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SWCS Southwest Catalysis Society

SOUTHWEST CATALYSIS SOCIETY

2026 SPRING SYMPOSIUM

Friday, May 1, 2026

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The SWCS officers and I welcome you to the 2026 Southwest Catalysis Society Spring Symposium, Friday, May 1, 2025, at the University of Houston.

We are delighted to present six invited speakers' presentations at this year’s symposium. The 2026 SWCS Excellence in Applied Catalysis Award will also be presented. Furthermore, meritorious posters presented by students and postdocs will be identified with Best Poster Awards. See Page 3 for an outline of the Program.

The 2026 Spring Symposium registration fee is $20 for students and post-doctoral researchers, and $60 all other attendees. The fee includes North American Catalysis Society and SWCS annual membership dues, coffee/snack break, and lunch. Event tickets and receipts will be sent via e-mail, so please be prepared to enter your e-mail address when you register.

Please see page 4 for meeting venue and parking locations.

If you have colleagues who cannot attend the Symposium and wish to continue their membership in the NACS/SWCS, please forward this program to them. Membership dues (same pricing as the registration fee above) and corporate donations should be sent to our Treasurer, Prasanna Dasari (see contact information at left).

We hope you enjoy the Symposium!

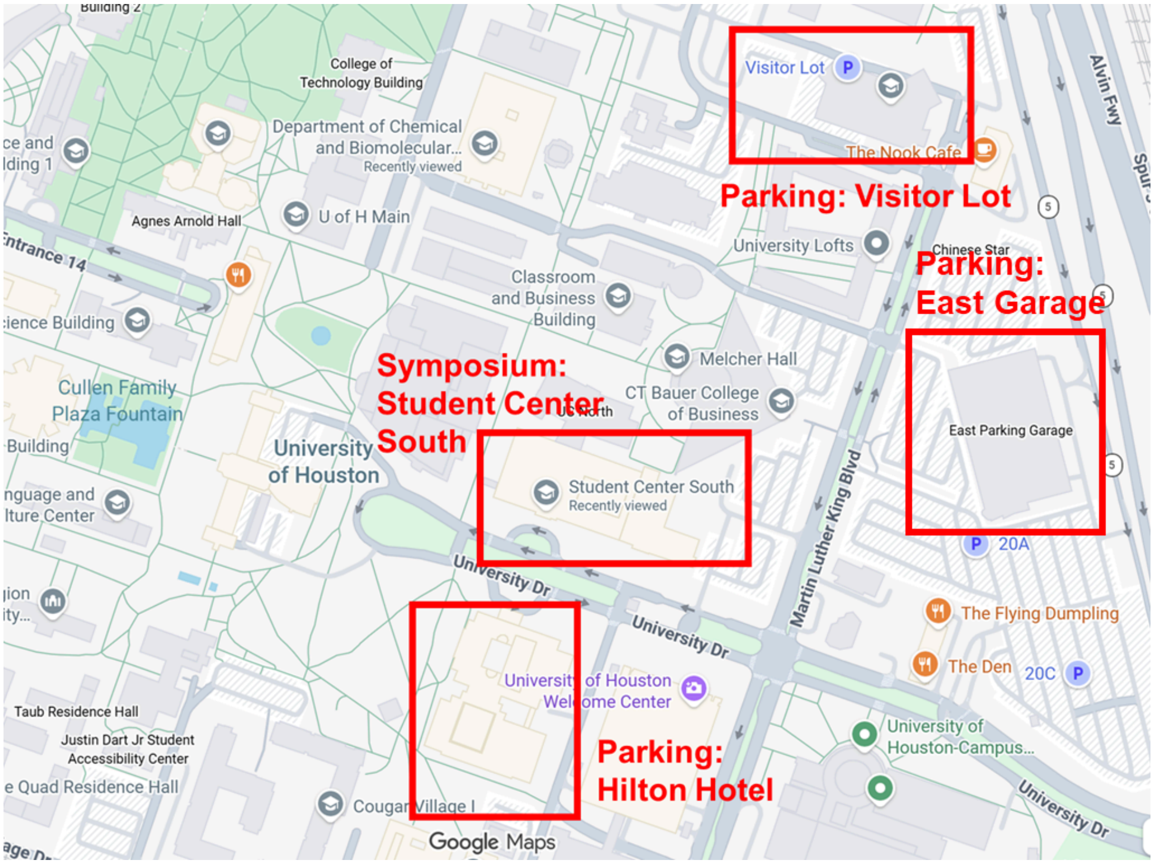
Joaquin Resasco

SWCS Chair
Assistant Professor
Department of Chemical Engineering
University of Texas at Austin

