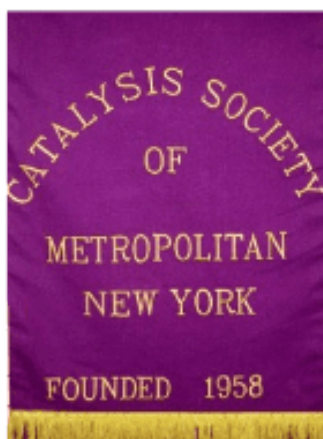


The Catalysis Society of Metropolitan New York 2025 Annual Spring Symposium



Lehigh University
Ben Franklin Conference Facility
Wednesday March 12th, 2025

Acknowledgements

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2025 Annual Symposium

The Catalysis Society of Metropolitan New York
 Wednesday, March 12th, 2025

8:00 AM	Registration (Coffee/Tea available)
8:45 AM	Opening Remarks Dr. Boris Sheludko <i>Chair</i>
Session I <i>Chair: Michele Sarazen</i>	
8:50 AM	Keynote Address – Catalytic Conversion of Polyolefins to Fuels, Lubricants, and Olefins Dr. Dion Vlachos <i>University of Delaware</i>
9:40 AM	Cation Solvation Effects for Zeolite Catalyzed Oxidation Reactions Dr. Chris Paolucci <i>University of Virginia</i>
10:10 AM	Catalytic approaches to selectively breaking C-F bonds: lessons learned from breaking C-O bonds Dr. Rachel Austin <i>Barnard College</i>
10:40 AM	Coffee Break
Session II <i>Chair: Kaitlyn Lawrence</i>	
11:00 AM	Leveraging hydrogen bonds in catalyst design Dr. Marcella Lusardi <i>Princeton University</i>
11:30 AM	Cobalt Catalyst on Siliceous Zeolite for Non-Oxidative Ethane Dehydrogenation Dr. Dongxia Liu <i>University of Delaware</i>
12:00 PM	Achieving a 100% Drop-in Sustainable Aviation Fuel: Technological Pathways and Challenges Dr. Mahluli Moyo <i>Air Company</i>
12:30 PM	Lunch Break
1:20 PM	Poster Session
Session III <i>Marco Castaldi</i>	
2:50 PM	Development of Electrocatalysts for the Conversion of CO₂ to High-Value Chemicals Dr. Andrey Smirnov <i>Rutgers University</i>

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3:20 PM	Automated reasoning in chemical science and engineering Dr. Tyler Josephson <i>University of Maryland, Baltimore County</i>
3:50 PM	Designing Heterogeneous Catalysts with Free-Atom-Like Electronic States Dr. Andrew Rosen <i>Princeton University</i>
4:20 PM	Understanding and Controlling Reaction Pathways in Organic Electrosynthesis Dr. Miguel Modestino <i>New York University</i>
4:50 PM	Poster Awards
5:00 PM	Adjourn

Poster Presentations

#	Presenter	Abstract Title	Affiliation
1	Aojie Li	Elucidating the essential role of hydrogen bonding and direct H-transfer in transfer hydrogenation of biomass oxygenates on transition metal catalysts	Lehigh University
2	Bohyeon Kim	Designing bimetallic heterogeneous catalysis by electrochemical polarization	Lehigh University
3	Damilola Awotoye	Molecular Structure of Na-WO _x /SiO ₂ Catalysts: Dispersed vs. Crystalline Phases for Selective Methane Activation in Oxidative Coupling of Methane (OCM)	Lehigh University
4	Dang Nguyen	Oxidative Dehydrogenation of Ethane (ODHE) to Ethylene by the Bulk MoVNbTe (M1 Phase) Mixed Oxide Catalyst: Surface and Bulk Properties	Lehigh University
5	Dominic Caracciolo	Multimetallic Nanoalloy Catalysts in Proton Exchange Membrane Fuel Cells	Binghamton University
6	Eli Ream	Tuning Molecular Structure and Reaction Mechanism of Olefin Metathesis by Model Bilayered Supported MoO _x /AlO _x /SiO ₂ Catalyst	Lehigh University
7	Emmanuel Aransiola	Elucidating the Structural and Electronic Effects of Ni and Mn Cationic Impurities on CoOOH for Efficient Benzyl Alcohol Electrooxidation	Lehigh University
8	Erin Sobchinsky	Ethylene Dimerization to n-butene with Nickel Sulfate on Zirconia: Investigation of the Molecular Structure and Activity of Surface Nickel and Sulfate Species	Lehigh University
9	Henry Jin	Selective Electroreduction of CO ₂ to C ₄ Products on Molybdenum Phosphide through a Novel Dimerization Mechanism	Rutgers University
10	Johari Dramiga	DFT-derived Insights of CO ₂ Reduction in Solid Oxide Electrolysis Cells and Inhibition by S-containing Molecules	Lehigh University
11	John Sackey	Understanding the mechanisms of catalyst deactivation during hydrothermal gasification	Syracuse University
12	Joseph I. Thompson	DFT and Microkinetic Study of the Mechanism of Propene Metathesis on MoO _x /SiO ₂ and MoO _x /(AlO _y -SiO ₂) Catalysts	Lehigh University
13	Joshua Miller	Insights into MOF Stability, Coordination Environment, and Active Site Structure during Oxidative and Non-Oxidative Transformations	Princeton University
14	Kaitlyn Lawrence	Efficacy of Waste-to-Energy Ash in NO _x Abatement	The City College of New York
15	Meheryar R. Kasad	Exploring the Electrocatalytic Dehydrogenation of Ethanol for Liquid Organic Hydrogen Carrier Applications	The City College of New York
16	Merry Madiou	Synthesis and Characterization of Intermetallic and Random Alloy Catalysts for CO Oxidation	Binghamton University
17	Moses Chilunda	The role of potential in enhancing the electrocatalytic dehydrogenation of benzyl alcohol	City College of New York
18	Neelesh Kumar	Surface/Bulk Chemistry of La-based perovskite oxides	Lehigh University

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19	Nicholas Scrofano	Styrene to Benzaldehyde with an oxidant, a study in enzyme and heterogeneous catalysis	Lehigh University
20	Olivia De Luca	Breaking the C-X Bond: A Kinetic Analysis of the Room Temperature Dehalogenation of Halobenzenes Catalyzed by Rh/Al ₂ O ₃	Barnard College of Columbia University
21	Rehan Ali Qureshi	Transition Metal Phosphates as Next-Generation Electrocatalysts for Overall Water Splitting	New Jersey Institute of Technology
22	Seyed Danial Mousavi	NiCo@Pt Core-Shell Catalysts: Synthesis and Characterization Using Hydrogen Temperature-Programmed Reduction	Binghamton University
23	Shubham Gupta	Selective CO ₂ electro-reduction to acetate on nickel arsenides	Rutgers, The State University of New Jersey
24	Sonia Arumuganainar	Design of ordered aluminosilicates for dielectric barrier discharge-assisted catalysis of ammonia reactions	Princeton University
25	Yaqin Tang	Kinetic Analysis of CO Methanation Over PtSn/ γ -Al ₂ O ₃ Catalysts	Syracuse University
26	Zeqi Li	Characterization of structure and composition in membrane electrode assembly with nanoalloy catalysts ultralow platinum loading in correlation with PEM fuel cell performance	Binghamton University

Oral Presentations

**Keynote Address:
Catalytic Conversion of Polyolefins to Fuels, Lubricants, and Olefins**

Dion Vlachos

Department of Chemical and Biomolecular Engineering, Catalysis Center for Energy Innovation, RAPID Manufacturing Institute, Delaware Energy Institute, University of Delaware, Newark, DE 19716

This talk will provide an overview of the different approaches for converting polyolefins to various products, including fuels, lubricants, and small olefins. It will also provide mechanistic insights into methane formation pathways and ways to minimize its formation. The talk will discuss the need for earth-abundant catalysis, additives, mixed plastics, and the role of heat transfer in product distribution. It will introduce novel reactors, and electrification to advance the catalytic conversion.

