Dow reports. Dan was named the Mid-Michigan AIChE Chemical Engineer of the Year in 2014, received the CRE Practice Award from the Catalysis and Reaction Engineering Division of AIChE in 2015, was named an AIChE Fellow in 2023, and currently serves the global reaction engineering community on the board of directors for International Symposium on Chemical Reaction Engineering, Inc.

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From Biomass to Recyclable Polymers for a Circular Economy

Raul F. Lobo, Alan Allgeier, Bala Subramanian and Dionisios Vlachos, Marianthi Ierapetritou
Center for Catalytic Science and Technology, Department of Chemical and Biomolecular
Engineering, University of Delaware, Newark, DE USA
Center for Environmentally Beneficial Catalysis, Chemical and Petroleum Engineering
The University of Kansas, Lawrence, KS USA

Abstract

The transition to a circular economy requires the development of materials designed to work within this paradigm and the development of manufacturing processes that are scalable, economical, and ultimately, competitive. In this talk, I will use the preparation of the monomer 4,4'-dibenzyl-dicarboxylic acid DBDC as a case study of the potential and the challenges faced when using biomass-derived species to prepare a desirable molecule in comparison to fossil-fuel-derived equivalents. We will compare alternative pathways to the preparation of DBDC from methylfuran and furoic acid and describe a process to integrate techno-economic analysis and laboratory work to improve synthesis steps, identify better catalysts, and scale up reactions and separations for potential large-scale manufacture. We will also compare the synthesis and properties of blends of DBDC and terephthalic acid polyesters and assess their recyclability using glycolysis powered by microwave reactors. A life-cycle analysis of the process—from biomass to monomers to polymers and back to monomers—will help quantify the potential benefits of new materials for a circular economy.

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Raul F. Lobo

**Claire D. LeClaire Professor of Chemical and Biomolecular Engineering
And Associate Chair**

Department of Chemical and Biomolecular Engineering
University of Delaware

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 with Mark Davis. 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.

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Organic-Inorganic Interface Enhanced CO₂ Capture and Conversion

Fanglin Che, Department of Chemical Engineering, University of Massachusetts Lowell

Abstract

CO₂ in air increases from 280 to 417 ppm from 1760 to 2022, changing climate, rising sea level, and inducing ocean acidification. The CO₂ in air is estimated to rise to 450 ppm by 2050 without the installation of newer Carbon Capture, Sequestration, and Utilization technologies. CO₂ capture (e.g., air, ocean release, and industrial point source) is the most critical technology to pave the way for facilitating decarbonization. Industrially, CO₂ is selectively captured by liquid monoethanolamine solution due to the strong C-N bond formation with a capture capacity of 0.5 mol CO₂/mol amine. The **main challenges** are (1) high CO₂ releasing temperature in a range of 100-120°C; and (2) a huge amount of degraded solvent waste.

To overcome the above challenges, *combining amine-based ligands with solid catalysts* to achieve CO₂ capture and directly transformation from the captured state to value-added multi-carbon products (C₂, e.g., ethylene, ethanol) are very attractive. However, the mechanism of CO₂ reactive capture and direct conversion to valuable hydrocarbons and alcohols at such organic-inorganic interface is unclear.¹

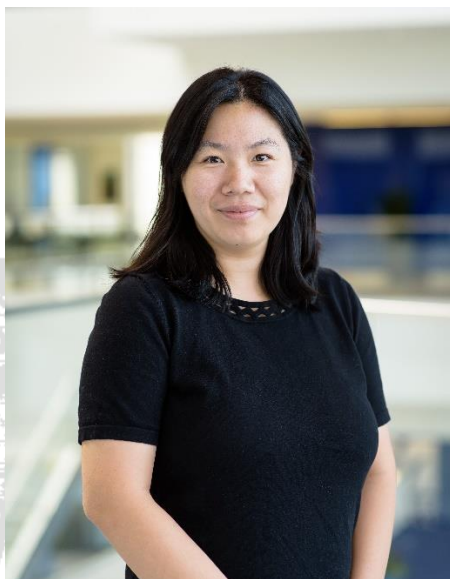
To mitigate the above mechanism challenge, we designed aminothiolate self-assembled monolayer (SAM)-modulated Cu interface (i.e., Cu-S-C_nH_{2n}-NH₂, n = 2, 6, 11). Grand canonical density functional theory (GC-DFT) simulation is applied to prove that dual-active sites (organic nitrogen site (-NH₂), inorganic Cu site) at the interface promoted CO₂ capture, first-proton transfer activation (i.e., COOH* formation), and its selectivity to C₂ (i.e., carbon-carbon (C-C) coupling).^{2,3} More specifically, our results show that (1) the ligands are stable over the Cu surface when the coverage is lower than ¼ ML. In addition, the ligand with a longer alkyl chain length is more stable; (2) aminothiolate ligands provide H bond and active N site to promote COOH* formation at Cu and N site, respectively, thus improving the activity; and (3) low coverage of aminothiolate ligand at flat-lying configuration decreases the activation barrier of C-C coupling up to 0.64 eV compared to that of bare Cu, facilitating the selectivity of C₂ species. The simulation results are further validated with CO₂ electroreduction experiments. Overall, this research provides an innovative picture of CO₂ reactive capture and conversion at hybrid organic-inorganic interfaces, and specifically their roles in increasing catalytic activity and selectivity.

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1. Xu, Y.; Ross, M. B.; Xin, H.; Che, F., Engineering bimetallic interfaces and revealing the mechanism for carbon dioxide electroreduction to C₃+ liquid chemicals. *Cell Reports Physical Science* **2023**, *4* (12), 101718.
2. Wan, M.; Yang, Z.; Morgan, H.; Shi, J.; Shi, F.; Liu, M.; Wong, H.-W.; Gu, Z.; Che, F., Enhanced CO₂ Reactive Capture and Conversion Using Aminothiolate Ligand–Metal Interface. *Journal of the American Chemical Society* **2023**, *145* (48), 26038-26051.
3. Wan, M.; Gu, Z.; Che, F., Hybrid Organic-Inorganic Heterogeneous Interfaces for Electrocatalysis: A Theoretical Study of CO₂ Reduction to C₂. *ChemCatChem* **2022**, *14* (4), e202101224.

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Fanglin Che

Department of Chemical Engineering

University of Massachusetts Lowell

Biography

Dr. Fanglin Che joined in Chemical Engineering department at UMass Lowell as an Assistant Professor in September 2019. Dr. Che earned her Ph.D. in Chemical Engineering at Washington State University in 2016. From 2017 to 2018, she worked on electrocatalysis at University of Toronto as a Postdoctoral Researcher. From 2018 to 2019, she worked on computational fluid dynamics simulation as a Postdoctoral Researcher in the Department of Chemical and Biomolecular Engineering at University of Delaware. The overarching goal of Dr. Che's research at UMass Lowell is to advance the knowledge of electrified interfacial phenomena via building data-driven multi-scale and multi-physics computational models. A special focus is placed on field-enhanced chemistry, electrocatalysis, plasma catalysis, and microwave catalysis. Dr. Fanglin Che has received the prestigious DOE Early Career in Catalysis Science at Basic Energy Science Division in 2023. And her group is also currently funded by National Science Foundation, Army, and Office of Navy Research.

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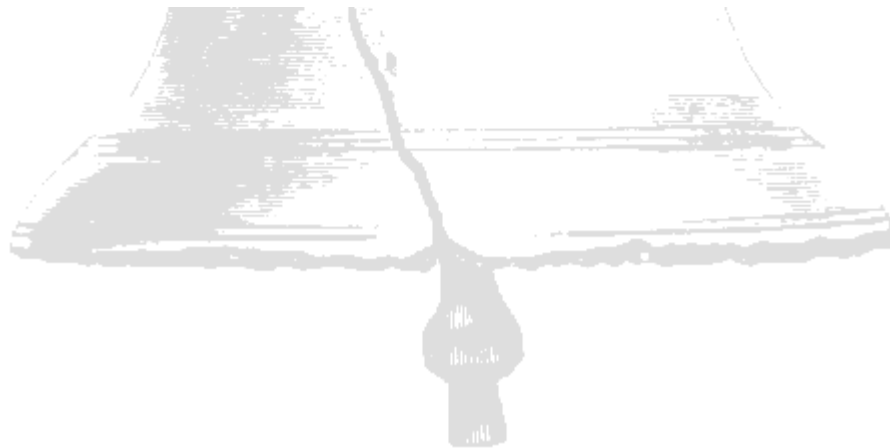
Scalable Continuous Flow Hydrogenation using Structured Catalyst Reactor

Vladimiro Nikolakis, W.L. Gore & Associates, Inc.

Abstract

Manufacturing of pharmaceuticals, agrochemicals, and other specialty chemicals proceed through multistep transformations (reactions, crystallization, extraction etc.) that are operated in a batch mode. Frequently one of the reaction steps is a three-phase catalytic hydrogenation using supported pgm powder catalysts in stirred batch reactors. There is significant interest in the industry to convert from batch to continuous manufacturing for a variety of reasons (i.e. improve yields, safety, reduce waste etc.). Despite the significant progress achieved for chemistries that do not involve solid catalysts (i.e. L, L/L, G/L etc.), carrying out continuous three phase hydrogenations with powder catalysts, especially at manufacturing scale, is challenging.

In this talk we present a scalable solution for continuous heterogeneous catalytic hydrogenations. First, we discuss the Gore Structured Catalyst, a 3-dimensional PTFE mesh-based structure embedded with particles of supported catalyst. This 3-dimensional structure has tunable properties, such as porosity and catalyst loading, thus allowing for the construction of a structure with high catalyst mass loading and low resistance to flow. We discuss then a new modular and scalable reactor design conceived to take full advantage of the Structured Catalyst substrates. We present design principles, scalability arguments, and experimental results with a model hydrogenation reaction. This case study highlights high catalyst utilization, tight temperature control, operation under high pressure, moderate pressure drop, quick scalability of the process, and no loss of catalyst material.



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Vladimiros Nikolakis

W.L. Gore & Associates, Inc.

Biography

Dr. Vladimiros Nikolakis is a scientist at W.L. Gore and Associates Inc. Before joining Gore (2015), he was a Principal Researcher at the Institute of Chemical Engineering Sciences; Patras; Greece and the Associate Director of Research at the Catalysis Center for Energy Innovation; Univ. of Delaware. He got his Chemical Engineering Diploma from Aristotle University of Thessaloniki (1995) and his Ph.D. from University of Massachusetts Amherst (2001). His research interests are in the areas of materials development, & characterization coupled with reaction engineering to improve catalytic conversions or separations. He co-authored more than 65 publications in peer-reviewed journals, and he's a co-inventor in two patents. He has served the CCP for five seasons through various officer positions.

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Micro-CT Imaging of Four-Way Catalysts and Quantitative Analysis via Computer Vision

Robert M. Palomino*¹, Ke-Bin Low¹, Florian Waltz², Chunxin Ji¹, Thomas Schmitz² and Ivan Petrovic¹

¹ BASF Corporation, Iselin, NJ, 08830

² BASF Catalysts Germany GmbH, Hannover, Germany, 30173

*Corresponding Author, robert.palomino@basf.com

Abstract

Materials characterization is a core part of catalysts development at BASF. Characterizing our catalysts materials helps us to understand what specifically affects our catalyst performance to aid in improving and developing better catalysts. Most of our materials characterization is based around standard characterization, which provides a wealth of information about the catalysts and provides strong guidance for fast decision making in catalysts development. These standard measurements can be broken down into following categories: Physical Measurements, Elemental Analysis, Spectroscopy, Microscopy and Thermal Analysis. However, not all issues are addressed by these techniques, and, in these circumstances, “advanced” methods are required to help answer more complex questions. The focus of this presentation highlights one of those “advanced” materials characterization studies undergone at BASF using X-ray Computed Micro-Tomography (XMT).