2026 Program

All talks & posters will be held in the Ballroom at the Student Center South

8:00 AM	**Ballroom Opens**
8:15-8:55 AM	**Registration and Poster Setup**
8:55 AM	**Welcoming Remarks – Joaquin Resasco, Chair**
	Session Chair: Tsatsa Battsengel, DOW Chemical
9:00 AM	**Randall Meyer**, Exxon Mobil *Early Stage Research for Propane Dehydrogenation Catalysts*
9:45 AM	**Eranda Nikolla**, University of Michigan *Engineering Cationic Centers in Mixed Metal Oxides for Enhanced Catalysis*
10:30 AM	**Coffee Break**
	Session Chair: Tom Senftle, Rice University
10:45 AM	**Manish Shetty**, Texas A&M University *Beyond 'Closer is Better': Proximity Effects in Tandem CO_2 Hydrogenation*
11:30 AM	**Lunch Break and Poster Session**
	Session Chair: Omar Abdelrahman, University of Houston
12:50 PM	**Applied Catalysis Award, presented by Omar Abdelrahman** **James Brazdil** **Winner, 2026 SWCS Excellence in Applied Catalysis Award** *Perspectives on Heterogeneous Catalyst Design Strategies: Past, Present, and Future*
1:45 PM	**Ian McCrum**, City College of New York *Solvation at the Electrode/Electrolyte Interface: Connecting DFT, UHV, and Electrochemistry*
2:30 PM	**Coffee Break**
	Session Chair: Jason Adams, Rice University
2:45 PM	**Julie Rorrer**, University of Washington *Advancing Chemical Upgrading of Complex Waste Streams through Mechanistic Insight and Automation of Analytical and Reactor Platforms*
3:30 PM	**Presentation of Poster Awards**
3:45 PM	**Closing Remarks**
4:00 PM	**Meeting concludes**



Symposium location:

University of Houston

Ballroom – Student Center South

Parking location:

Several visitor parking lots are available on the UH Campus. Information regarding visitor parking and rates for campus lots can be found here:

https://www.uh.edu/parking/parking-on-campus/visitor/

The parking lots closest to the Student Center South are the UH Hilton Hotel, the Welcome Center North Garage, the East Garage, and the Elgin Street Garage

An map of parking at the University of Houston can be found here:

https://www.uh.edu/parking/_images/maps/campus-parking-map-8.21.jpg

Early Stage Research for Propane Dehydrogenation Catalysts

Randall Meyer

Senior Research Associate – Active Materials Development and Scale Up, ExxonMobil Technology and Engineering Company

ExxonMobil has a long history of using X-ray Absorption Spectroscopy to aid their catalyst development programs. We will detail a few examples of studies designed to improve our understanding of zeolite encapsulated metal catalysts with specific application in alkane dehydrogenation. In order to assess the potential regenerability of metal catalysts, *in-situ* studies have been performed at both the Advanced Photon Source (APS) and at National Synchrotron Light Source (NSLS). Specifically work in collaboration with the Instituto de Tecnología Química (ITQ) has examined the creation of Pt and Pt alloy nanoparticles in CHA [1] and MFI [2] frameworks and their stability under multiple cycles of oxidation and reduction. More recently we have examined at PtSn/hydrotalcite catalyst which shows promising regeneration properties. Challenges associated with the commercialization of these materials will be discussed.

[1] M. Moliner, J. E. Gabay, C. E. Kliewer, R. T. Carr, J. Guzman,. G. L. Casty, P. Serna, A. Corma *Journal of the American Chemical Society* **138** (2016) 15743

[2] L. Liu, M. Lopez-Haro, C. W. Lopes, S. Rojas-Buzo, P. Concepcion, R. Manzorro, L. Simonelli, A. Sattler, P. Serna, J. J. Calvino, A. Corma *Nature Catalysis* **3** (2020) 628

Biography

Randall J. Meyer obtained his PhD degree in Chemical Engineering at the University of Texas at Austin in 2001, under the joint supervision of Prof. David Allen and Prof. Buddie Mullins.