Cation Solvation Effects for Zeolite Catalyzed Oxidation Reactions

Christopher Paolucci

Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22903

Ion exchanged zeolites are used in catalytic applications ranging from hydrocarbon upgrading to emissions abatement. Under some conditions, ions can be liberated from the zeolite framework and mobilized by solvent molecules, coupling attractive features of homogeneous and heterogeneous catalysis. Here, I discuss our recent results for metal-exchanged zeolite catalyzed Wacker oxidation and oxidative activation of ethane where we show that metal ions are solvated under reaction conditions, and solvation impacts the reaction mechanism.

The first example, Wacker oxidation, is a well-known redox process involving Cu and Pd ions where the formation of acetaldehyde is speculated to occur on Pd²⁺ ions. While the homogeneous counterpart proceeds by having Cl⁻ stabilize the metal ions, the anionic AlO₂⁻ sites of metal-exchanged zeolites can charge compensate Pd, eliminating the need for Cl⁻. A major challenge with the heterogeneous catalyst is deactivation due to coking and sintering. We show that the Pd ions are solvated by H₂O and NH₃ under reaction conditions, and relative fractions of these two molecules compete with C₂H₄ adsorption, consequently suppressing oligomerization and coke formation.

Similarly, NH₃-solvated Co ions supported on MFI zeolites catalyze oxidative activation of ethane. Rates measured by the Flaherty group at different characteristic separations between cobalt ions demonstrate reactions among C₂H₆ and O₂ occur at isolated mononuclear cobalt sites, however, the addition of NH₃ forms oxygen-bridged binuclear cobalt-amine complexes. Computational results and UV-vis spectroscopy show that these binuclear species form by dimerization of mobile Co-amine complexes. Interestingly, confinement within zeolite frameworks stabilizes these complexes relative to their homogeneous analogues.

Catalytic approaches to selectively breaking C-F bonds: lessons learned from breaking C-O bonds

Rachel Narehood Austin

Department of Chemistry, Barnard College, New York, NY 10027

C-F bonds play an important role in modern medicine and commerce. Their unique properties – strength, hydrophobicity, limited reactivity – endow the molecules they decorate with functions not found with other functional groups. These same properties, however, pose challenges to efforts to selectively break C-F bonds. In this talk, we will describe some of the broad lessons learned from our work developing and studying catalysts for selective C-O bond-breaking and highlight work in our research group to understand catalytic mechanisms of C-F bond breaking carried out by both heterogeneous catalysts and metalloenzymes. Both efforts support our long-standing goal of contributing to the development of a circular material economy.

Leveraging hydrogen bonds in catalyst design

Marcella Lusardi

Department of Chemical and Biological Engineering and the Materials Institute, Princeton University, Princeton, NJ 08540

Advancements in catalyst design will play a critical and transformative role in the redevelopment of global chemical and energy infrastructures in the face of growing populations and increasingly stringent cost and sustainability targets. Realizing these advancements in practice hinges on the development of tailored synthetic methods to enable finer-grained control over catalyst structure and functionality across length scales. In this talk, we demonstrate how hydrogen-bonding interactions in the form of functionalized N-heterocycles can be leveraged to create small, highly dispersed metal nanoparticles (NPs) on a supramolecular support. Moreover, we show that the supported Au NPs prepared in this way give rise to competitive turnover and outperform comparands prepared using conventional impregnation-reduction and sol-immobilization techniques in a model oxidative dehydrogenation reaction. We conclude with opportunities to tune hydrogen-bonding interactions more broadly to introduce porosity, anchor single-atom active sites, and modulate the electronic environment at the metal-support interface towards enhanced reactivity in diverse catalytic applications.

Cobalt Catalyst on Siliceous Zeolite for Non-Oxidative Ethane Dehydrogenation

Dongxia Liu

Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716

Dispersed metal species in siliceous zeolites have been actively studied for non-oxidative dehydrogenation of light alkanes. Fundamental insights into the dynamics of metal centers in zeolites under reaction conditions have been rarely explored. Herein, we report an atomic level understanding of the dynamics and activity of cobalt (Co) centers in dealuminated Beta (DeAl-BEA) zeolite for non-oxidative dehydrogenation of ethane for on-purpose production of ethylene. In Co@DeAl-BEA samples with 0.5 mass% Co loading, highly dispersed Co²⁺ cations in four-fold coordination form upon exposure to hydrogen in induction and persisted through the dehydrogenation reaction. Increasing the Co loading to 3.0 mass% yielded Co sites with similar electronic structures and coordination numbers but slightly elongated Co-O bonds. After cooling to room temperature, the Co atoms persisted at the same site. Still, the disappearance of a feature in the Co K-edge near-edge region revealed changes in the active site electronic structure coinciding with modest shifts in bond lengths. The electronic structure and activity of the majority sites, mononuclear Co²⁺ sites, and the minority dinuclear -Co-O-Co- sites were investigated in various coordination environments with electronic structure calculations and microkinetic simulations. The simulations show that the ethane dehydrogenation is controlled by the β -hydride elimination that follows the C-H bond activation, and that Co-sites possessing flexibility on account of neighboring silanol defects are more active. Interestingly, the minority dinuclear sites Co-O-Co are more active than the majority sites because of favorable hydrogen bonding with the vicinal silanol groups. The present study provides the knowledge on the active sites under reaction conditions in alkane dehydrogenation chemistry.

Achieving a 100% Drop-in Sustainable Aviation Fuel: Technological Pathways and Challenges

Mahluli Moyo

Air Company, Brooklyn, NY 11211

The aviation industry has set an ambitious goal to decarbonize, with sustainable aviation fuel (SAF) positioned as a key driver to reduce carbon emissions from existing airline fleets. Achieving this goal will involve transitioning from conventional crude oil refining to technologies that can utilize renewable feedstocks. However, a critical challenge remains i.e. achieving 100% drop-in SAF, a fuel that can seamlessly replace conventional jet fuel without requiring modifications to current aircraft, engines, or infrastructure.

In this talk we will delve into the concept of what is 100% drop-in SAF, addressing what qualifies a fuel as truly drop-in and further exploring promising technologies that enable its production and compare how these technologies stack up against one another, examining their respective advantages and challenges. Additionally, we will emphasize the importance of fuel certification and how its achieved, ensuring that drop-in SAF meets the same performance and safety standards as traditional jet fuel, paving the way for its large-scale adoption.

Development of Electrocatalysts for the Conversion of CO₂ to High-Value Chemicals

Andrey Smirnov^{1*}, Anders Laursen², G. Charles Dismukes^{1,3}

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Carbon dioxide (CO₂) is a vital renewable feedstock for synthesizing high-value chemicals, that if used to replace unsustainable fossil feedstocks would eliminate greenhouse gas emissions. The electrochemical reduction of CO₂ can produce oxyhydrocarbon products (C₁ to C₄) and polymers from water under ambient conditions using renewable electricity. Suppressing the fast H₂ evolution reaction and controlling the C_x product selectivity are the major impediments to commercialization. Binary compounds comprised of transition metals with group-15 elements (TM_aX_b; X = P, As, Sb, Bi) have emerged as leading electrocatalysts [1]. Group-15 elements in the center of the P-block of the Periodic Table have incomplete valence electron shells that form ionic charge transfer intermediates. These intermediates enable deoxygenation by exchange reactions between surface *hydrides and substrate hydroxyls, e.g. formic acid/formaldehyde: *X-H/HC(=O)OH ↔ *X-OH/H₂C=O. The choice of TM, X and electrolyte dictates the reaction yield based on the reaction free energy.

To make more complex products, exothermic aldol C-C coupling reactions occur on many electrocatalysts to make C₂-C₄ products. For example, C₂-glycolaldehyde: 2*H₂C=O $\xrightarrow{\text{[Lewis acid]}}$ HOC-C(=O)H. Depending on choice of the TMP plus Lewis acid co-catalyst, subsequent *X-H hydride additions forms C₂-ethylene glycol, C₂-ethylene oxide or C₂-acetic acid, in competition with sequential aldol couplings to C₃-glyceraldehyde then C₄-furanediol. We shall illustrate selectivity changes across the family of TMXs [2].