XMT combined with Artificial Intelligence (AI) assisted image analysis or Deep Learning (DL) was utilized to visualize Four-Way Catalyst (FWC) filters via 3D volume rendering and quantify the resulting 3D morphology to correlate microstructural features with backpressure. FWC catalysts provide three-way conversion efficiency and filtration of particulate matter at the same time, which is a requirement in emission control as restrictions get tighter. By introducing filtering, backpressure generated by an FWC filter becomes a concern and must be carefully controlled. It is suspected that 3D morphology of the FWC filter has the largest effect on the backpressure, but characterization of 3D morphology via 2D imaging (e.g., SEM) can be very limited. XMT allows 3D imaging of relatively large samples, which provides relevant information with respect to the 3D morphology of the FWC filters. However, quantification of microstructural features is required if correlation of 3D morphology with backpressure is to be obtained. Segmentation of the 3D image is required to obtain the quantitative information, but manual processing of even a few slices would take hours, which is highly inefficient and impractical when expanding this to a full 3D image of 1000-2000 slices. DL trains a neural network to recognize image feature classes as a human brain would and, after training with a few representative images pre-labeled via classic machine learning, allows the segmentation to occur in a few hours for the entire dataset. By imaging and analyzing filters with increasing washcoat loading, we were able to correlate what morphological features are affected by the increased loading and correlate that to the resulting backpressure changes. Fundamental research projects such as this help us understand which morphological features require more focus and allow us to facilitate rational design in developing improved catalysts by better understanding how different coating parameters affect the 3D morphology and ultimately performance.

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Robert M. Palomino
Senior Chemist II
BASF

Biography

Robert Palomino is a Senior Chemist II at BASF Corporation located in Iselin, NJ since 2018. He conducts X-ray Spectroscopy and Microscopy studies in the Materials Characterization group of the Catalysts department. His research focuses on X-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Spectroscopy and X-ray Micro-computed Tomography (XMT) along with AI-assisted segmentation of the resultant 3D images. This is employed for various fields, including environmental catalysts, battery materials, refining catalysts, pigments, and coatings. His work at BASF involves collaborations with universities and synchrotron facilities globally. He received his B.S. in Chemistry from St. John's University and his Ph.D. from State University of New York Stony Brook. He has given numerous invited talks and recently received the 2023 CRE Pioneer Award from AIChE, where he gave an invited talk on "Advanced" Materials Characterization at BASF. He is on the National Synchrotron Light Source II (NSLS-II) User Executive Committee (UEC) and served as the Outreach Officer from 2022 – 2023.

Prior to joining BASF, Robert was a Postdoc at Brookhaven National Laboratory (BNL), joint between the Chemistry Division and the NSLS-II. During this role, he served as Authorized beamline staff at the *In situ* and Operando Soft X-ray Spectroscopy (23-ID-2, IOS) beamline. While at BNL, he also worked on characterization of catalysts for alcohol synthesis, environmental catalysts, CO oxidation, ethanol decomposition, and nerve agent decontamination using Ambient Pressure XPS, X-ray Absorption Spectroscopy, and Infrared Reflective Absorption Spectroscopy.

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Catalytic upcycling and recycling of polyolefin plastic wastes via microwave and joule-heated processes

Esun Selvam

Department of Chemical and Biomolecular Engineering
University of Delaware

Abstract

Chemical upcycling of polyolefins offers a promising strategy for mitigating their accumulation in landfills and the environment. However, the high energy demand associated with these processes can lead to significant carbon dioxide emissions. Furthermore, achieving true recyclability of polyolefins into light olefins with high yields under realistic polymer-to-catalyst ratios still remains elusive. Here, we present two single-step electrified processes utilizing Microwave heating (MW) and Rapid Joule Heating (RJH) over solid acid catalysts to selectively deconstruct polyolefin plastic waste into olefins. We demonstrate that coupling microwave heating with suitable solid acid promoters in a slurry reactor coupled with a distillation unit can overcome the energy-related challenges of conventional pyrolysis by operating at modest temperatures (350-375°C), enhancing transport, and furnishing a high yield of olefins (~88%) in seconds, with medium-sized olefins (>75%) composing a significant fraction. We also demonstrate that Rapid Joule Heating (RJH) of polyolefins over an H-ZSM-5 catalyst can produce light olefins (C₂-C₄) with high selectivity and conversion in milliseconds at a much higher polymer-to-catalyst ratio than prior work. Pulsed operation and steam co-feeding enable highly selective deconstruction with minimal catalyst deactivation compared to continuous Joule heating. This technology demonstrates effective deconstruction of various real-life waste materials, resilience to additives and impurities, and versatility for circular polyolefin plastic waste management.

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Esun Selvam

Department of Chemical and Biomolecular Engineering
University of Delaware

Biography

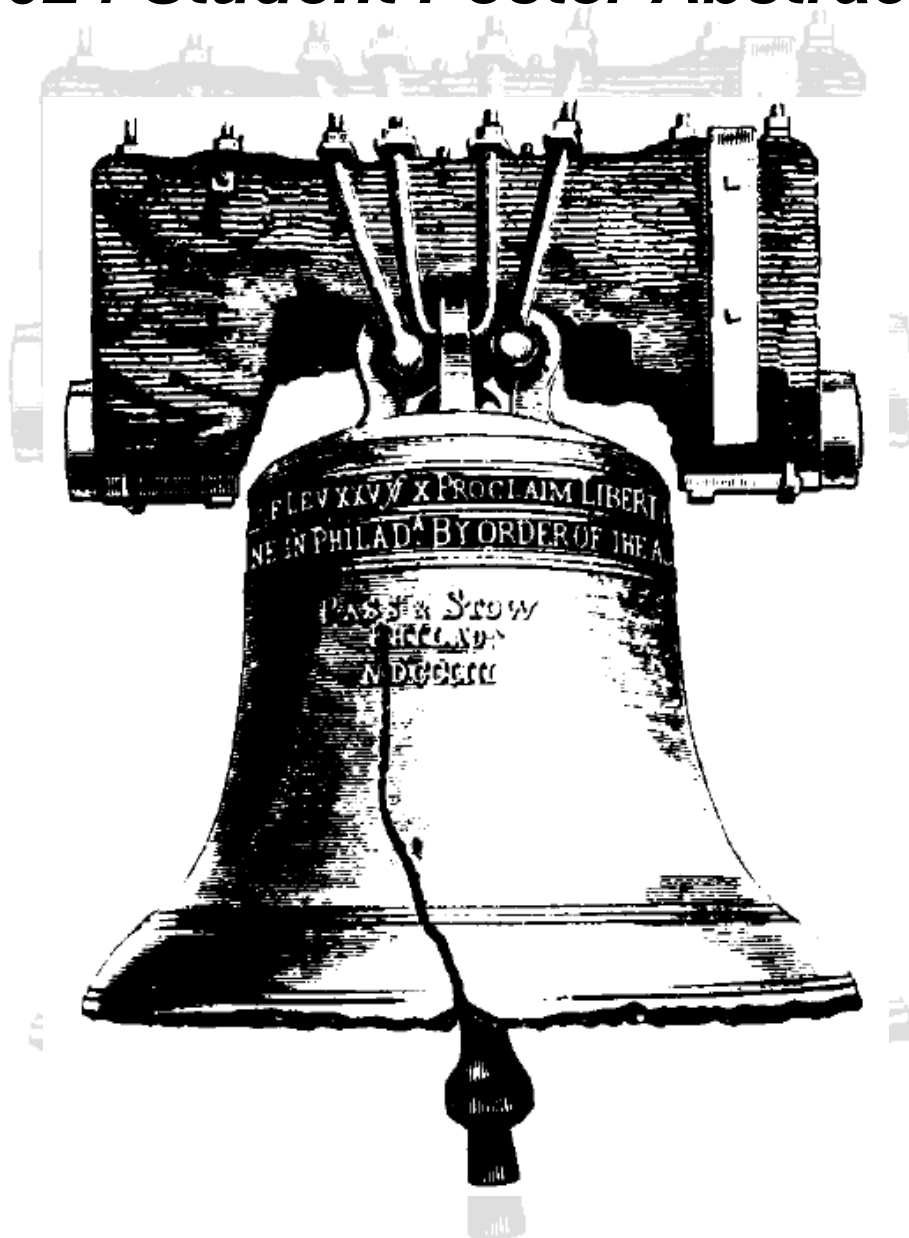
Esun Selvam is a fifth-year PhD candidate at the University of Delaware, working under the guidance of Prof. Dion Vlachos. His research primarily focuses on the development of active and selective heterogeneous catalysts for the deconstruction of plastic waste into high-value products such as fuels, monomers, and olefins. Additionally, his work explores the electrification of these processes using unconventional heating methods, including microwaves and Joule heating. Before joining UD, Esun earned his Bachelor's degree in Chemical Engineering from the National Institute of Technology, Trichy, in India.

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Catalysis Club of Philadelphia

2024 Student Poster Abstracts



Promoting the science of catalysis since 1949

Thursday, April 18, 2024

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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: (Yes)

Spectroscopic Elucidation of Phase Evolution in NiO/YSZ and LaFe_{0.9}Ni_{0.1}O₃ Electrocatalysts under Oxidative and Reductive Gas Environments

Neelesh Kumar¹, Bar Mosevitzky Lis¹, Musa Najimu², Kandis Leslie Abdul-Aziz², Eranda Nikolla³, Israel E. Wachs¹

¹*Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical & Biomolecular Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, United States*

²*Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, California 90007, United States*

³*Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, 48109*

High temperature co-electrolysis of CO₂ and H₂O serves a viable, energy efficient, and scalable route to produce syngas (CO + H₂). The solid oxide electrolysis cell (SOEC) has proven to be a promising technology for CO₂ utilization and a carbon neutral route to curb CO₂ emissions. The design of the cathode catalyst is critical as it must facilitate the activation of CO₂ and H₂O while maintaining redox stability and exhibiting high electronic and oxygen ion conductivity¹. The state-of-the-art cathode materials used in SOECs are Ni/YSZ (8 mol% Ytria Stabilized Zirconia) ceramic composite and novel perovskite LaFe_{0.9}Ni_{0.1}O₃ (LFNO), with performances dependent on various operating factors including temperature, composition of feed gas stream, presence of contaminants like SO_x/NO_x, etc². With the aim of tracking electrocatalyst's structural evolution and surface chemistry under oxidative and reductive gas compositions at high temperature, the cathode materials Ni/YSZ and LFNO were studied using *in situ* Raman spectroscopy and High Sensitivity-Low Energy Ion Scattering (HS-LEIS). Typical flue gas composition is chosen on the basis of the concentration of different components like 15% CO₂, 10% H₂O, 5% O₂ with argon. Under H₂, metallic Ni is formed in the Ni/YSZ cathode while the YSZ phase is stable under these conditions at elevated temperature. Exposure to oxidative environments on Ni/YSZ resulted in the formation of a defective NiO_x phase on the stable YSZ. For the LFNO cathode, *in situ* Raman spectroscopy reveals the reversible nature exsolution of metallic NiFe nanoparticles under H₂ and dissolution in the host lattice under O₂. Surface compositional analyses of the perovskite LaFe_{0.9}Ni_{0.1}O₃ cathode revealed that the surface is dynamic and strongly dependent on the gaseous environmental conditions. The results from this study provide the fundamental insights on the effects of temperature and gas phase composition upon the surfaces and bulk phase of the Ni/YSZ and LFNO cathodes, which serve as a rational guide for the process level design and operation of SOECs.