After graduation, Randall was awarded an Alexander von Humboldt post-doctoral fellowship to continue his education at the Fritz Haber Institute in Berlin where he worked in the department of Chemical Physics for Prof. Hajo Freund until Spring of 2004 whereupon Randall moved to the University of Virginia where he worked as a post-doctoral researcher under Prof. Matt Neurock.

Randall began his career as a faculty member in the Chemical Engineering Department at the University of Illinois at Chicago in January of 2006. In 2007 Randall won the NSF CAREER award. In 2011, he was promoted to the level of Associate Professor with tenure. However, in summer of 2014 Randall moved from industry to academia, joining the Catalysis Section in Corporate Strategic Research at ExxonMobil Research and Engineering facility in Annandale NJ. In summer of 2025, Randall was relocated to Spring TX where he now serves as a Senior Research Associate in Active Materials Development and Scale Up. He has authored over 100 publications and 6 patents in which he has used a variety of techniques to study heterogeneous catalysis focusing mostly on a combination of density functional theory, kinetic modeling and X-ray absorption spectroscopy.

Engineering Cationic Centers in Mixed Metal Oxides for Enhanced Catalysis

Eranda Nikolla
Professor, Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan

Controlling the nature and uniformity of catalytic sites is critical for optimizing the reactivity of heterogeneous catalysts for targeted reactions. However, achieving consistent site uniformity in conventional supported catalytic systems presents a significant synthetic challenge. Emerging alternatives are compositionally versatile, non-stoichiometric mixed metal oxides belonging to the perovskite family (general formula $A_{n+1}B_nO_{3n+1}$). These oxides are highly tunable platforms for hosting well-defined catalytically active cationic sites, while simultaneously providing tailored ionic, electronic, and optical functionalities. Their flexible frameworks enable precise control over cation composition, defect chemistry, and structure-property relationships. Moreover, the intrinsic cation mobility within these oxides allows for reversible structural transformations that dynamically reshape catalytic function, capabilities difficult to access with conventional catalyst materials.

In this talk, I will illustrate how cations in non-stoichiometric mixed metal oxides can be engineered to: (i) drive electron-mediated oxygen reduction/evolution with high efficiency, (ii) leverage photon-induced excitations to modulate adsorbate binding on oxide surfaces, and (iii) undergo exsolution/reincorporation through reversible cation mobility to drive fundamentally different reaction pathways, each demanding a distinct active-site architecture. These examples will highlight the potential of tuning mixed metal oxide stuctures belonging to the perovkite family for enhanced catalysis.

Biography

Eranda Nikolla is a Professor of Chemical Engineering, Materials Science and Engineering, and Macromolecular Science and Engineering at the University of Michigan-Ann Arbor, MI. Her research interests focus on the development of heterogeneous catalytic materials for chemical and electrochemical energy conversion/storage processes. As an integral part of engineering catalytic/electrocatalytic structures, Dr. Nikolla has implemented a paradigm which involves a combination of controlled synthesis, advanced characterization, kinetic measurements and quantum chemical calculations to unearth the underlying mechanism that governs their catalytic performance for targeted reactions. Her group's impact to catalytic science has been recognized through the National Science Foundation CAREER Award, the Department of Energy Early Career Research Award, Camille Dreyfus Teacher-Scholar Award, the Young Scientist Award from the International Congress on Catalysis, the 2021 Michigan Catalysis Society Parravano Award for Excellence in Catalysis Research and Development, the 2022 ACS Catalysis Lectureship for the Advancement of Catalytic Science, the 2023 Maria Flytzani-Stephanopoulos Award for Creativity in Catalysis and 2024 Excellence in Catalysis Award, Catalysis Society of Metropolitan New York.

Beyond ‘Closer is Better’: Proximity Effects in Tandem CO_2 Hydrogenation

Manish Shetty
Assistant Professor, Department of Chemical Engineering, Texas A&M University, College Station, Texas

For catalysis to play a pivotal role in the construction of a sustainable chemical industry, engineering catalytic materials that are earth-abundant, active, selective, and stable are desirable. Development of such transformational catalytic technologies requires fundamental understanding of the underlying chemical transformations on a molecular level. The insights can then be exploited towards tailored synthesis of molecular architectures that can modulate chemical transformations.