We have developed electrocatalysts that prevent C-C coupling, thus allowing selective formation of C₁-formic acid using Bi-based catalysts. Elemental Bi corrodes under electrocatalysis, limiting its lifetime. We show that NiBi and Ni-doped Bi electrocatalysts are more stable against corrosion and suppress the H₂ evolution reaction, while forming formic acid as the sole product. The best turnover rates are sufficient to support current densities > 100 mA/cm², a threshold for early commercialization. These findings highlight the versatility and reactivity of group-15 TM compounds to produce multi-carbon products via carbon-negative electrocatalysis. Funded by the NSF-STTR program.

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[2] Li, Y.; Calvino, K. U. D.; Dhiman, M.; Laursen, A. B.; Gu, H.; Santorelli, D.; Clifford, Z.; Dismukes, G. C. *EES Catalysis* 2024, 2 (3), 823-833.

Automated reasoning in chemical science and engineering

Tyler Josephson

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Baltimore County, Baltimore, MD 21250*

Large language models (LLMs) like ChatGPT are powerful text-generation tools. They are increasingly relevant in chemical science and engineering, but are unreliable in solving complex, practical problems faced by scientists and engineers. This is fundamentally about gaps in their *reasoning* capabilities.

In this talk, I will illustrate how engineers solve problems using reasoning skills that go beyond pattern-matching, in which current memorization-based machine learning algorithms excel. I will highlight old and new approaches in AI for reasoning, and highlight opportunities for scientists and engineers to leverage these approaches. Examples from the AI & Theory-Oriented Molecular Science (ATOMS) Lab at UMBC will be highlighted, including prompting LLMs for chain-of-thought reasoning for solving NMR spectra, writing bug-free software for adsorption calculations using formal theorem provers, and incorporating reasoning tools into methods for discovering equations describing force fields for acid-base interactions.

Designing Heterogeneous Catalysts with Free-Atom-Like Electronic States

Andrew Rosen

Department of Chemical and Biological Engineering, Princeton, NJ 08540

Single-atom alloys—solid-state materials composed of a spatially isolated “guest” metal embedded on the surface of a typically less-reactive “host” metal—have garnered substantial interest due in part to their ability to break conventional linear scaling relationships. Recently, a few single-atom alloys have also been shown to exhibit an unusual phenomenon wherein the *d*-band of the dopant metal is extremely narrow in terms of its energetic distribution, making it behave more like a free metal atom rather than a typical solid. This "free-atom-like" electronic character has typically been assumed to be relatively rare, which begs the question: what factors govern this unique electronic structure behavior, and how might it be leveraged for new types of catalysis? Through a data-mining and high-throughput density functional theory approach, we identify an incredibly diverse range of metallic compounds that are predicted to have transition metals with free-atom-like electronic states. Importantly, we note that site isolation is necessary but that the dilute limit, as in most single-atom alloys, is not a prerequisite. From density functional theory calculations and the *d*-band model of chemisorption, we predict that localized *d* states play a critical role in modulating the binding strength of CO on the surface. We conclude by discussing how these findings may open up new avenues for theory-driven catalyst design.

Understanding and Controlling Reaction Pathways in Organic Electrosynthesis

Miguel A. Modestino

Department of Chemical and Biomolecular Engineering, New York University, New York, NY 10011

The chemical industry produces more than 70,000 products (1.2 billion tons in total) via thermal processes powered by fossil fuel combustion, accounting for ~5% of the US energy utilization and >30% of the US energy-derived industrial CO₂ emissions. Amongst these processes, the production of organic chemical commodities accounts for most of the energy utilization (>1200 TBTU/y), and the electrification of these processes via the implementation of electro-organic reactions coupled with green hydrogen production could enable the integration of renewable electricity sources with chemical plants and accelerate the decarbonization of the chemical industry. Most of these reactions are oxidations in nature and if performed electrochemically could be coupled with the reduction of water to potentially produce H₂. These paired electrolysis approaches for the production of basic organic chemicals would result in the production of large amounts of emissions-free H₂ which could support other processes in the industry. Currently, however, two major challenges prevent the deployment of electro-organic reactions at scale: their low selectivity and their low production rates. To circumvent these barriers, my group combines electrochemical reaction engineering principles and machine-learning methods to accelerate the development of high-performing electro-organic reaction processes.

In this presentation, I will discuss our work on understanding and improving the production of adiponitrile (ADN), a precursor to Nylon 6,6, via the electrohydrodimerization of acrylonitrile (AN). This is the largest and most successful electro-organic reaction deployed in industry and serves as a test case for the development of large-scale organic electrochemical processes. Our investigations on ADN are aimed at uncovering the relationship between the electrochemical environment at and near the electrical double layer (EDL) and reaction performance metrics (i.e., selectivity, efficiency, and productivity). I will discuss general guidelines for electrolyte formulation and provide insights into the role of different electrolyte species (e.g., buffer ions, chelating ions, selectivity-directing ions, and supporting ions) in achieving conversions of AN to ADN with selectivity as high as 83%. I will also present how carefully controlling pulsed electrosynthesis conditions guided by active machine learning can help mitigate mass transport limitations, control the concentration of AN near the EDL and enhance the production rate of ADN by >30%. Our learnings on ADN electrosynthesis helped us to also engineer the electrocatalytic hydrogenation of ADN to hexamethylenediamine (a Nylon 6,6 monomer), achieving the highest reported selectivity to date for this reaction (>95%). This electrochemical hydrogenation process avoids sourcing hydrogen from fossil sources and brings sustainability to hydrogen utilization in chemical production. To further accelerate the development of high-performing electro-organic processes, my group has recently developed new machine-learning methods for rapid reactor outflow analysis using inexpensive spectroscopic tools and Bayesian optimization methods that leverage physical models to maximize process performance. These new tools will help us accelerate the electrification of petrochemical processes with large carbon footprints.

Poster Presentations

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

Aojie Li and Srinivas Rangarajan*

Chemical and Biomolecular Engineering, Lehigh University, 124 E Morton St, Bethlehem, PA, 18015, USA

Hydrogenation and hydrogenolysis processes, pivotal in biomass conversion and otherwise, traditionally employ molecular hydrogen as hydrogen source under significant pressures. Catalytic transfer hydrogenation (CTH) presents an alternative using organic hydrogen donors like alcohols and formic acid (FA), offering a safer and milder approach suitable for small-scale distributed processing. Mechanistically, CTH may involve indirect H-transfer via metal hydrides, or direct H-transfer akin to MPV reductions on lewis acid catalysts. While evidence for direct H-transfer on transition metal catalysts is limited, several studies demonstrate higher rates and conversions using formic acid as H source compared to molecular hydrogen under identical conditions. Here, we show that direct hydrogen transfer between a donor and acceptor (or derived intermediates) is kinetically feasible on transition metal catalysts, especially facilitated by hydrogen bonding interaction. This mechanism opens up new hydrogenation pathways inaccessible to molecular hydrogen and could explain higher CTH rates vis-a-vis conventional hydrogenation.

In this work, we combine density functional theory (DFT) with coverage-cognizant microkinetic modeling to conceptually explain the mechanism of catalytic hydrogen transfer between a common donor, viz. HCOOH, and a model acceptor, viz. HCHO (the smallest carbonyl compound), on Cu(111) to explicate the role of indirect and direct hydrogenation routes and the effect of surface coverages and concomitant destabilization. Our results show that (1), hydrogen bonded complexes are formed when HCOOH and HCHO are both present, they enable direct hydrogen transfer which is kinetically relevant, resulting in three times higher reaction rate (compared to using molecular H₂ under the same conditions). (2), hydrogen bonded complexes arise in a number of other CTH systems (furfural and lignin hydrogenolysis, reduction of nitrates, nitriles, etc.) and transition metal catalysts, potentially indicating the generality of our results to more practical chemistries in biomass conversion and beyond.