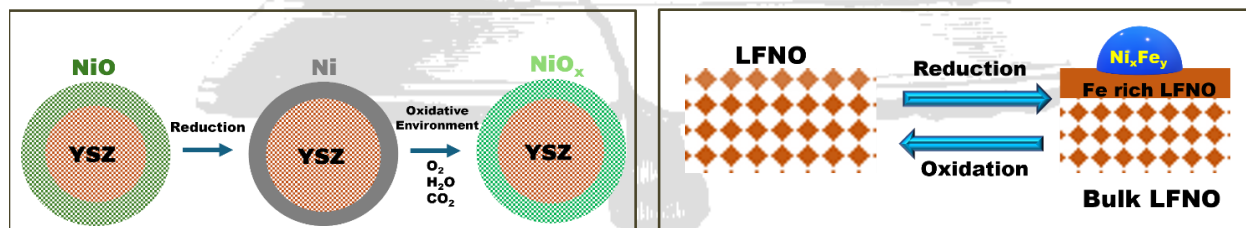


Fig. 1 Phase Transformations in NiO/YSZ and LaFe_{0.9}Ni_{0.1}O₃ (LFNO) under reductive & oxidative gas environments

References

- [1] Juliana Carneiro, Xiang-Kui Gu, Elif Tezel, and Eranda Nikolla, *Industrial & Engineering Chemistry Research* 2020 59 (36), 15884-15893.
- [2] John Kirtley, Anand Singh, David Halat, Thomas Oswell, Josephine M. Hill, and Robert A. Walker, *The Journal of Physical Chemistry C* 2013, 117 (49), 25908-25916.

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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

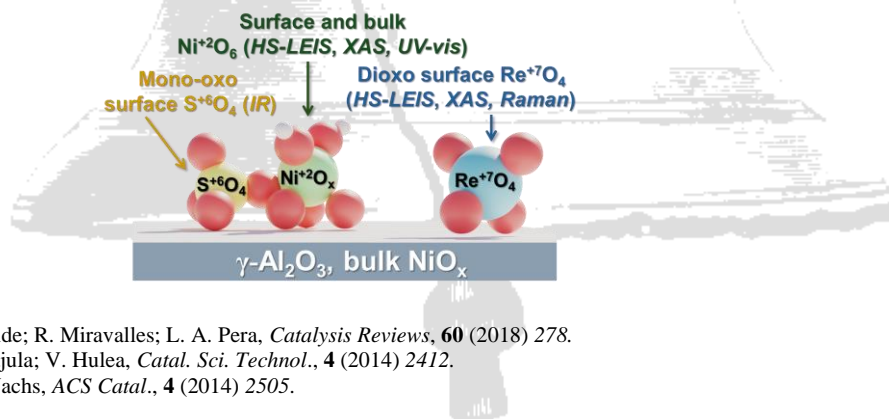
Direct Conversion of Ethylene to Propylene Through Simultaneous Ethylene Dimerization and Olefin Metathesis with Dual-Site Supported 8%NiSO₄/8%ReO₄/γ-Al₂O₃ Catalyst

Eli Ream, Israel E. Wachs*

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Propylene is an important petrochemical building block that has historically been produced as a byproduct of propane steam cracking. However, with an increase in shale gas production, steam cracking processes are switching to lighter feedstocks that produce less propylene.¹ Thus, there is a need for the development of new “on-purpose” methods of propylene production to meet the growing propylene demand. The direct conversion of ethylene to propylene (ETP) through simultaneous ethylene dimerization and olefin metathesis is a promising method for propylene production that is currently in development. In ethylene dimerization, ethylene reacts to form butenes, and in olefin metathesis, ethylene and 2-butene react to form propylene. Many catalysts have been proposed for this reaction. One way to design a catalyst for ETP is to combine aspects of ethylene dimerization and olefin metathesis catalysts. Ethylene dimerization catalysts are typically Ni-based and olefin metathesis catalysts are typically Mo-, W-, or Re-based.^{2,3} In this study, a supported 8%NiSO₄/8%ReO₄/γ-Al₂O₃ dual-site catalyst was synthesized for the direct conversion of ethylene to propylene, in which NiSO₄ performs ethylene dimerization to butenes (primarily 2-butene) and ReO₄ performs olefin metathesis of ethylene and 2-butene to propylene.

The supported 8%NiSO₄/8%ReO₄/γ-Al₂O₃ catalyst was extensively physically characterized at the molecular-level (*in situ* Raman, IR spectroscopy, UV-vis spectroscopy, X-ray absorption spectroscopy, High Sensitivity-Low Energy Ion Scattering (HS-LEIS)) and chemically probed (C₂=-TPSR, C₃=-TPSR, and steady state ethylene dimerization and olefin metathesis reactions). The physical characterization studies revealed that rhena and sulfate are present as surface (O=)₂ReO₂ and O=SO₃ sites, respectively, on the alumina support. The nickel oxide was primarily present as NiO₆ sites that are distributed between the surface and alumina bulk lattice. The individual surface SO₄ and NiO₆ sites did not perform ethylene dimerization and only performed ethylene dimerization when they were both present suggesting a synergistic interaction between them. Neither of the surface SO₄ and NiO₆ sites performed olefin metathesis. The surface ReO₄ sites were not able to perform olefin dimerization and only performed olefin metathesis. Addition of surface ReO₄ to the NiSO₄/Al₂O₃ catalysts modestly enhanced the rate of ethylene dimerization while the addition of NiSO₄ to ReO₄/Al₂O₃ significantly enhanced the rate of olefin metathesis. These promotional activity changes are related to the competitive adsorption of these oxides on specific surface hydroxyls of the alumina support. These results provide new insights about the structure-function relationship of the dual site supported 8%NiSO₄/8%ReO₄/γ-Al₂O₃ catalyst for direct conversion of ethylene to propylene.



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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

Oxidative Dehydrogenation of Ethane (ODHE) to Ethylene by the Bulk MoVNbTe (M1 Phase) Mixed Oxide Catalyst: Surface and Bulk Properties

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ODHE is an alternative method to circumvent thermodynamic limitation, coke formation, and greenhouse gas emissions associated with conventional steam cracking of ethane to produce ethylene. Recently, the bulk M1 phase of the crystalline MoVNbTe mixed oxide catalyst has gained popularity over other types of ODHE catalysts due to its high ethylene selectivity (> 90%) and good ethane conversion (up to 65%). In the present study, bulk-sensitive (Raman) and surface-sensitive (*in situ* High Sensitivity-Low Energy Ion Scattering (HS-LEIS)) techniques are employed to characterize the MoVNbTe mixed oxide catalyst.

The bulk MoVTenb mixed oxide catalyst was hydrothermally prepared from aqueous $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, NH_4VO_3 , $\text{Nb}(\text{OCH}_2\text{CH}_3)_5$, and H_6TeO_6 precursors with a stoichiometric Mo/V/Nb/Te ratio of 1/0.2/0.15/0.15. The aqueous solution was transferred into a Parr vessel and kept at 175 °C for 48 h. The resulting sample was filtered, dried at 120 °C overnight, calcined at 275 °C under O_2/He for 2 h, and heat-treated at 600 °C under He for 2 h.

In situ Raman spectroscopy confirmed the existence of the MoVNbTe bulk M1 phase by the characteristic band at $\sim 870\text{ cm}^{-1}$. Sharp bands at $\sim 820\text{ cm}^{-1}$ and $\sim 992\text{ cm}^{-1}$ associated with small amounts of MoO_3 and V_2O_5 nanoparticles were also detected due to Raman's high sensitivity to crystalline constituents. This finding reveals the existence of other non-M1 phases, which require further purification to remove them from the sample.

Under dehydrated condition (10% O_2/Ar), *in situ* HS-LEIS depth profile suggested surface enrichment of Te and surface depletion of V and Mo/Nb in the outermost surface layer ($\sim 0.2\text{ nm}$). HS-LEIS also detected Co as a contaminant in this sample, but its contribution was insignificant and its signal weakened near the surface region threshold ($< 2\text{ nm}$). The *in situ* HS-LEIS findings demonstrate the complex nature of the surface region of the MoVNbTe M1 phase in an oxidative environment, enabling opportunities to conduct experiments in other environments (activation and reaction).

The present results highlight the complexity of the bulk MoVNbTe catalytic system. *In situ* and *operando* Raman spectroscopies are essential tools to study the contributions from different phases of the bulk MoVNbTe catalyst. *In situ* HS-LEIS is the most surface-sensitive technique to elucidate the intricacies of the surface regions under various environments.

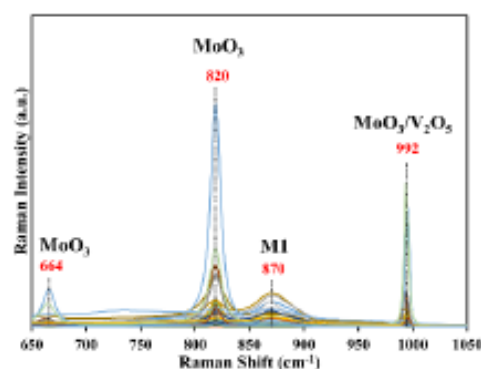


Figure 1. *In situ* Raman mapping (532nm) of the synthesized bulk M1 phase catalyst after dehydration at 400 °C under 10% O_2/Ar for 1 h. After the pretreatment, the temperature was cooled down to 120 °C and the spectra were acquired 15 minutes after reaching 120 °C.

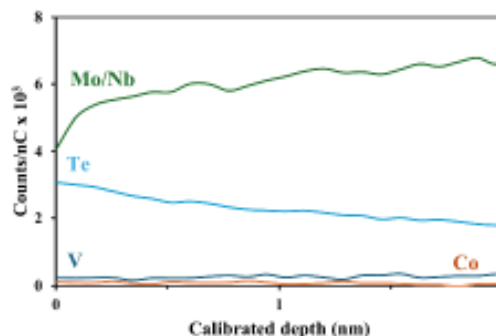


Figure 2. HS-LEIS depth profile spectra of M1 catalyst, acquired with 5 keV Ne^+ ions during simultaneous sputtering by 0.5 keV Ar^+ ions (sputter rate of $1.17 \times 10^{15}\text{ cm}^{-2}$, which corresponds to ~ 1 monolayer) after heating at 400 °C for 1 h at 12 mbar of 10% O_2/Ar . After the pretreatment, the chamber was pumped down and the catalyst was cooled to room temperature and transferred to the analysis chamber.