For instance, tandem chemical conversions underpin both conventional and emerging processes, from alkane isomerization to CO_2 upgrading to fuels. These conversions are often treated as sequential reactions and guided by the qualitative proximity-criterion “the closer the better”, overlooking how reaction networks, thermodynamics, and transport govern site-proximity effects, in addition to mobility of catalytic moieties (e.g., cations or oxide clusters).

We investigate their origins for CH_3OH-mediated tandem CO_2 hydrogenation (TCH) over oxide/zeolite catalysts by analyzing reaction pathways, thermodynamics, and transport processes across length-scales. We reveal molecular-scale nuances that influence overall rates and selectivity. Specifically, we show that CH_3OH decomposition to HCHO and CO on redox sites influences hydrocarbon-pool mechanism in zeolite micropores through Prins condensation and carbonylation pathways, respectively. To elucidate how transport dictates rates at reactor-scale, we propose a transport-resistance model quantifying intrapellet and zeolite intrapore diffusion at different proximities. Crucially, the approach is generalizable to other tandem and multicomponent systems, where diffusion constraints and catalyst design remain a critical factor in the production of sustainable fuels and chemicals.

Biography

Prof. Manish Shetty is an Assistant Professor in the Artie McFerrin Department of Chemical Engineering at Texas A&M University, since Fall 2021. He obtained his bachelor’s in chemical engineering from the Indian Institute of Technology Bombay in 2011 and his Ph.D., also in Chemical Engineering, from the Massachusetts Institute of Technology in 2017. Post PhD, he completed his postdoctoral training at the University of Minnesota and the Pacific Northwest National Laboratory (PNNL) between 2017- 2021. His research has centered around a wide range of kinetic, synthetic, spectroscopic, and theoretical approaches to study chemical transformations at catalytic surfaces. At Texas A&M, two of his research thrusts focus on utilizing chemical precursors such as carbon dioxide, and converting them into fuels, chemicals, and liquid carriers, and enhancing catalytic recycling and upcycling of plastics. His work has been recently recognized by the Ralph E Powe Junior Faculty Enhancement Award and ACS PRF Doctoral New Investigator Award. He is also on the Early Career Advisory Boards of ChemCatChem, ACS Sustainable Chemistry and Engineering, and Journal of Catalysis.

Perspectives on Heterogeneous Catalyst Design Strategies: Past, Present and Future

James Brazdil
Adjunct Professor, Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas

The heart and soul of heterogeneous catalysis science have always been the alchemy behind finding the right combination of inorganic materials that would catalyze a targeted chemical transformation. The arc of history around the discovery and improvement of heterogeneous catalysts for commercial chemical processes reaches back to the very beginning of the 20th century with the discovery and commercialization of the Haber-Bosch process for ammonia synthesis. The osmium and uranium used by Haber in the laboratory to catalyze his process were not practical for commercial application. It took the work of Alwin Mittasch to painstakingly identify, through trial and error, an iron/calcium/silica/alumina catalyst for the first commercial plant in 1913. This heralded the Age of Discovery and Synthesis in catalyst development that stretched from Mittashch's work through about 1970. This was an era of catalyst development that was largely based on brute force testing of large numbers of known and synthesized inorganic materials for desired chemical transformations including hydrocarbon oxidation, hydrogenation, polymerization, hydrocarbon reforming and others, until the right one was identified that could be scaled to multi-ton chemical production for extended periods of operation. Many, if not most, of the commercial chemical processes we operate today are still based on catalysts discovered using this approach. The rapid development and application of both new and enhanced analytical instruments then made the characterization and physical understanding of known catalytic materials possible. This has made the ability to understand the structure and chemical environment of heterogeneous catalysts at the atomic-level possible. This new Golden Age of Catalyst Characterization, in combination with detailed understanding of the reaction mechanisms of catalytic transformations, produced the next stage for catalyst design methodology. This period focused, primarily, on ways to improve yield and selectivity of catalysts already used commercially. A new era we entered this century is based on the application of computers for both catalyst improvement and discovery that target new chemical reactions including those using bio-based feedstocks. This work is in its nascent stage of development and includes combinatorial experimentation, data mining, and the emerging field of artificial intelligence (AI). This presentation will provide examples of the application of the three catalyst design strategies over time from the scientific and patent literature and from personal research in the selective ammoxidation of propylene to acrylonitrile. Some perspectives will be provided on what the future may hold with respect to approaches to both the discovery and improvement of heterogeneous catalysts and processes for commercial application.