Designing bimetallic heterogeneous catalysis by electrochemical polarization

Bohyeon Kim¹, Isaac Daniel², James Spragg², Samuel Pattisson², Richard J. Lewis², Mark Douthwaite², Christopher J. Kiely³, Graham J. Hutchings², and Steven McIntosh^{1,*}

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Traditionally, thermocatalytic reactions have been considered as processes driven purely by thermal energy without electrochemical driving forces or mechanistic steps. Herein, we challenge this view by demonstrating that aqueous-phase thermocatalytic reactions can be effectively analyzed through coupled electrochemical half-reactions. Our tailored electrochemical measurements support excellent alignments between the estimated electrochemical activity and the observed thermocatalytic performance across multiple reactions and catalytic systems.

Furthermore, we introduce a different but efficient way of designing thermocatalysts by harnessing electrochemical driving forces. We can deliberately segregate redox half-reactions to the favorable active sites in dissimilar catalysts, significantly enhancing catalytic performance through a mechanism known as Cooperative Redox Enhancement (CORE). Another advantage of CORE-based catalysts is also presented as enhanced half-reaction activities by spontaneous polarization. Real-time electron transfer measurements provide direct evidence of charge transfer between catalysts during thermocatalytic turnover, strongly supporting the role of electrochemical interactions and the mechanism of CORE.

Molecular Structure of Na-WO_x/SiO₂ Catalysts: Dispersed vs. Crystalline Phases for Selective Methane Activation in Oxidative Coupling of Methane (OCM)

Damilola Awotoye, Srinivas Rangarajan, and Jonas Baltrusaitis*

Lehigh University, Department of Chemical and Biomolecular Engineering, Bethlehem, PA, 18015, US

The oxidative coupling of methane (OCM) represents a promising route for the direct conversion of methane into valuable chemical feedstocks, such as ethylene. Currently, the supported Mn₂O₃-Na₂WO₄/SiO₂ catalyst is the benchmark catalyst with promising performance (~30% methane conversion and ~70% C₂ selectivity). However, the nature of the active sites governing methane activation and selectivity remains poorly understood. Our hypotheses suggest that the dispersed Na-WO_x/SiO₂ sites promote selective methane activation by generating atomic oxygen species (O*) that facilitate C₂H₆ formation while suppressing overoxidation. In contrast, crystalline Na₂WO₄/SiO₂ transitions into a molten phase under reaction conditions, favoring molecular oxygen species (O₂*), which enhance CH₃O· formation and lead to unselective oxidation pathways. To investigate these effects, we synthesize Na-WO_x/SiO₂ catalysts using individual Na and W precursors to allow precise control over the ratio of dispersed Na-WO_x and crystalline Na₂WO₄ phases. The catalysts are prepared via incipient wetness impregnation and characterized using Raman spectroscopy to elucidate their molecular structure. This study provides fundamental insights into the structure–function relationships of Na-WO_x/SiO₂ catalysts, offering a rational approach for designing more efficient and selective OCM catalysts.

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

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Oxidative Dehydrogenation of Ethane (ODHE) is an alternative method that addresses the thermodynamic limitations, coke formation, and greenhouse gas emissions associated with the conventional and energy-intensive steam cracking of ethane to produce ethylene. Recently, the bulk M1 phase of the crystalline MoVNbTe mixed oxide catalyst has become popular among ODHE catalysts due to its high ethylene selectivity (over 90%) and good ethane conversion rates (up to 80%). While the bulk structure of the crystalline MoVNbTe mixed oxide M1 phase catalyst has been well-studied, less is known about its surface properties under controlled ODHE reaction conditions. In the present study, we employ multiple surface-sensitive techniques, including in situ Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) and quasi-in situ High Sensitivity-Low Energy Ion Scattering (HS-LEIS), along with bulk-sensitive methods such as in situ Raman spectroscopy and ambient X-ray Diffraction (XRD), to characterize the bulk MoVNbTe mixed oxide M1 phase catalyst. These studies provide new insights into both the surface and bulk properties of the crystalline MoVNbTe mixed oxide M1 phase catalyst.

Multimetallic Nanoalloy Catalysts in Proton Exchange Membrane Fuel Cells

Dominic Caracciolo¹, Zeqi Li¹, Zhipeng Wu¹, Dong Dinh², Guojun Shang¹, Megan Barber¹, Niko Vidakovic¹, Ylith Peck¹, Jessica Tao¹, Gary Han¹, Jin Luo¹, Susan Lu², Chuan-Jian Zhong^{1,*}

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The understanding of structures and electrocatalytic properties of multimetallic nanoalloy catalysts in proton exchange membrane fuel cells (PEMFCs), a vector for alternative clean energy conversion, is critical for the optimization of membrane electrode assembly design and fabrication. We have been investigating different wet-chemical and solid-state synthesis routes for the preparation of Pt and/or Pd-alloyed transition metal catalysts towards achieving enhanced high performance and durability. Key to the investigations is the correlation of the phase structures of the nanoalloys with the electrocatalytic properties in the PEMFC. In this presentation, recent results from using in-situ high-energy x-ray diffraction (XRD) to characterize the phase structures and monitoring fuel cell performance of the nanoalloy catalysts in PEMFC to determine the durability will be discussed. Examples of Pt and Pd alloyed with Cu, Ni, Fe, etc. will be highlighted. The effect of dealloying and realloying processes on the PEMFC performance and electrocatalytic durability will be discussed. Both DFT-based theoretical modeling and AI-driven data processing and simulation are used for assessing the experimental results for better understanding the composition-performance relationship of the multimetallic nanoalloy catalysts in fuel cells.

Tuning Molecular Structure and Reaction Mechanism of Olefin Metathesis by Model Bilayered Supported MoO_x/AlO_x/SiO₂ Catalyst

Eli M. Ream, Joseph I. Thompson, Adhika Setiawan, Srinivas Rangarajan, Israel E. Wachs*

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Supported MoO_x catalysts are commonly used for the cross-metathesis of ethylene and 2-butene to produce propylene ($C_2H_4 + C_4H_8 \rightarrow 2 C_3H_6$). The molecular structure and activity of supported MoO_x catalysts is heavily impacted by the choice of catalyst support. Supported MoO_x/Al₂O₃ is very active but contains several different MoO_x sites depending on MoO_x loading. The nonuniform nature of this catalyst makes it difficult to draw conclusions about the active site. Supported MoO_x/SiO₂ is less active and requires high temperature activation for olefin metathesis but contains only isolated dioxo (O=)₂Mo(-O-Si)₂ sites. The uniform nature of MoO_x/SiO₂ allows it to serve as a model catalyst. Supported MoO_x/(SiO₂-Al₂O₃) has demonstrated improved olefin metathesis performance over MoO_x/SiO₂ or MoO_x/Al₂O₃, but there has been limited characterization of the surface sites which has prevented the establishment of the structure-function relationship.

In this study, surface modification of the SiO₂ support with AlO_x was used to tune the structure and activity of surface MoO_x, resulting in a supported MoO_x/AlO_x/SiO₂ catalyst with significantly enhanced activity over MoO_x/SiO₂. The surface structure of MoO_x and the origin of this enhanced activity were investigated through extensive in situ molecular characterization, chemical probing, and density functional theory (DFT) calculations. In situ IR spectroscopy and DFT calculations reveal that AlO_x anchors on surface Si-OH silanols on SiO₂ and that MoO_x anchors extensively to Al-OH hydroxyls on AlO_x/SiO₂. In situ UV-vis spectroscopy, in situ Raman spectroscopy, and DFT calculations reveal that MoO_x/AlO_x/SiO₂ consists of well dispersed isolated dioxo (O=)₂Mo⁶⁺(-O-Al)(-O-Si) sites. Mechanistic insights from DFT indicate that the enhanced activity of MoO_x/AlO_x/SiO₂ over MoO_x/SiO₂ is the result of a more energetically favorable mechanism that arises from the formation of six-membered metallacycle intermediates attached to both Mo and a neighboring Al atom.