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Multiscale modelling framework to understand the effect of site heterogeneity on activity in paramagnetic single atom catalysts

Authors: Sanjana Srinivas, Dr. Stavros Caratzoulas, Prof. Dionisios Vlachos

Supported atomically dispersed metals and sub-nanometer metal clusters have been garnering attention on account of the high activity and selectivity they impart to reactions. Of particular interest is the dehydrogenation (DH) of small alkanes to alkenes, as the latter are used in the synthesis of several commodity chemicals and the recent shale gas boom in the US has made dehydrogenation economically viable. Common catalysts of the reaction are Pt-Sn alloys and alumina-supported chromium oxides, both of which have several shortcomings. The burgeoning activity in replacing supported Pt-group metal atom/sub-nanometer cluster catalysts with earth abundant metals is driven by the lower biological toxicity and cost of the latter. Experimental reports have demonstrated that highly dispersed Co(II) single sites on am-SiO₂, both as single sites and sub-nanometer CoO_x clusters, exhibit high activity and selectivity for alkenes (>95%)¹. We use DFT calculations and microkinetic modelling to explore the theoretical efficiencies due to spin-crossing kinetics shown by Co of varying nuclearity, for small alkane DH. We develop reaction mechanisms and rank them in kinetic importance using micro-kinetic analysis for single site and di-nuclear Co(II)/SiO₂ active sites. Our electronic structure calculations showed that the β-hydride elimination step is rate limiting, and is accelerated by 2 spin crossings on account of Co(II) being paramagnetic. We derived expressions to compute the rate of spin-crossing events in the limit of high-spin orbit coupling to integrate them into our microkinetic model. We use insights from the mechanistic model to study the effect of the amorphous silica support on the activity and to compute site-averaged activation energies. To this end, we sampled the site distribution from a representative am-SiO₂ slab and employed linear and non-linear feature selection methods, particularly the PLS (Partial Least Squares regression) and RIVI (Regression and Independence based Variable Importance) to identify reactivity relevant geometric features. We use these descriptors to construct a subset of single-site models from the distribution on which we evaluate the complete reaction mechanism and build surrogate models to compute the site-averaged apparent activation, which showed a close match with experiments. Our electronic structure analysis shows the planar sites to be more active than the tetrahedral sites on account of higher Lewis acidity. These insights guided our study on the Co/BEA catalyst (zeolitic support), where we show that support defects promote activity by increasing the planarity of the sites.

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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

Size and structure effects of carbon-supported ruthenium nanoparticles on waste polypropylene hydrogenolysis

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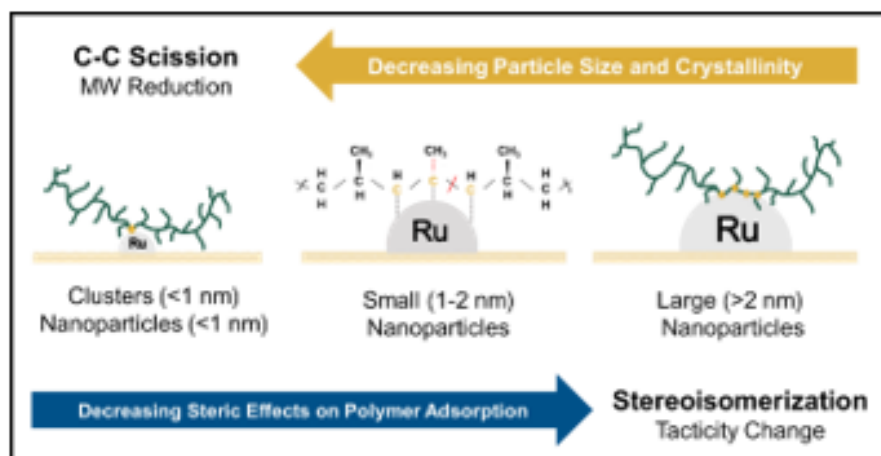
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Hydrogenolysis of plastic waste using Ru-based catalysts is promising for deconstructing polyolefins (PO) into lower molecular weight products. Yet, the effect of catalyst atomic structure and size on activity and product selectivity is poorly understood. Herein, we expose the effect of metal particle size and atomic structure on *isotactic*-polypropylene (*i*-PP) hydrogenolysis over Ru supported on carbon. Despite similar molecular weight distributions of solid and liquid products, their physical properties are distinct due to different chain regio-irregular CH₃ sequences of steric pentads containing *racemo* configurations. We propose that *i*-PP hydrogenolysis entails an interplay of C-C bond scission and stereoisomerization. The active site's local electronic environment and structure dictate the former, whereas polymer-catalyst surface interactions creating suitable polymer conformations control the latter. C-C scission and stereoisomerization are structure-sensitive. Small, disordered nanoclusters are effective in C-C bond scission, whereas larger metal nanoparticles promote stereoisomerization. We hypothesize that a heterogeneous distribution of metal active sites is essential for deconstruction and product (lubricant base oil) quality control.



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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

Hydrogenolysis of Poly(Ethylene-co-Vinyl Alcohol) and Related Polymer Blends over Ruthenium Heterogeneous Catalysts

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The hydrogenolysis of polymers is emerging as a promising approach to deconstruct plastic waste into valuable chemicals. Yet, the complexity of plastic waste, including multilayer packaging, is a significant barrier to handling realistic waste streams. Herein, we reveal fundamental insights into a new chemical route for transforming a previously unaddressed fraction of plastic waste – poly(ethylene-co-vinyl alcohol) (EVOH) and related polymer blends – into alkane products. We report that Ru/ZrO₂ is active for the concurrent hydrogenolysis, hydrogenation, and hydrodeoxygenation of EVOH and its thermal degradation products into alkanes (C1-C35) and water. Detailed reaction data, product analysis, and catalyst characterization reveal that the in-situ thermal degradation of EVOH forms aromatic intermediates that are detrimental to catalytic activity. Increased hydrogen pressure promotes hydrogenation of these aromatics, preventing catalyst deactivation and improving alkane product yields. Calculated apparent rates of C-C scission reveal that the hydrogenolysis of EVOH is slower than low-density polyethylene. We apply these findings to achieve hydrogenolysis of EVOH/polyethylene blends and elucidate the sensitivity of hydrogenolysis catalysts to such blends. Overall, we demonstrate progress towards efficient catalytic processes for the hydroconversion of waste multilayer film plastic packaging into valuable products.

2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

Microkinetic Modeling-driven Density Functional Theory Exploration of Ethylene Epoxidation on Partially Oxidized Silver Catalyst Surfaces

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Overcoming the selectivity challenge in the selective oxidation of ethylene has been an ongoing decades-long journey which has been partially addressed through the utilization of a slew of Ag catalyst promoters from across the periodic table. Despite their proven efficacy, there is a lack of systematic understanding in the promotion of the catalyst, and detailed effects of combinations of promoters are not well understood. Additionally, there has been a reinvigorated push towards a more careful study of the oxidic reconstruction of the Ag surface during the reaction. These concerns guide the three focal points of the current study: 1) Extension of the ethylene oxidation (EO) reaction mechanism to account for partially oxidized surfaces, 2) Analysis of promoter effects on specific elementary steps in the extended mechanism, and 3) ab-initio simulations supplement for atomic-level details in both unpromoted & promoted cases.

One pathway to oxidize C_2H_4 involves the surface lattice O atom of a partially oxidized Ag surface, through which an oxygen vacancy ($/O^*$) is generated. A subsequent adsorption of O_2 into the $/O^*$ site, forms a new oxygen species (O_2/O^*). An extended MKM is constructed to validate the possible kinetic relevance of these new intermediate species to the EO reaction system, featuring the currently-accepted common-intermediate mechanism, additional reaction pathways involving both the $/O^*$ and O_2/O^* species, and ethylene oxidation on Ag_6 patches. Here, the ' Ag_6 ' notation is used to represent the metallic portion of the p(4x4)-O-Ag(111) surface, which features 6 exposed Ag atoms. The current work explores the competition between these three pathways, along with the effects of common catalyst promoters on them.

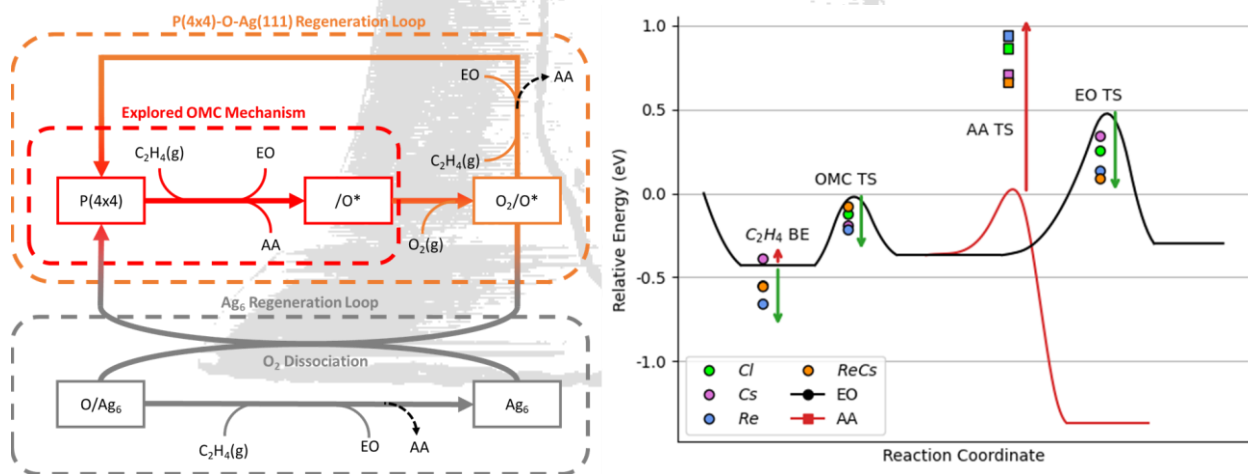


Figure 1: (a)LEFT: Schematic of extended EO reaction mechanism (b)RIGHT: Promoter effects on OMC-based pathway for ethylene oxidation.

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2024 CCP Poster Abstract

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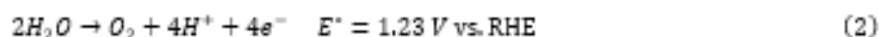
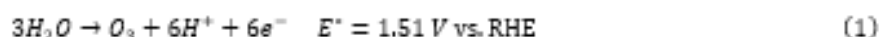
Consideration in poster competition: Yes

Insights into 6-e⁻ water oxidation on tin oxide-based catalyst

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Rapid global urbanization has created a pressing need for clean and accessible water supplies. Traditional water treatment methods are often limited by the increasing demands and complexities associated with human population growth.¹⁻³ A critical factor widening the gap between industrial progress and environmental sustainability is the inability of current technologies to effectively address the growing issue of water contamination.^{4,5} Advancements in electrochemical water treatment methods could provide a promising path towards bridging this gap and offer sustainable solutions to global water scarcity.



6-e⁻ EOP (eq-1) and 4-e⁻ OER (eq-2)

Among water treatment methods, the 6-electron electrochemical ozone production (EOP) reaction stands out. EOP offers a significant advantage because it allows for the on-site generation of ozone (O₃), a powerful oxidizer with a minimal environmental footprint compared to other disinfectants.⁶ However, EOP is plagued by selectivity issues due to the competing and more thermodynamically favored oxygen evolution reaction (OER). Nickel and antimony doped tin oxide (Ni/Sb-SnO₂) is one of the most selective catalysts for EOP under normal operating conditions.⁷⁻¹⁰

Interestingly, un-doped tin oxide (SnO₂) does not generate O₃.