Biography

James F. Brazdil currently holds the position of Adjunct Professor at the University of Houston in the Cullen College of Engineering, William A. Brookshire Department of Chemical and Biomolecular Engineering. Prior to this, he served as Group Director, Process Chemistry and Catalysis research with Archer Daniels Midland Company in Decatur, Illinois before retiring in 2020. In this role he was responsible for the leadership of ADM's catalysis Research & Development (R&D) activities. This included oversight of internal and external laboratory programs, high throughput screening, and catalyst technology demonstration through the pilot phase and commercial scale-up. He previously was Research and Development Manager with INEOS Technologies in Naperville, Illinois where he was responsible for all the catalyst development efforts for INEOS's acrylonitrile business and tasked to support the business in maintaining its world-wide leadership position in technology, manufacturing, and catalyst sales.

He received his B.S. in chemistry from John Carroll University, summa cum laude, and his M.S and Ph.D. degrees in physical chemistry from Case Western Reserve University. He joined SOHIO in 1975 and has conducted both fundamental and applied research in the areas of hydrocarbon ammoxidation and oxidation catalysis, surface spectroscopy, solid state chemistry, and inorganic synthesis. He has over 100 patented inventions, largely in the field of selective oxidation catalysis and the commercial production of acrylonitrile, as well as several other pending U.S. and global patent applications. His patent portfolio also encompasses the emerging field of the catalytic conversion of bio-based feedstocks to produce industrial chemicals and nutrition additives. He has published extensively and presented numerous invited lectures on oxidation catalysis science. He has held technology leadership positions directing teams of technical professionals in the development of commercial catalysts and processes for SOHIO, BP and INEOS. He has been responsible for technical program delivery for his teams, as well as development and execution of the intellectual property strategy for the business. Jim currently consults part-time with client projects ranging from fundamental research to technology commercialization.

For his many technical accomplishments, Jim has received the Distinguished Researcher Award of the Energy and Fuels Division of the American Chemical Society in 2020. He has also received awards for his technical and leadership accomplishments including the 1989 Technical Achievement Award of the Cleveland Technical Societies Council, the 1990 PittsburghCleveland Catalysis Society Award in Catalysis, The Catalysis Society of Metropolitan New York 2001 Excellence in Catalysis Award, the 2002 Herman Pines Award in Catalysis from the Catalysis Club of Chicago and the 2020 Distinguished Researcher Award of the Energy and Fuels division of the American Chemical Society. He was selected as an American Chemical Society Fellow in 2014. He is a member of the American Chemical Society (ACS,) and has held numerous leadership positions in the organization including secretary, treasurer, and chairman of the Petroleum Division (now the Energy and Fuels Division), and secretary, treasurer, and chairman of the Cleveland Section. He has served as secretary, treasurer, and chairman of the Pittsburgh-Cleveland Catalysis Society and on the Editorial Board of Applied Catalysis.

Solvation at the Electrode/Electrolyte Interface: Connecting DFT, UHV, and Electrochemistry

Ian McCrum
Assistant Professor, Department of Chemical Engineering, City College of New York, New York, New York

The structure and dynamics of solvent and ions present at the electrode/electrolyte interface impact the activity and selectivity of the catalytic reactions which occur at this interface. The behavior of solvent is particularly important, as it dictates the ion and electric-field spatial distribution and can stabilize adsorbed reactive intermediates through electrostatic and hydrogen-bonding interactions. Interfacial solvent is difficult to study however due to the "buried" nature of this interface. We have recently developed an approach to quantify solvent-adsorbate interactions at the electrode/electrolyte interface through quantitative comparison of experimental measurements made in the solvated electrochemical environment with density functional theory calculations in a solvent-free environment. This quantitative comparison is enabled by careful consideration of sources of DFT error, including that from the choice of exchange-correlation functional. Results using this approach to understand how molecular and electronic properties of the adsorbate, such as its dipole moment and charge, impact adsorbate-solvent interactions will be discussed. We will additionally highlight what can be learned upon comparison with measurements made in ultra-high vacuum. Recent work from our group examining the electrode side of this interface – specifically the unique behavior of defect sites on alloy (electro)catalysts – will also be briefly discussed.