Elucidating the Structural and Electronic Effects of Ni and Mn Cationic Impurities on CoOOH for Efficient Benzyl Alcohol Electrooxidation

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Transition metal oxides, such as cobalt oxyhydroxide (CoOOH), are cost-effective electrocatalysts for partial electrooxidation of organic molecules, offering a durable and affordable alternative to expensive and less stable iridium oxide for low-potential H₂ synthesis and the co-generation of valuable oxidized products in alkaline media. Recent findings in electrochemical water splitting demonstrate that cationic impurities can cause structural and electronic reconstruction of electrocatalysts during electrochemical reactions for green H₂ production. It remains unclear if this promotional effect is also present in organic molecule electrooxidations. Here, we report an investigation of the effects of two common cationic impurities (Ni and Mn) incorporated in cobalt oxyhydroxide electrocatalysts (2NMC@NF) on the electrooxidation of benzyl alcohol. Electrochemical measurements of the 2NMC@NF catalyst, synthesized in the presence of both Ni and Mn, revealed an increased number of active sites. This enhancement in activity is attributed to the incorporation of Ni³⁺ active sites, which facilitated the high electrocatalytic performance. Meanwhile, Mn³⁺ was observed to improve the structural stability during 24 hours of continuous chronoamperometry (CA) as confirmed via SEM and STEM-EDS maps after CA. Liquid product analysis revealed that 2NMC@NF achieved selective oxidation to benzoic acid, with a 77.6% yield during a 24-hour CA test at 1.5 V vs. RHE. Furthermore, the 2NMC@NF model catalyst also showed excellent performance not only during BAOR but also during water oxidation with a 296 mV overpotential after 24 h CA. This work showed that transition metal ion contaminants, potentially present in the electrodes via deposition from liquid handling equipment, can modify the structure and electrochemical properties of cobalt oxyhydroxide catalysts as a result, enhancing their activity and stability. Specifically, we show that both Ni and Mn cation impurities in the electrolyte incorporate into the cobalt oxyhydroxide structure, enhancing activity and long-term stability of the catalyst surface under electrochemical conditions, respectively.

**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. This has stimulated interest in the dimerization of shale gas derived ethylene to butene. In industry, ethylene dimerization is carried out in homogeneous systems which can face several operational and environmental challenges. Consequently, there is interest in developing heterogeneous ethylene dimerization catalysts with comparable performance to their homogeneous counterparts. Nickel sulfated zirconia is a promising heterogeneous ethylene dimerization catalyst due to its high activity and selectivity for 2-butene under mild reaction conditions as well as its high surface acidity and well dispersed nickel phase. However, little is known about the nature of the 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 LEIS) were applied under different environments. Dehydrated IR and Raman spectra indicated the presence of $\text{O}=\text{S}(\text{O}-\text{Zr})_3$ sulfate species which preferentially anchor to terminal hydroxyls on the zirconia support at low loadings. At high loadings, a second sulfate species anchors to the tri-bridging hydroxyls. XAS and UV-vis spectra collected under dehydrated conditions indicated that nickel is present as Ni^{2+}O_6 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 NH_3 also revealed that the order of impregnation of nickel and sulfate alters the Bronsted to Lewis acid ratio and temperature for butene formation.

Selective Electroreduction of CO₂ to C₄ Products on Molybdenum Phosphide through a Novel Dimerization Mechanism

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Electro-catalytic conversion of CO₂ into chemicals and fuels offers a carbon negative approach to sustainable use of petroleum resources that has not yet been implemented commercially despite major advances in research. Transition metal phosphides (TMPs) have emerged as a major class of electrocatalysts for converting CO₂ into a range of multi-carbon products, spanning C₁ to C₄ oxyhydrocarbons and polymers [1, 2, 3] suitable for upgrading to diesel and feedstock chemicals. Exceptional electrochemical performance is possible for the simplest products. However, commercialization of higher molecular products is constrained by electrical overpotentials, product selectivity, and complex reaction mechanisms.

Nickel phosphides are exceptional TMP electro-catalysts for CO₂RR that produce a mixture of formic acid, (C₁), methylglyoxal (C₃) and 2,3-furandiol (FD, C₄). [1] All three products arise from intermediate formate. Here, we demonstrate molybdenum phosphide's highly selective, carbon-negative pathway to reduce CO₂ to a C₄ product, predominantly 2,3-furandiol and furan. By changing the transition metal to Mo, a more electron-deficient element, the selectivity of the CO₂ reduction pathway is altered. Specifically, MoP₂ redirects the C₂ glycolaldehyde intermediate to form FD via ethylene glycol and ethylene oxide as confirmed intermediates. This mechanism undergoes a novel C₂-C₂ dimerization step to form the C₄ product distinct from the aldol coupling mechanism that forms FD on the nickel phosphides. This study contributes to the fundamental understanding of CO₂RR on transition-metal phosphides and their analogues based on periodic trends. It also provides a simple binary material as alternative to the use of co-catalysts to tune the selectivity of TMPs [4]. Further scale-up of this process to higher current densities and commercial product rates is feasible by overcoming CO₂ mass transport.

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DFT-derived Insights of CO₂ Reduction in Solid Oxide Electrolysis Cells and Inhibition by S-containing Molecules

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Solid Oxide Electrolysis Cells (SOECs) have become a system of interest due to their efficiency of splitting H₂O and reducing CO₂ into useful, high-energy products. The most common SOEC cathode is Ni/YSZ with YSZ as the solid electrolyte for O₂- conduction. The active site for SOEC, at sufficiently high applied potential, is often postulated to be a triple phase boundary (TPB) between metallic Ni nanoparticle and the YSZ surface. In particular, CO₂ can adsorb at the interface, undergo electrochemical C-O scission leading to CO and O₂- ions. However, the catalytic activity on Ni/YSZ cathodes can be hampered by the presence of S constituents in feed flows due to their strong adsorption, minimal barriers to bond activation and surface persistence, even at high temperatures. Modeling the thermodynamics and kinetics in the local environment of the electrode TPB can elucidate the mechanism of CO₂ electroreduction on the cathode half reactions. To this end we seek to analyze surface reactions which produce desired, useful, products of CO₂ and potentially harmful products of SO₂ on Ni, Ytria-stabilized Zirconia (YSZ), and Ni/YSZ.

Comparative analysis of the enthalpy of CO₂ and SO₂ adsorption on Ni(111), YSZ(111), and Ni/YSZ shows CO₂ binds weakly on Ni(111) and YSZ(111) while strongly at the interface, while SO₂ binds significantly more strongly on all sites indicating strong competitive inhibition. SO₂ dissociation (leading to SO and S) has lower thermodynamic barrier than CO₂ dissociation, indicating that persistent S-containing species can occupy active sites on Ni nanoparticle as well as the TPB. The adsorption of CO₂ at the interface results in charge transfer from Ni to CO₂ subsequently, CO₂ dissociates to form (CO+O) whose Bader charge is -1.77e indicating a charge transfer and a potential-dependent step. Subsequently, a subsurface O diffuses to the bulk leaving behind a vacancy and CO desorbs, thereby completing the cycle.

Understanding the mechanisms of catalyst deactivation during hydrothermal gasification

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The development of effective and stable catalysts is essential for hydrothermal gasification (HTG) processes, which convert mixed organic compounds into methane under water-rich conditions. In this system, supported nickel catalysts are both active and selective for methane production. However, their long-term stability and performance are hindered by severe deactivation, which occurs through several modalities under typical working conditions of high temperature (500°C), pressure (>20 bar), and water content (> 50 wt%). Specifically, coke formation, sintering, nickel oxidation, and pore structure collapse are all problematic. Our aim is to understand the extent to which each process contributes to the deactivation of supported Ni catalysts and how each deactivation mechanism responds to changes in operating conditions. Further, we aim to mitigate each to the extent possible, as addressing catalyst degradation is vital for advancing commercial applications. To this end, we consider modulation of the Ni support structure and composition, techniques for Ni deposition, and strategies for Ni protection and passivation. The physicochemical properties of all samples are characterized before and after exposure to hydrothermal gasification conditions using X-ray diffraction, inert gas physisorption, H₂ chemisorption, and temperature-programmed oxidation, and we provide insights into how variations in material composition, synthetic methodology, and operating conditions can impact various modes of deactivation.