This study delves into the mechanism of electrochemical ozone production (EOP) using Ni/Sb-SnO₂ catalysts. Our findings suggest that antimony (Sb) primarily enhances electrical conductivity, leading to better electrochemical performance. Conversely, nickel (Ni) dopants are linked to the catalytic activity for EOP.^{9,11-13} Additionally, we show that O₃ is generated from water and the metal oxide lattice. Leveraging this mechanistic understanding, we explored the possibility of substituting Ni with other transition metals like iron (Fe) and cobalt (Co). Similarly, we investigated replacing Sb with alternative n-type dopants such as tantalum (Ta) and tungsten (W). These explorations open doors for the development of a wider range of EOP catalysts. Additionally, we addressed methods for improving catalyst stability, a crucial aspect for practical applications. This work establishes a framework for designing improved EOP catalysts with superior performance. By elucidating the mechanism and exploring alternative dopants, we pave the way for significant advancements in electrochemical water treatment technology.

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2024 CCP Poster Abstract

Type: Postdoc

Consideration in poster competition: (No)

Identifying and Controlling Defects in Si-LTA Zeolite in Presence of F⁻

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Controlling defects in zeolites is crucial for tuning their adsorption and catalytic properties. However, as of today, precise control of number of defects in zeolites still remains a challenge. Herein, in order to address this problem an integrated zeolite synthesis, spectroscopy, and density functional theory study was performed. First, the limit of F⁻ as a charge-balancing agent that mitigates defects in siliceous zeolites was tested in the synthesis of siliceous zeolite LTA at 150 °C, which used 1,2-dimethyl-3-(4-methylbenzyl) imidazolium as the primary organic structure-directing agent (OSDA) and tetramethyl ammonium (TMA) as the secondary OSDA.¹ Then, it was discovered that by varying the amount of TMA in the synthesis gel, positive charges could be titrated into the resulting as-made Si-LTA, but the greater TMA concentration does not induce more F⁻ to enter into the zeolite to fulfill the charge balance.² ²⁹Si solid-state MAS NMR, Raman spectroscopy, and density functional theory³ all suggested that this system has surpassed its capacity for F⁻ to balance OSDA charge, and those additional positive charges are balanced by Si-O⁻ framework defects. The number of defects in the as-made Si-LTA can be precisely titrated by the amount of TMA in the zeolite structures. For the Si-LTA synthesized without TMA, framework defects formed in the early stage of crystal growth were found to heal during later crystallization, leading to defect-free Si-LTA. However, for the Si-LTA synthesized with TMA, the defects formed in early stages do not heal. A DFT thermodynamic analysis explains that crowding of Si-LTA pores by TMA impedes defect healing; this prediction is corroborated by synthesis experiments at an elevated temperature (170 °C). These results indicate that F⁻ can have a limited capacity to balance OSDA charge in zeolite synthesis, opening up a third route to zeolite synthesis intermediate between the fluoride and hydroxide routes.

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2024 CCP Poster Abstract

Type: Postdoc

Consideration in poster competition: No

Pt supported on W-modified alumina and zirconia for *n*-dodecane hydroisomerization reaction.

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The use of green fuels is an interesting alternative towards the transition to clean and renewable energy. These fuels can be obtained from biomass residues and drop-in in the current infrastructure, transport, and storage. The use of this green fuels reduces the CO₂ emissions and employes residues in a circular economy. Furthermore, the use of green fuels will play a critical role in the decarbonization of the economy in some niches which are difficult to be electrified in medium term. Among them, the use of sustainable aviation fuels is essential for the decarbonization of air transport. Hydrotreatment of vegetal oils (HVO) is an interesting process to reach this goal.

The present work is related with the second step of HVO process, which is the hydroisomerization (HISO) reaction. In the hydroisomerization step, the mixture of lineal hydrocarbons is converted in branched hydrocarbons and this new mixture has exceptional properties as fuel. Considering the results published in the literature for long chain paraffin hydroisomerization and our previous study on the influence of the reduction temperature and nature of the support on hydroisomerization, this work aims to study the influence of W loading, preparation method and nature of the support during the hydroisomerization of *n*-dodecane in order to improve the quality of linear alkane fuels obtained by HVO or Fischer-Tropsch synthesis, producing a suitable fuel.

Thus, in this study, the hydroisomerization of *n*-dodecane is mainly discussed with respect to the use of bifunctional catalysts with different W loadings (3-18 wt. % W) (**Figure 1**). Pt supported (0.3 wt.% Pt) on W-modified alumina and zirconia were used as the catalysts¹.

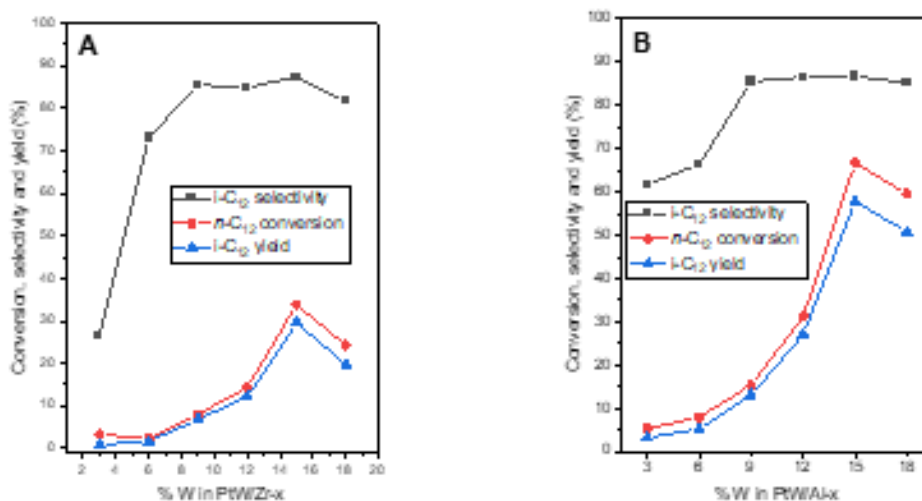


Figure 1. *n*-C₁₂ Conversion, *i*-C₁₂ selectivity and *i*-C₁₂ yield in the HISO of *n*-dodecane for (A) PtW/Zr-3 to 18 and (B) PtW/Al-3 to 18 (*T_r* = 350 °C, *P* = 2.0 MPa, liquid flow = 0.1 mL·min⁻¹, H₂ flow = 340 mL·min⁻¹).

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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

Transient Behavior of the Oxygen Reduction Reaction (ORR) for PEMFCs

Carolyn Spaulding,¹ **Ramchandra Gawas**², **Joshua Snyder**^{1,*} {11 pt. Arial, Bold}

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Cost is prohibitive for the expansion of fuel cell technology. For hydrogen fuel cells the catalyst is the source of this issue as platinum is used to improve the kinetics of the oxygen reduction reaction (ORR) at the cathode[1]. To explore avenues to further improve platinum's kinetics we have looked at the transient behavior of ORR. While transient current decay has been discussed regarding membrane electrode assemblies (MEAs), transients are rarely considered for rotating disk electrode (RDE) experiments[2]. We have found that Pt(111) transients in the ORR potential window last in the order of hundreds of seconds, notably longer than what is typically observed for polycrystalline electrodes. During these transients, initially slow current decay occurs until a critical point, where an inflection point indicates the transition to more rapid decay. We hypothesize that these dynamic transients are caused by 2D nucleation and growth of adsorbed spectator hydroxide islands. To test this 2D nucleation and growth theory we will examine the effect of potential and temperature, as well as the addition of hydrophobic cations. Studying this transient provides an avenue to better understand the roles of adsorbed hydroxide and interfacial water and inform the development of alternative surface interface modifiers.

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Non oxidative ethane dehydrogenation in carbon membrane reactor with dealuminated beta supported cobalt catalyst

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Ethylene (C₂H₄) is a crucial petrochemical feedstock with global annual production exceeding 180 million tons. Steam cracking is the leading technology for ethylene production, in which pyrolysis of ethane (C₂H₆) or naphtha takes place in a cracking furnace with process heat supplied by fossil fuel in burners. The process entails 10-35% ethylene selectivity with regular decoking (e.g., every 14-100 days for ethane and every 15-40 days for naphtha) which has the most energy consumption in the chemical industry (e.g., globally uses ~8% of the sector's total primary energy demand) and copious carbon dioxide (CO₂) emissions (i.e., 300 million tons per year). An attractive solution is ethylene production via decarbonized (i.e., green) ethane dehydrogenation (NDE), which is non-oxidative conversion of ethane (C₂H₆) to ethylene (C₂H₄) and hydrogen (H₂). The endothermic NDE is thermodynamically limited ($\Delta H = +137 \text{ kJ mol}^{-1}$). Unfortunately, high activity and selectivity to C₂H₄ is challenged by coke deposition from side reactions and thermal sintering of active species in the EDH catalysts. Supported platinum (Pt) and chromium oxide (Cr₂O₃) are the state-of-the-art NDE catalysts, among which the Pt-based catalysts have higher specific activity and longer stability than the Cr₂O₃-based ones. Although Pt-based NDE catalysts have shown great performances, the scarcity and cost of Pt material is a concern for the bulk chemical synthesis. Therefore, development of earth-abundant-based catalysts to minimize cost in ethylene production is needed. For this purpose, we synthesized dealuminated Beta zeolite supported Cobalt catalysts (Co/DeAl-BEA) for the NDE reactions. This catalyst has been coupled with an asymmetric carbon molecular sieve (CMS) hollow fiber membrane to develop first stable, active, selective, and low-CO₂-emissive on-purpose ethane dehydrogenation MR technology. The absence of Brønsted acidic centers in the siliceous zeolite eliminates acid-catalyzed side reactions such as cracking and oligomerization that lead to low ethylene selectivity and catalyst deactivation due to coke deposition. The small metal clusters are effective for ethane activation, and suppression of side reactions involving hydrogenolysis (C-C cleavage) and/or coke formation (C-C coupling) occurred on geometrically complex and large ensembles of metal atoms. For the first time, asymmetric CMS hollow fine fiber (300 mm outer diameter) membranes are used for MRs. Their thin separation layer allows rapid H₂ removal from the reaction mixture, thereby upshifting the reaction equilibrium to reach high conversions at low reaction temperatures. In comparison to catalysts and membranes that were used in NDE MRs in literature, the CMS MR reaches up to 2.5 times as high as ethane equilibrium conversion and achieves a record-low deactivation rate and excellent long-term durability. The small diameter of the CMS hollow fibers gives significantly higher packing density and flexibility than conventional tubular or monolith inorganic membranes used for NDE MRs and therefore are more suitable for large-scale applications.

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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

Synthesis of renewable insecticides possessing tailored functional groups

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With the continuous increase in food production to support the growing population, ensuring agricultural sustainability using crop-protecting agents, such as pesticides, is vital. Conventional pesticides benefit agricultural systems but threaten biodiversity and the ecosystem. They are derived from fossil fuels via unsustainable manufacturing practices. Here, we synthesize new amide-based insecticidal active ingredients from biomass-derived monomers, furfural and vanillin, via reductive amination followed by carbonylation, scoring 8 out of 12 green chemistry principles. Insecticidal activity evaluations against a known pest demonstrate competitive potency. Ecotoxicity predictions showcase lower toxicity levels and bioavailability toward non-target aquatic and terrestrial species. These biomass-derived insecticides are economically promising and could promote the preservation of biodiversity.

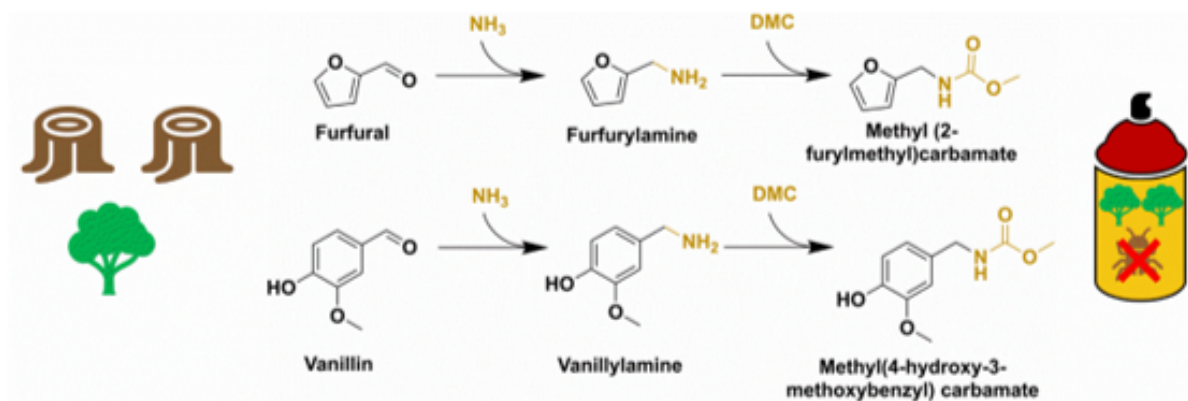


Fig 1. A two-step synthetic pathway to biobased insecticides, FC and VC, from furfural and vanillin. Reductive amination was conducted over an Rh/Al₂O₃ catalyst in liquid ammonia and carbonylation over a La(Otf)₃ catalyst with DMC as the solvent and reactant.



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2024 CCP Poster Abstract

Type: Graduate

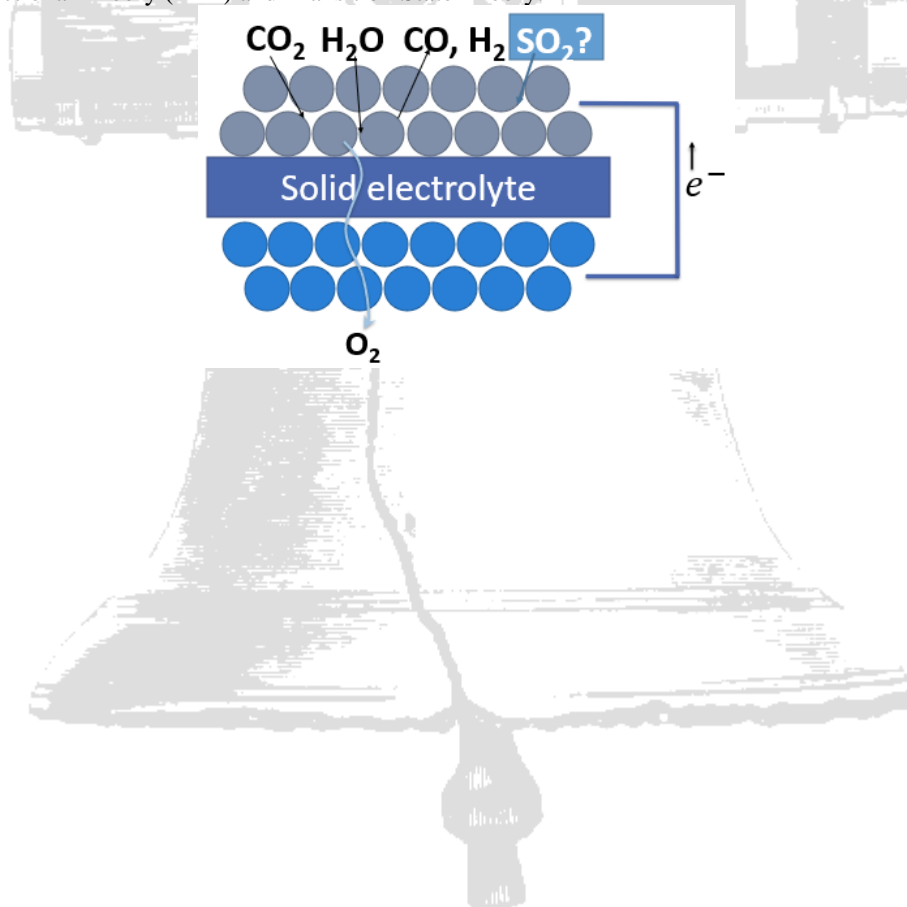
Consideration in poster competition: Yes

Thermodynamic and Kinetic Investigation of S Impurities in Solid Oxide Electrolysis Cell Feed Flow

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¹ *Chemical Engineering, Lehigh University, 27 Memorial Drive West, Bethlehem, PA 18015*

Solid Oxide Electrolysis Cells (SOECs) have become a system of interest due their efficiency of splitting H₂O and reducing CO₂ into useful products. Catalytic activity on Ni/YSZ cathodes can be hampered by the presence of S constituents in feed flows. Here, we seek to analyze the surface reactions which produce desired, useful, products and undesired products on Ni(111), Ytria-stabilized Zirconia (YSZ), and Ni/YSZ facets. The reduction of H₂O, the reduction of CO₂, and the dissociation of S containing species under reaction conditions (~1070K) are investigated to quantify the energetics of these reactions and their intermediates. Using these findings a microkinetic model can be created to understand the effects of S and S containing species on cathode reactions using a combination of Density Functional Theory (DFT) and Transition State Theory.



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2024 CCP Poster Abstract

Type: Postdoc

Consideration in poster competition: No

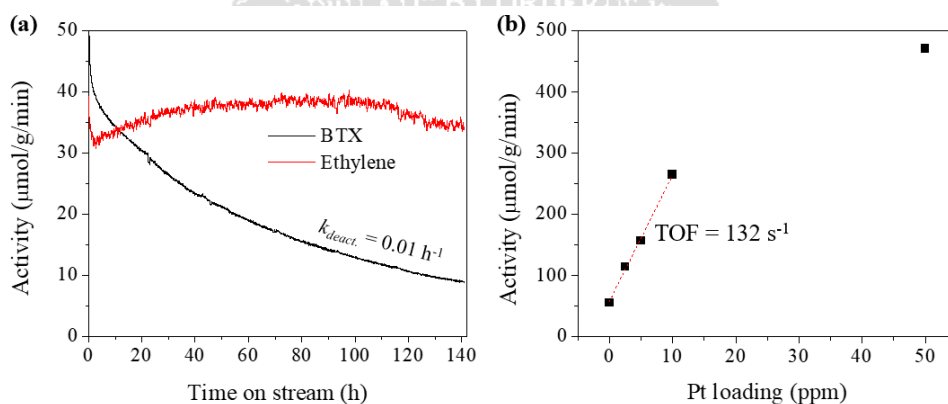
Light Alkane Dehydroaromatization over Pt-Zn/HZSM-5 Catalyst with Ultralow Pt Loading

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Minimizing Pt loading in dehydroaromatization (DHA) catalysts is critical to the cost-efficient transformation of abundant light alkanes for energy and chemical production. This work investigated the bimetallic Pt-Zn/HZSM-5 catalysts with ultralow Pt loading of 0.0001-0.05 wt% (1-500 ppm) for both ethane and propane DHA. For propane DHA, the results show that the bimetallic Pt-Zn/HZSM-5 catalysts with Pt loading of 50-500 ppm are significantly more active and/or stable than the monometallic counterparts. Such enhancement becomes less significant when decreasing Pt loading to ≤ 10 ppm. For ethane DHA, the mass-specific activity of the Pt-Zn/HZSM-5 catalysts decreases linearly with decreasing Pt loading from 10 to 2.5 ppm, indicating a constant molar-specific activity (TOF) of up to $132 \text{ s}^{-1} \cdot (\text{mol}_{\text{ethane}}/\text{mol}_{\text{Pt}})$.¹ This breakthrough in higher activity and stability during the DHA process is achieved owing to the formation of $[\text{Pt}_1\text{-Zn}_n]^{\delta+}$ ensemble in the micropores of ZSM-5 zeolite.²



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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

Ethylene Dimerization to n-butene with Nickel Sulfate on Zirconia: Investigation of the Molecular Structure and Activity of Surface Nickel and Sulfate Species

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Due to the growing abundance of shale gas, industry has shifted to processing lighter hydrocarbon feedstocks which has contributed to a decrease in the production of butene.¹ This has stimulated interest in the dimerization of shale gas derived ethylene to butene, where two ethylene molecules are exothermically dimerized to 1-butene which is then isomerized to form 2-butene. In industry, ethylene dimerization is typically carried out in homogeneous systems which can face several operational and environmental challenges.² Consequently, there is interest in developing heterogeneous ethylene dimerization catalysts with comparable performance to their homogeneous counterparts. Ethylene dimerization can be carried out heterogeneously on several metal oxide promoted solid acid catalysts, with Ni-based catalysts typically reported to have the highest activity and selectivity to n-butene due to nickel's ability to prevent further oligomerization of butene to higher chain hydrocarbons.² Nickel oxide promoted sulfated zirconia is a promising heterogeneous ethylene dimerization catalyst due to its high activity and selectivity for 2-butene under mild reaction conditions (20 °C) as well as its high surface acidity and well dispersed nickel phase.³ However, little is known about the nature of the surface sulfate and nickel sites as well as the structure-activity relationships that are responsible for ethylene dimerization activity. To address these gaps in the literature, this work focuses on determining the nature of the surface structures and the interactions between the nickel and sulfate species that increase the dimerization activity and butene selectivity. Several characterization techniques (*in situ* IR, Raman, and UV-vis spectroscopy, ethylene-TPSR, *in-situ* XAS and HS-LEIS) were applied under different environments. *In-situ* IR and Raman spectra collected under dehydrated conditions indicated the presence of O=S(O-Zr)₃ surface sulfate species which preferentially anchor to terminal hydroxyl groups on the zirconia support at low sulfate loadings. At high sulfate loadings, a second surface sulfate species anchors to the tri-bridging hydroxyl groups. *In-situ* XAS and UV-vis spectra collected under dehydrated conditions indicated that nickel is present as Ni²⁺O₆ in a distorted octahedral geometry while spectra collected during ethylene dimerization indicated that these sites are stable during reaction. Ethylene-TPSR also demonstrated that both nickel and sulfate are necessary for ethylene dimerization activity. IR spectra of adsorbed NH₃ also revealed that the order of impregnation of nickel and sulfate alters the Bronsted to Lewis acid ratio and the temperature for butene formation. Ethylene-TPSR and IR spectra of adsorbed NH₃ also demonstrated that the activity is closely linked to the Bronsted to Lewis acid ratio, where a lower Bronsted to Lewis ratio results in higher ethylene dimerization activity and a decreased production of propylene.

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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

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

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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 CO₂ emissions in 2021[1] and it is important that chemical manufacturing processes are electrified. As compared to conventional thermochemical reactors, joule-heated reactors (JHR) provide local uniform heating, which maximizes 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 [2]. While JHR has demonstrated improved reaction yields and efficiencies, many technical aspects remain as challenges, including scalability, temperature control, and mass and heat transfer.