DFT and Microkinetic Study of the Mechanism of Propene Metathesis on MoO_x/SiO₂ and MoO_x/(AlO_y-SiO₂) Catalysts

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Heterogeneously catalyzed olefin metathesis is an important route to making olefins in the chemical industry and is an emerging route to upcycle plastics. While there has been substantial interest in this chemistry, the precise active site requirements, reaction mechanism, and molecular structure-function relationships for these catalysts still remain unclear. In this context, this contribution focuses on studying the energetics of propene metathesis on silica supported molybdena catalyst (MoO_x/SiO₂), a model catalyst with isolated MoO₄ clusters and a bilayer MoO_x/AlO_y/SiO₂ with isolated MoO_x grafted on to isolated AlO₄ structures on silica. The thermochemistry of incorporating AlO_x and MoO_x species on SiO₂ (and MoO_x on AlO_x/SiO₂) showed that molybdate preferentially anchors on the alumina (relative to pure silica). In the MoO₄/SiO₂ free energy pathway, cycloaddition of Mo=CH₂ (or Mo=CHCH₃) results in a four-membered metallocycle intermediate that then undergoes cycloreversion to produce an olefin (ethylene or 2-butene respectively) and forming the complementary Mo-alkylidene species. The activated MoO₄/AlO₄/SiO₂ metathesis pathway shows formation of six-membered metallocycle rings comprising both Mo and Al which were found to be more stable than the four-membered counterparts. Further, the olefins (ethylene, propylene, and 2-butene) all preferred to bind to Al, thereby resulting in a modified Chauvin mechanism. Comparison of the two potential energy diagrams shows that the relative energy of transition and intermediate states are significantly stabilized compared to MoO₄/SiO₂ indicating higher activity. This contribution will discuss the catalyst structure, activation of the site, the chemistry of olefin metathesis on these sites, the associated DFT energetics, and the results of microkinetic modeling.

Insights into MOF Stability, Coordination Environment, and Active Site Structure during Oxidative and Non-Oxidative Transformations

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Metal-organic frameworks (MOFs) have high metal contents and a proposed high degree of site homogeneity, making them well-suited for rigorous kinetic and mechanistic investigation in metal-catalyzed reactions like oxidations. Here, iron-based MIL-100(Fe) is selected for styrene oxidation by hydrogen peroxide (HP) or tert-butyl hydroperoxide (TBHP) in acetonitrile. Styrene oxidation over MIL-100(Fe) leads to the formation of styrene oxide and benzaldehyde, with further secondary reactions to styrene glycol, phenylacetaldehyde, and benzoic acid. Initial oxygenate formation rates were ~10x higher with HP than TBHP, though TBHP was more selective for styrene oxide formation (52% for TBHP vs. 4% for HP). HP exhibited more secondary reaction, resulting from higher MIL-100(Fe) defect densities generated by iron and linker leaching during reaction. The secondary ring opening reaction of styrene oxide was further investigated in the presence of water, which is proposed to be catalyzed by either the Lewis acidic Fe site or Brønsted acidic ancillary (defect) sites. Styrene oxide ring opening over MIL-100(Fe) resulted in selective formation of styrene glycol (96-97%) over phenylacetaldehyde (3-4%). In-situ MIL-100(Fe) titrations with various pyridine analogs were employed to elucidate the active site in the reaction, where pyridine can access both Fe sites within MIL-100(Fe) micropores and surface Brønsted acid sites, while 2,4,6-trimethylpyridine can only access the latter. Altogether, this work utilizes kinetic and spectroscopic techniques to gain insights into the local structure of MOF catalysts during reaction.

Efficacy of Waste-to-Energy Ash in NO_x Abatement

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Municipal solid waste (MSW) combustor ash, a byproduct of waste-to-energy (WtE) processes, contains metal oxides that can serve as catalysts for NO_x reduction. This study explores the feasibility of using WtE ash as a catalyst for the non-selective catalytic reduction (NSCR) of NO_x using CO. Catalytic activity was evaluated in a packed-bed flow-through reactor under simulated flue gas conditions with oxidative and reductive pretreatments applied to enhance performance. Hydrogen pretreatment improved NO_x conversion by up to 35% in the highest range (>~400°C) of temperatures investigated (150–600 °C) while carbon monoxide pretreatment resulted in greater activity at lower temperatures (<~400 °C).

H₂-temperature programmed reduction (H₂-TPR) analysis revealed that the reducibility of the ash aligns with the temperature dependence of the equilibrium reduction potential of its metal constituents, with iron, aluminum, silicon, and calcium accounting for most of the observed reduction behavior. The temperature of maximum reducibility increased after pretreatment and catalytic testing, with a greater shift in the reductively pretreated sample. Additionally, H₂ consumption was highest in the oxidatively pretreated and spent ash, lowest in the reductively pretreated and spent ash, and intermediate in the as-received sample, indicating lasting effects of pretreatment on the redox properties of the catalyst.

These findings suggest that iron oxides, species known to be active in NSCR, are primarily responsible for the ash's catalytic activity. Given its effectiveness and availability, WtE ash presents a promising, low-cost alternative for NO_x abatement in harsh exhaust environments. Further optimization of catalyst formulation and industrial-scale testing are needed to assess long-term feasibility.

Exploring the Electrocatalytic Dehydrogenation of Ethanol for Liquid Organic Hydrogen Carrier Applications

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The growing production of renewable electricity from solar and wind energy requires the deployment of suitable storage and transportation infrastructure to provide the flexibility needed to harness energy from these sources and utilize it at different times and locations. Liquid organic hydrogen carrier (LOHC) systems are essential for achieving this goal. LOHCs cycle between two states: a hydrogen-lean state for storing hydrogen derived from water and a hydrogen-rich state that releases the stored hydrogen at the point of application.

The ethanol-acetic acid pair appears promising for use in LOHC systems and presents several advantages for this application compared to traditional hydrocarbon-based LOHCs. These include favorable thermodynamics for oxidation (“dehydrogenation”), higher hydrogen-carrying capacity, the ability to source ethanol renewably from biomass, and the use of environmentally benign molecules. Deploying an electrochemical pathway for the oxidation of ethanol to acetic acid is particularly promising as it can be tuned to selectively produce the acid rather than the ester, which is the likely product in thermocatalytic processes.

The present study aims to explore the electrocatalytic dehydrogenation of ethanol to acetic acid on Pt-based catalysts. Rotating disk electrode (RDE) techniques were employed to identify the number of electrons transferred during oxidation of each ethanol molecule (2e⁻ for acetaldehyde, 4e⁻ for acetic acid, and 12 e⁻ for carbon dioxide). This approach will be used in future experiments to screen catalysts that selectively convert ethanol to acetic acid. Furthermore, carbon felt-supported Pt was synthesized and used to gather data on the reaction, including ethanol conversion and product yields. The data collected from these experiments serve as a benchmark to inform future electrocatalyst design and help identify optimal reaction conditions for enhancing acetic acid formation.