This work describes the development of a JHR that uses 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). A highly active Mn-containing ZSM-5 zeolite catalyst has been chosen for this reaction [3]. Using a wash-coated catalytic structure, we demonstrate how integrated electrical heating can improve thermal conductivity across the catalyst film. Computational Fluid Dynamics (CFD) results revealed that porcupine coil geometry produces turbulent-like flow conditions, alleviating mass-transfer limitations. The principles developed here could be applied to other heterogeneous endothermic reactions, such as methane dry reforming.

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2024 CCP Poster Abstract

Type: (Graduate)

Consideration in poster competition: (Yes)

Light Olefin Production via Catalytic, Melt, Electrified Pyrolysis of Polyethylene

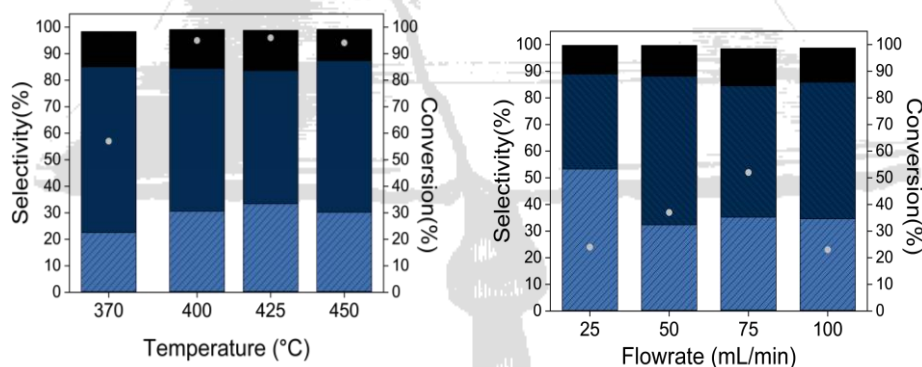
Jacqueline Ngu^{1,2}, Esun Selvam^{1,2}, Arun Sundaramoorthy², Pavel Kots¹, Dionisios G. Vlachos^{1,2*}

¹ Center for Plastics Innovation, University of Delaware, Newark, DE,

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Plastic waste has become a huge burden on our environment, with less than 10% being recycled and the remaining incinerated or thrown into landfills(1). Most recycled plastic is mechanically recycled. This process cannot handle mixed plastics. Catalytic pyrolysis is an appealing method for plastic deconstruction as it can be feedstock agnostic. However, converting plastic into light olefins (C₂-C₄) is challenging, sometimes requiring a two-step process(2).

Here, we introduce an electrified pyrolysis slurry reactor operat at low temperatures to produce a narrow distribution of light olefins at high yield. Increasing the operating temperature increases the selectivity of light olefins (C₂-C₄). We demonstrate an optimum flow rate to tune product distributions. We also explore reactor optimization via process intensification to further control light olefin yields. Increasing the temperature increases selectivity toward light olefins. At 370 °C and 100 mL/min of N₂, the LDPE conversion was 58% with 22% and ~100% selectivity to C₂-C₄ and C₂-C₁₂ olefins, respectively. At 400 °C, the overall yield to olefins of ≤C₁₂ is a remarkable ≤ 90+%. This slate of products is very valuable because light olefins are used for various products like lubricant base oils, cosmetics, etc. The effect of N₂ flowrate on light olefin selectivity at 400 °C at low conversion is shown in Figure 1b. Decreasing the flowrate increases the residence times of the heavier products in the reaction zone, leading to more cracking and a higher selectivity toward lighter products. At low flowrates, conversions are low due to ineffective mixing, causing inefficient heat and mass transfer. Hence, an optimal flowrate exists for light olefin production and high conversion. To tune the product distribution, we introduce an intensified hybrid setup to recirculate heavy products and further improve the yield to light olefins. To tune the product distribution, we introduce an intensified hybrid setup to recirculate heavy products and further. A condenser enables heavier products to condense back into the reaction zone to react further. We have found that once the products are light enough, such that they cannot be further condensed, they exit the reaction zone. We will also present results on the effect of acid catalyst.



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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

Elucidating the essential role of hydrogen bonding and direct H-transfer in transfer hydrogenation on transition metal catalysts.

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Hydrogenation and hydrogenolysis, two important catalytic chemistries employed in the chemical industry, are typically carried out at high pressure using gaseous molecular hydrogen as the hydrogen source. Catalytic transfer hydrogenation (CTH), is an alternative process that employs organic hydrogen donors such as alcohols and formic acid (FA) as the hydrogen source, offering a safer and milder option for small-scale and distributed processing, such as for biomass conversion. The underlying mechanism of such reactions is not fully understood. In particular, CTH may occur through an indirect “metal hydride route” where the donor dehydrogenates on a metal surface and the surface hydrogen atoms get picked by the acceptor molecule; alternatively, donors may directly transfer hydrogen to the acceptor, especially on Lewis acid catalysts.

In this presentation, we use FA as a representative hydrogen donor and formaldehyde as a representative hydrogen acceptor to elucidate how hydrogen bonding affects the reaction mechanism for CTH of carbonyl bonds on Cu(111). Using dispersion-corrected periodic density functional theory (DFT, PBE-dDSC) calculations and coverage-cognizant mean-field microkinetic modeling, we develop a mechanistic model of this CTH system. We show that direct hydrogen atom transfer between a donor and acceptor is kinetically feasible on transition metal catalysts especially if the donor and the acceptor can interact via hydrogen bonding. Such direct transfer significantly enhances the rate of catalytic hydrogenation by 3 times while using a hydrogen donor relative to using molecular hydrogen as the hydrogen source. This work, thus, indicates the potential tuning of activity and selectivity of hydrogenation through judicious choice of hydrogen donors.

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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: No

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

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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.¹ 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.¹ 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.² 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 H_2SO_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 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.² 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 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.³ However, high yields of such products are difficult to achieve due to their high reactivity.⁴ 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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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

Hydrodeoxygenation of *m*-Cresol over WO_x-Pt/SBA-15 Using Alkanes as Hydrogen Carriers

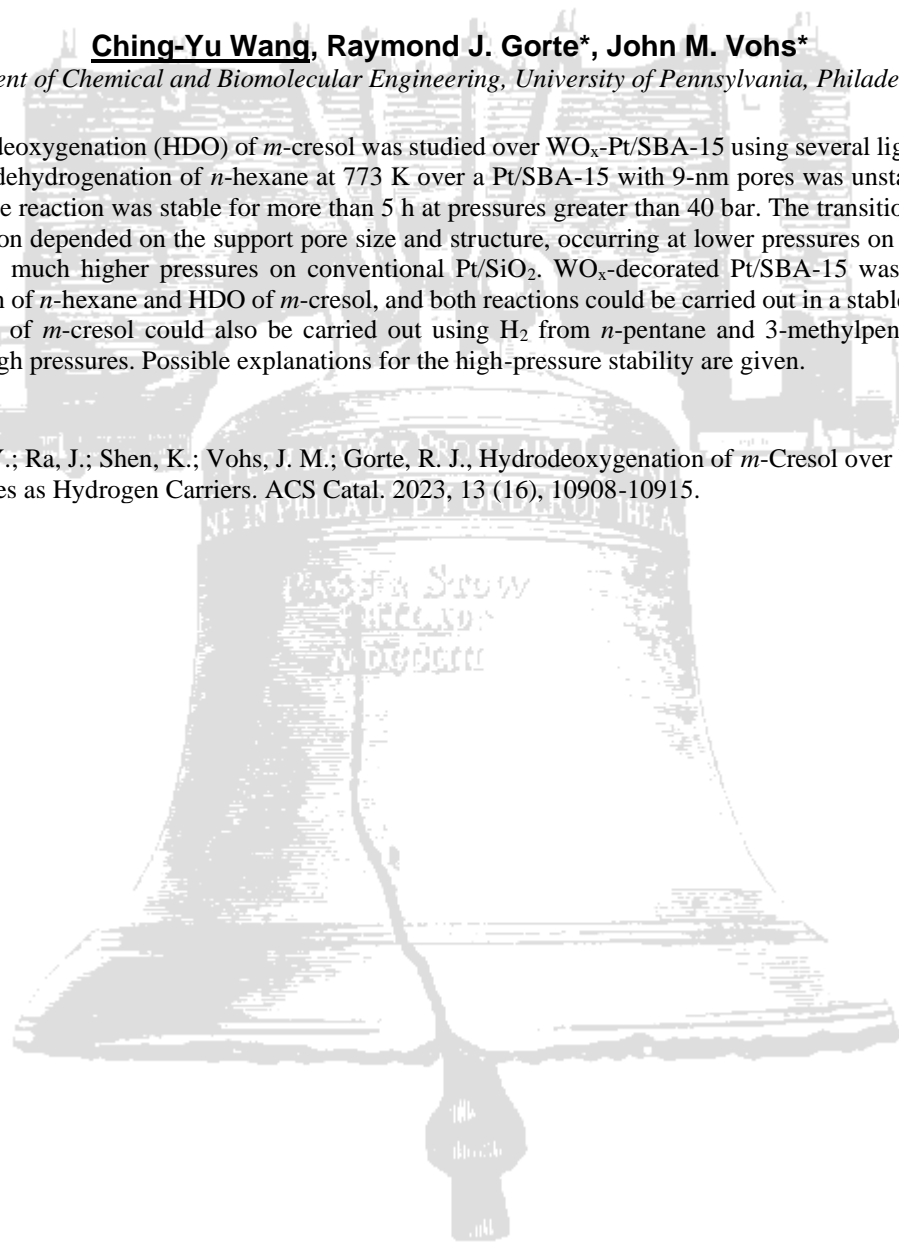
Ching-Yu Wang, Raymond J. Gorte*, John M. Vohs*

Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA

Hydrodeoxygenation (HDO) of *m*-cresol was studied over WO_x-Pt/SBA-15 using several light alkanes as H₂ 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/SiO₂. WO_x-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 H₂ from *n*-pentane and 3-methylpentane over WO_x-Pt/SBA-15 at high pressures. Possible explanations for the high-pressure stability are given.

References

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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: (No)

Comparison of batch reactor and flow reactor for Hydrogenolysis reaction of long-chain alkane

Zhuoming Feng,¹ Siwon Lee, John M. Vohs^{1,*}, Raymond J. Gorte

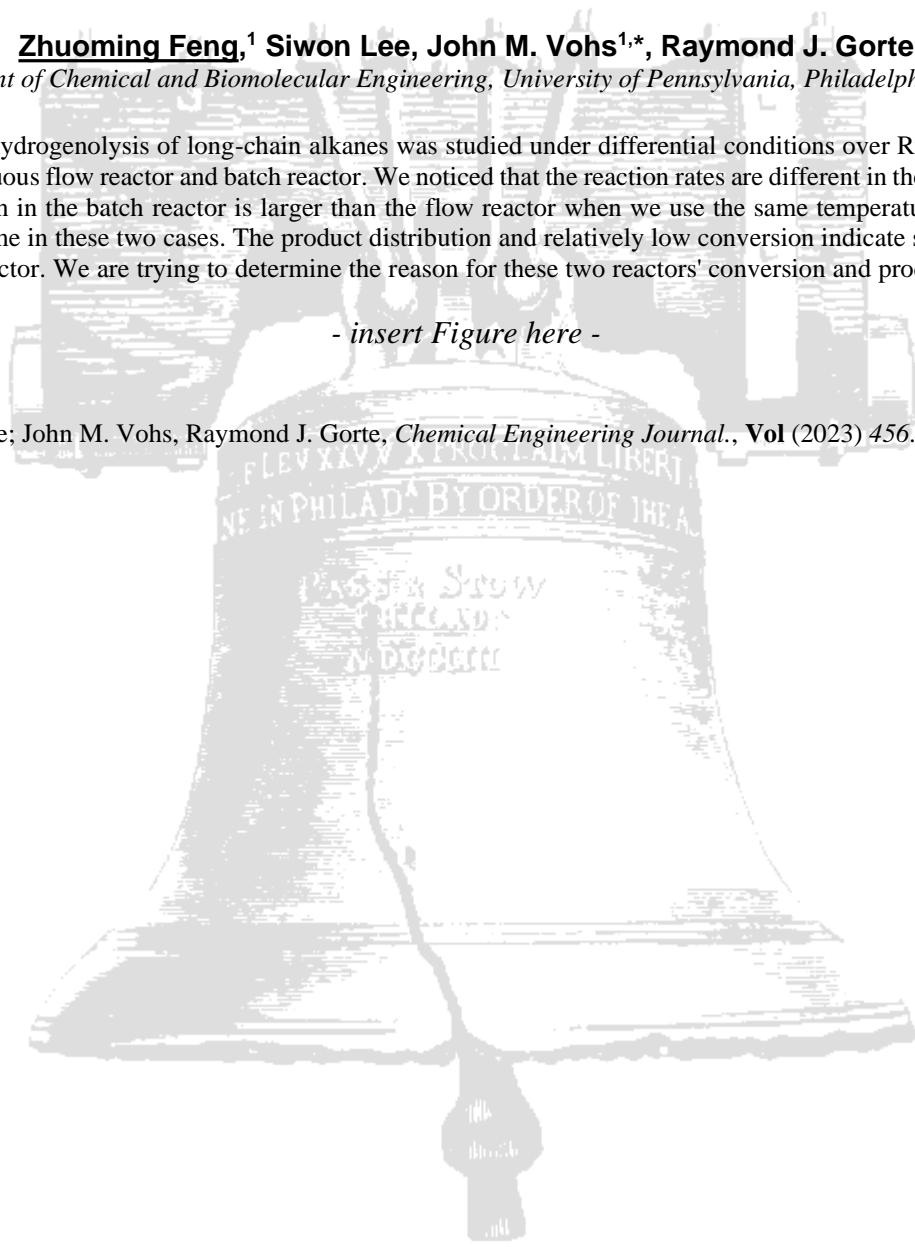
¹ *Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104*

The hydrogenolysis of long-chain alkanes was studied under differential conditions over Ru/SiO₂ catalysts using a continuous flow reactor and batch reactor. We noticed that the reaction rates are different in these two reactors. The conversion in the batch reactor is larger than the flow reactor when we use the same temperature and keep the WHSV the same in these two cases. The product distribution and relatively low conversion indicate some limitations in the flow reactor. We are trying to determine the reason for these two reactors' conversion and product distribution differences.

- insert Figure here -

References

[1] Siwon Lee; John M. Vohs, Raymond J. Gorte, *Chemical Engineering Journal.*, Vol (2023) 456.



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2024 CCP Poster Abstract

Type: Graduate

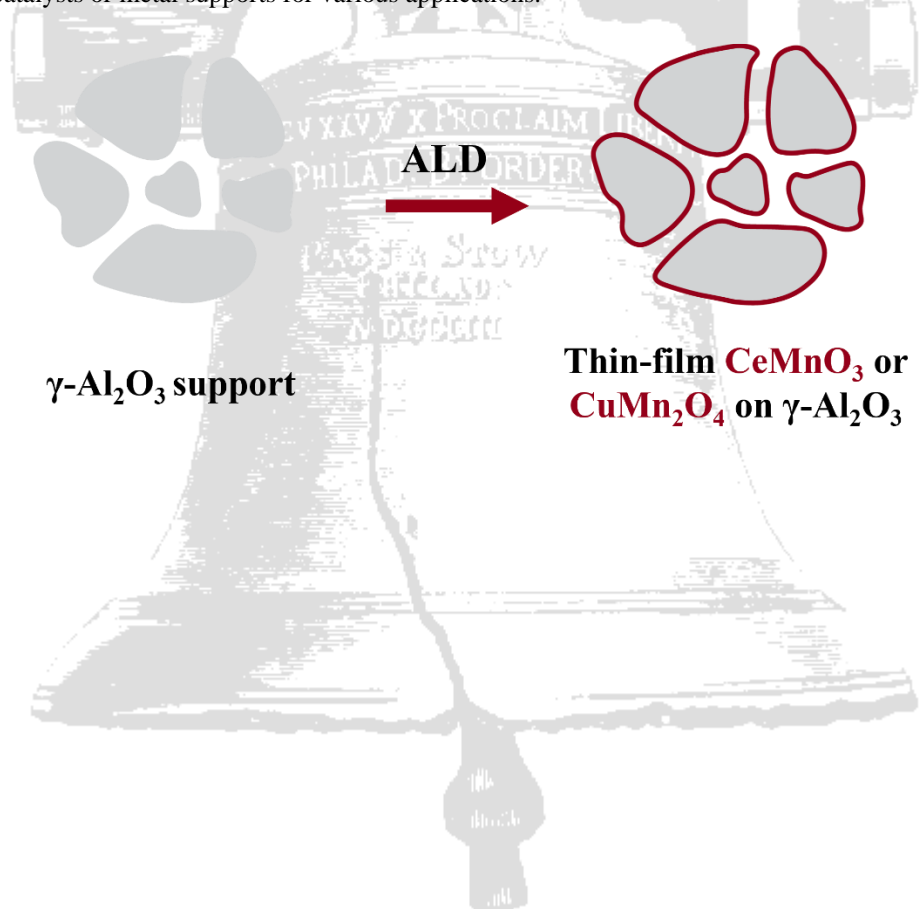
Consideration in poster competition: Yes

ALD-prepared thin-film CeMnO_3 and CuMn_2O_4

Kai Shen, R. Gorte, J. Vohs*

Department of CBE, University of Pennsylvania, 220 S 33rd St, Philadelphia, 19104

Thin films of CeMnO_3 and CuMn_2O_4 were deposited by atomic layer deposition (ALD) on high-surface-area $\gamma\text{-Al}_2\text{O}_3$. The films were 0.5 to 2 nm thick, uniformly covering the $\gamma\text{-Al}_2\text{O}_3$ surface, and the corresponding weight loadings of these mixed oxides were 25% to 60%. The CeMnO_3 films can reversibly transition between an oxidized $\text{CeMnO}_{3.5}$ and a reduced CeMnO_3 at 1073 K, with Ce cations swinging between +4 and +3 oxidation states while most Mn maintained +3 oxidation states. In the CuMn_2O_4 films, most Cu and Mn cations are locked in +2 and +3 oxidation states, respectively, under reduction at 973 K. The CO oxidation rates on thin-film CuMn_2O_4 are closely associated with its surface termination. The redox properties and catalytic activities of both materials make them promising candidates as catalysts or metal supports for various applications.



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2024 CCP Poster Abstract

Type: Graduate

Consideration in poster competition: Yes

Zinc-Imidazolate Films as an All-Dry Resist Technology

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The drive to further decrease microelectronic device dimensions has led to the expansion of extreme ultraviolet lithography (EUVL) and EBL processes which require next generation metal organic resist materials to maximize feature resolution and improve product throughput. Conventional solvent-based resist processes utilize organic resists which have several limitations such as typically requiring time consuming baking steps, poor EUV sensitivity, and the generation of organic solvent waste. Furthermore, mechanical stress induced by solution-based development can lead to pattern collapse, limiting the maximum possible density of patterned features. The process described herein (shown schematically in Figure 1) avoids the use of, and some issues associated with, organic solvents by depositing films using ALD/MLD to produce amorphous films from 2-methylimidazole and diethylzinc that are chemically similar to zeolitic imidazolate framework-8 (ZIF-8), a type of metal-organic framework commonly used in for applications in catalysis and gas separations. Following electron irradiation, areas of the film which were exposed to the electrons maintain the C:N:Zn ratio of the original film, but are slightly densified and are rendered resistant to etching by vapor phase 1,1,1,5,5,5-hexafluoroacetylacetone (hfacH). In contrast, unexposed areas can be readily removed by exposure to hfacH vapor at 120 °C, demonstrating the efficacy of aZnMIm films as a negative tone electron beam resist. The low temperature thermal etching conditions used in this study are notable in the context of lithography processes, as the typical requirement of high temperatures in other dry etching processes can be difficult to implement in nanofabrication processes. The use of a molecular etchant (hfacH) also avoids limitations of plasma-based processes, which require the photoresist to have high resistance to plasma etchants. This methodology produces a solvent free, EUV compatible process that allows for cost-effective and high-resolution resist development with critical dimensions down to 22 nm/30 nm pitch on SiN_x substrates and 29 nm/40 nm pitch on Si wafer substrates.

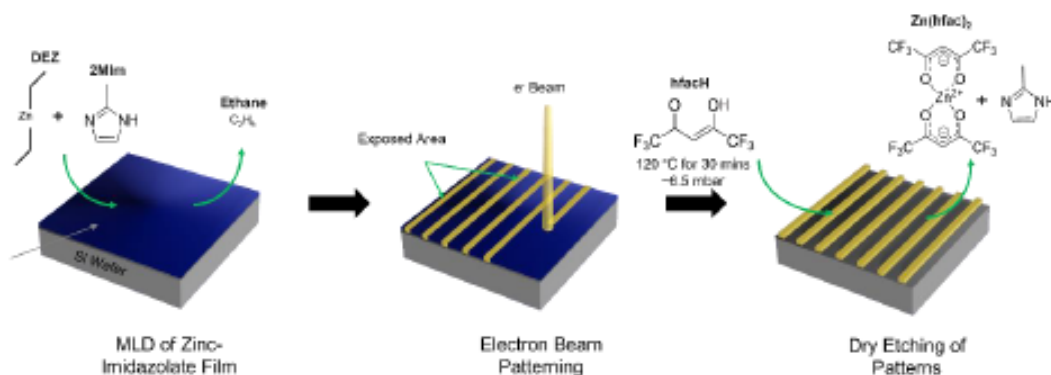


Figure 1. Overall process schematic of film deposition, patterning, and dry etching to create an all-vapor phase resist.

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2024 CCP Poster Abstract

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Consideration in poster competition: Yes

Growth of Conformal Carbon-MgO Composite via Magnesiothermic Reduction of Carbon Dioxide

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Carbon capture, sequestration, and utilization (CCSU) are crucial for achieving a sustainable carbon future. While current methods primarily involve geological storage of carbon dioxide (CO₂), there's immense potential in engineering high-value carbon materials from CO₂, termed "negative-carbon carbon" (NCC) materials. Previous research has explored metallothermic reduction reactions (MRRs) of CO₂, particularly the magnesiothermic reduction (MR) using Mg, yielding carbon and magnesium oxide (C-MgO) products with diverse morphologies. Initially investigated for space travel fuel in CO₂-rich environments, MR reactions have been studied for various applications including producing nanostructured carbon for supercapacitors. This study focuses on fabricating bulk carbon composites within porous monolithic carbon foam, necessitating control over reaction conditions for uniform deposition within the pores. A custom reactor was built utilizing radio frequency heating and with a control system to program reaction sequences. This research aims to advance the MR of CO₂ for CCSU, particularly for producing bulk C-MgO composite materials.