**Synthesis and Characterization of Intermetallic and Random Alloy Catalysts
for CO Oxidation**

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As fossil fuel vehicles sales increase, air pollution continues to rise. Emission control regulations in the automotive industry are becoming more stringent to curb the worsening climate crisis. Platinum and other noble metals are traditionally the choices of catalysts for emission control reactions, such as carbon monoxide (CO) oxidation. Platinum, however, is expensive and scarce, which makes it unsustainable in the long term. Platinum also requires a high activation temperature, worsening emissions during cold start. In this presentation, we will discuss recent findings of an investigation of Pt-based intermetallic and random compositions of ternary nanoalloys for lower temperature catalytic oxidation of CO. We seek to understand the relationship between composition, structure, and catalytic activity. X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) techniques are used for structural and morphological characterizations of the intermetallic and alloy catalysts. H₂-Temperature Programmed Reduction (H₂-TPR) technique is used to determine the oxygenation properties of the catalysts. Online Fourier Transform Infrared Spectroscopy (FTIR) is used for monitoring the catalytic activity of CO oxidation reaction over the catalysts. Correlations among the structure, composition, and catalytic properties of the ternary intermetallic and alloy catalysts will be discussed.

The role of potential in enhancing the electrocatalytic dehydrogenation of benzyl alcohol

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Benzyl alcohol (BA) electrocatalytic dehydrogenation (ECD) can serve as a model reaction for hydrogen discharge during liquid organic hydrogen carrier (LOHC) cycling. BA can undergo ECD, forming benzaldehyde (BzH) as the primary product. However, BzH can undergo further electrooxidation to form benzoic acid (BzA). BzA is undesirable for LOHC cycling because its carboxylic group makes hydrogenation back to BA difficult. Herein, we investigated how the applied potential can alter the electrocatalyst-electrolyte interfacial environment to favor the selective ECD of BA in a neutral phosphate electrolyte (pH 7.2). The electrocatalyst used was PdO/C on a carbon felt. Ex-situ characterization using x-ray photoelectron spectroscopy confirmed the presence of Pd²⁺ on the as-prepared catalyst surface. Chronoamperometry studies at 1.11, 1.61 and 2.11V vs RHE were performed in a continuous flow cell reactor at steady state conditions. BA ECD was not observed at 1.11V vs RHE, while increasing the potential to 1.61V vs RHE resulted in 13% BA conversion with 99% BzH selectivity. A further increase in potential to 2.11V vs RHE increased BA conversion to 18% but lowered BzH selectivity to 88% due to BzA formation. The overall Faradaic efficiency (FE) towards BA ECD decreased from 100 to 54% as the potential was increased from 1.61 to 2.11V vs RHE, due to the competition with the oxygen evolution reaction at higher potentials. This work elucidates how the applied potential can be tuned to selectively favor BzH formation. The applied potential likely influences the catalyst interfacial environment which plays a key role in the reaction pathway towards ECD that will allow efficient hydrogen cycling via LOHCs.

Surface/Bulk Chemistry of La-based perovskite oxides

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High temperature co-electrolysis of CO₂ and H₂O serves a viable, energy efficient, and scalable route to produce syngas (CO + H₂), which can be used to generate a variety of utility hydrocarbons. 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 a cathode catalyst is critical as it must facilitate the activation of CO₂ and H₂O and exhibit high electron and oxygen ion conductivity. The state-of-the-art cathode material used in SOECs is Ni/YSZ (8 mol% Ytria Stabilized Zirconia) ceramic composite (known as cermet), whose performance is dependent on various operating factors including temperature, composition of feed gas stream, presence of contaminants such as SO_x/NO_x, etc. that leads to deactivation due to coking, sulfidation, sintering, and oxidation. Perovskite oxides are considered as a promising alternative for cathode materials since they have better redox stability and high ionic/electronic conductivity at operational conditions. Here, La-based perovskite oxides are investigated with multiple in situ spectroscopic characterization techniques such as Raman, diffuse reflectance infrared Fourier transform spectroscopy- temperature programmed desorption (DRIFTS-TPD), high sensitivity-low energy ion scattering (HS-LEIS), and methanol-temperature programmed reaction spectroscopy (TPRS) to understand the surface/bulk structural evolution under environmental conditions and to identify the types of active sites and molecular structure of surface intermediates present under reaction conditions.

Styrene to Benzaldehyde with an oxidant, a study in enzyme and heterogeneous catalysis

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Molybdenzymes are an ancient class of oxotransferases ubiquitous to all living things. I have identified a popular enzyme mimic produced by Rupam Dinda et al. that has produced derivatives in subsequent papers used as catalysts in a styrene to benzaldehyde oxotransferase reaction with: the enzyme mimic catalyst, a 30% hydrogen peroxide oxidant, and an ethanol solvent (Shuang Yang). I will be synthesizing the original enzyme mimic produced by Dinda with the intent on recreating the styrene to benzaldehyde experiment, provide spectroscopic characterizations of the catalyst, and verify the mechanism of the reaction proposed in Yang's paper. I will then be attempting to characterize the same reaction run over a 4% MoO₃/SiO₂ common heterogeneous catalyst with the same type of oxidant and solvent, at only a marginally higher temperature. I will be doing this in order to illustrate any differences or similarities in reaction mechanism, and in the hope of clearly presenting data on the role of the oxidant in the reaction. This research will contribute to the understanding of low temperature styrene to benzaldehyde reactions, and I hope it will contribute to the uses of bioinspired catalysts. I am a graduate student currently performing these experiments and would like to present a poster summary of my research in order to not only spread my ideas to the field as a cross trained biologist and biochemical engineer but to get feedback, and possible new directions from the professional catalysis community.

**Breaking the C-X Bond: A Kinetic Analysis of the Room Temperature
Dehalogenation of Halobenzenes Catalyzed by Rh/Al₂O₃**

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Halogenated hydrocarbons are stable, persistent environmental pollutants that have been shown to accumulate in both humans and wildlife. Selected catalysts have emerged as a promising technique for the selective hydrogenolysis of the carbon-halogen bond. Rh/Al₂O₃ has been shown to hydrodehalogenate halobenzenes under mild conditions, but with a kinetic analysis that indicated that C-X bond strength was not rate-influencing. This project analyzes the kinetics of Rh/Al₂O₃-catalyzed breaking of the C-X bond in fluoro-, chloro-, and bromobenzene, and shows that reaction rates depend on C-X bond dissociation energy when rhodium is prereduced with H₂. Ultimately, this work seeks to elucidate the mechanism of action for the Rh/Al₂O₃ catalyst to guide the development of other catalysts capable of carrying out similar chemistry but comprised of more abundant metals.

Transition Metal Phosphates as Next-Generation Electrocatalysts for Overall Water Splitting

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Hydrogen energy is a greenhouse gas emission-free form of energy. Using the electrochemical water splitting (EWS) technique, hydrogen energy can be produced economically. Although various techniques are available, electrochemical methods are among the most promising. In this study, metallic phosphates—including cobalt phosphate, cobalt-nickel phosphate, cobalt-copper phosphate, and cobalt-iron phosphate (CIP)—were synthesized using the aqueous chemical growth method. Various characterization techniques were employed to analyze the morphology and physicochemical properties of these metallic phosphates. These techniques included X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and Fourier Transform Infrared Spectroscopy (FTIR). In addition to material characterization, electrochemical investigations were carried out to evaluate the bifunctional behavior of the synthesized electrocatalysts. Among them, CIP was identified as the optimized electrocatalyst for bifunctional activity toward the Oxygen Evolution Reaction (OER) and Hydrogen Evolution Reaction (HER). CIP exhibited a lower overpotential, with values of 300 mV for OER and 325 mV for HER at a current density of 10 mA/cm² in 1.0 M KOH alkaline media. It also demonstrated fast reaction kinetics, as indicated by its lower Tafel slopes of 53.6 mV/dec and 58.4 mV/dec for OER and HER, respectively. Additionally, CIP electrocatalyst was subjected to durability and stability testing for up to 45 hours for both HER and OER activities. The CIP exhibited enhanced intrinsic behavior, validated by higher Turnover Frequency (TOF) values and normalized data. Notably, significant hydrogen and oxygen production rates were achieved, measuring $470.6 \times 10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$ and $44.5 \times 10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$, respectively, due to its large electrochemically active surface area (ECSA) of 342.5 cm². This novel cobalt-iron (Co-Fe) phosphate-based electrocatalyst presents a promising alternative to platinum-group metal (PGM)-based electrocatalysts for practical applications.

**NiCo@Pt Core-Shell Catalysts: Synthesis and Characterization Using
Hydrogen Temperature-Programmed Reduction**

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Alloys and intermetallic compounds derived from nickel, cobalt, and platinum are used as catalysts in various industrial processes, including petroleum refining to the synthesis of fine chemicals, processing of various types of plant materials and biomasses, and various catalytic hydrogenolysis reactions. Modifying nickel-cobalt alloy-based catalysts with different metals greatly affects their catalytic activity and selectivity in processing biomass-derived feedstocks. We have been developing various nanoalloys and intermetallic nanoparticles for catalytic and electrocatalytic reactions. In this presentation, recent results from the investigation of the synthesis of nickel cobalt alloy decorated with platinum (NiCo@Pt) by wet-chemical and seeded growth methods will be described. Such core-shell type catalysts are characterized by hydrogen-temperature-programmed reduction (H₂-TPR) to obtain information on the reducibility of metal oxide species in the catalysts. By different heating rates, the activation energy was determined, showing strong dependence on the core-shell composition and structure. Implications of the results for the design of active and durable catalysts in different catalytic or electrocatalytic reactions will be discussed.

Selective CO₂ electro-reduction to acetate on nickel arsenides

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Electro-catalytic conversion of CO₂ into chemicals and fuels offers a carbon negative approach to sustainable use of petroleum products that has not yet been implemented commercially despite major advances in research. Commercialization remains constrained by electrical overpotentials, limited product selectivity, and complex reaction mechanisms. Transition metal phosphides (TMPs) have emerged as a promising class of electrocatalysts, demonstrating exceptional electrochemical performance—characterized by high Faradaic efficiency and reduced overpotentials. Notably, TMPs facilitate the conversion of CO₂ into a diverse range of multi-carbon products, spanning C₁ to C₄ oxyhydrocarbons and polymers [1, 2, 3], suitable for upgrading to diesel and feedstock chemicals.

Mechanistic investigations indicate that TMPs catalyze CO₂ reduction to complex products via the formate pathway, with surface hydrides (*H) serving as key reducing species, while additional reaction steps (e.g., substrate binding, C-C coupling, dehydration, and isomerization) are dictated by the TMP's atomic structure [4]. Under applied potential, electrons populate electronic states that mediate surface *H formation through proton or water reduction. This potentiometric activation enhances CO₂ adsorption and stabilizes intermediates via charge transfer processes. Phosphorus plays a crucial role in the formation of phosphino-hydrides that readily exchange with hydroxyl groups from intermediates (*H/*OH exchange) producing deoxygenated products.

This study further explores nickel arsenide (NiAs) to modulate the chemical potential of surface hydrides. Substituting phosphorus with arsenic yields more labile surface arsino hydrides (*H) with lower bond dissociation enthalpy and greater ionic character (Ar δ^+ H δ^-). The greater polarizability of arsenic enhances the CO₂ affinity, while the ionic character of the arsino-hydride bonds increases the chemical potential creating a stronger reductant. In various nickel phosphides, glycolaldehyde is an intermediate in the formation of C₃ products, including glyceraldehyde and methylglyoxal [1, 2, 3]; however, this pathway is notably absent in NiAs. Instead, C-C aldol coupling to C₃-glyceraldehyde is suppressed in favor of C₂ isomerization and hydride transfer to form acetate, prior to release of acetic acid. The electrocatalytic production of acetate from CO₂ represents a sustainable, carbon-negative approach for generating a versatile chemical feedstock with broad applications in polymer synthesis, solvent production, and chemical intermediates. Funded by the NSF-STTR program and Rutgers RCEI.

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Design of ordered aluminosilicates for dielectric barrier discharge-assisted catalysis of ammonia reactions

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Industrial Haber-Bosch ammonia synthesis entails centralized high temperature and pressure reactor systems with significant carbon emissions that can be reduced by direct electrification, e.g., dielectric barrier discharge (DBD)-assisted catalysis. These electrified strategies allow for the storage of disperse, intermittent green energy in the chemical bonds of the easily liquefied ammonia for harvesting at the point-of-use via electrified ammonia decomposition, sparking our interest in incorporating DBDs for both directions of the equilibrium-limited ammonia reaction. Packed beds with metal nanoparticles supported on porous oxides can have similar DBD-assisted ammonia yields as metal-free porous oxides alone, indicating significant support contributions that need to be understood to overcome the current low energy yields. Ordered silicas (i.e., SBA-15 and MCM-41) have shown relatively high ammonia synthesis energy yields; however, γ -alumina is more desirable than silica due to ammonia adsorption on Lewis acid sites that potentially shields ammonia from DBD-assisted decomposition. Here, we explore bulk amorphous oxides against (Al-incorporated) ordered silica: synthesized γ -alumina-coated SBA-15 and Al-MCM-41 (with isolated Brønsted acid sites) and their siliceous parents. Ordered materials exhibited higher ammonia yields than non-ordered oxides, extending literature insights for silica to γ -alumina, and the Al-incorporation into ordered silica improved performance and increased ex situ ammonia uptake. We further explored this ammonia adsorption-desorption and its decomposition under DBD environment on aluminosilicate zeolites with the added benefit of high dielectric constants. We systematically probed ammonia decomposition rates on a suite of zeolites with varying structure (i.e., framework type and pore size) and elemental composition (i.e., Si/Al ratio and cation identity) for a range of dilute feed concentrations mimicking the ammonia synthesis effluent. Together, these results inform the rational design of aluminosilicates to optimize DBD properties, catalytic activity, ammonia adsorption/desorption, and energy yield of DBD-assisted ammonia reactions.

Kinetic Analysis of CO Methanation Over PtSn/ γ -Al₂O₃ Catalysts

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Biomass is an important renewable resource, and the technology to produce energy and chemicals from biomass has developed rapidly over the past two decades. The key requirement for converting biomass into industrial products is the removal of oxygen atoms and the reduction of carbon atoms. - Past studies have shown that the bimetallic catalyst PtSn₂/ γ -Al₂O₃ has significantly improved selectivity for alcohols and aldehydes (desired products) in the hydrodeoxygenation (HDO) reaction of propionic acid compared to monometallic catalysts, from 50% to about 95%. In addition, the desired reaction rate also increased during the run, indicating that the catalyst underwent surface reorganization during the run. This phenomenon challenges the definition of basic kinetic parameters such as the reaction rate per active site (TOF), which are necessary for reactor design and scale-up. As the active sites change over time, characterization techniques applied to fresh catalysts may no longer be an accurate description of the reaction process. Here, we probe the interactions of key functional groups in the HDO mechanism (i.e., carbonyl, double bond, and CO) with bimetallic catalysts by using independent reactions such as acetone hydrogenation, olefin hydrogenation, and CO methanation to better understand the effect of tin on the catalytic performance.

Characterization of structure and composition in membrane electrode assembly with nanoalloy catalysts ultralow platinum loading in correlation with PEM fuel cell performance

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Proton Exchange Membrane (PEM) fuel cells are promising electrochemical energy conversion devices, where the membrane electrode assembly (MEA) with platinum catalysts plays a critical role in achieving high performance. A major challenge in PEM fuel cell performance is to achieve activity and durability of the catalyst at low loading of platinum. We have been developing nanoalloy catalysts by alloying platinum (Pt) with different transition metals (e.g., Ni, Fe, and Co) with ternary compositions for electrocatalytic oxygen reduction. This poster presents recent results of our investigation of the catalysts and MEA, with the goal of optimizing Pt usage, reducing costs, and improving performance. In addition to achieving precise control over Pt loading on the nanoalloy catalysts supported by carbon materials, we systematically studied the structural changes of the catalysts in MEA before and after fuel cell operation using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The ultralow Pt-loading MEAs are shown exhibit superior catalytic activity and good durability compared with traditional high-Pt loading MEAs, underscoring their potential for cost-effective fuel cell commercialization upon an in-depth understanding of the factors controlling the durability.