Biography

Ian T. McCrum is an Assistant Professor of Chemical Engineering at The City College of New York (CCNY) in New York, NY. He received his B.S. in Chemical Engineering from Clarkson University in 2012, his Ph.D. in Chemical Engineering from the Pennsylvania State University in 2017, and was then a postdoctoral fellow at Leiden University in the Netherlands from 2017-2020. He started his academic career as an Assistant Professor at Clarkson University in 2020, before moving to CCNY in 2025. He was awarded the NSF CAREER Award in 2024 and serves on the Early Career Editorial Board of the Journal of Catalysis. His research group is interested in using fundamental approaches to understand electrochemistry, surface science, and catalysis to enable the predictive design of better performing materials for renewable energy storage and sustainable chemical production.

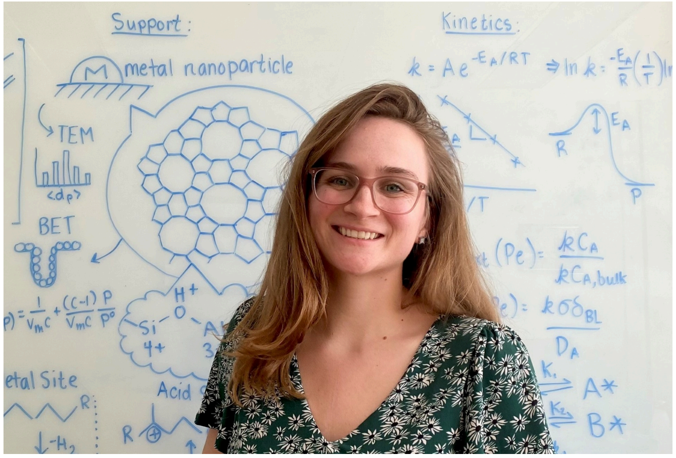
Advancing Chemical Upgrading of Complex Waste Streams through Mechanistic Insight and Automation of Analytical and Reactor Platforms

Julie Rorrer

Assistant Professor, Department of Chemical Engineering, University of Washington, Seattle, Washington

Advances in catalytic chemical recycling have enabled the conversion of low-value feedstocks, such as biomass and plastic waste, into fuels and chemicals to meet growing demand for energy and materials. The complexity and heterogeneity of mixed plastic waste pose several key challenges in developing scalable and economical technologies for its deconstruction and upgrading. These challenges include: (1) evaluating and promoting catalyst stability in the presence of contaminants and moisture, (2) rapidly identifying and quantifying product compositions to enable the development of explicit and rigorous kinetic models, and (3) developing reactor systems that respond to fluctuations in feedstock composition, availability, and cost. In this talk, we present recent work in the Rorrer group aimed at addressing these challenges through an integrated approach spanning catalysis, data analysis, and reactor design. We will begin by examining the impact of water on the mechanisms of polyethylene hydrocracking over metal-acid catalysts. We will then introduce custom analytical software we developed to accelerate reaction analysis using hydrogen-free polyethylene depolymerization as a case study. Finally, we will describe our progress in developing an automated, adaptive chemical reactor platform that is self-optimizing and responsive to variable feed conditions. Together, this work establishes a comprehensive framework driven by fundamental catalysis, product analytics, and reactor automation to address critical bottlenecks in the chemical conversion of waste plastics and complex feeds to produce high-quality hydrocarbon products.

Biography



Julie E. Rorrer is an Assistant Professor of Chemical Engineering at the University of Washington, Seattle. Her research group focuses on using heterogeneous catalysis for the chemical recycling of waste plastics and the production of renewable fuels and chemicals. She received her PhD in Chemical Engineering from UC Berkeley and her BS from Arizona State University. Prior to UW, she was a Beckman Postdoctoral fellow at MIT. Her recent awards include the ARPA-E IGNIITE Award, and the American Institute of Chemical Engineers 35 Under 35 Award. In addition to her work in catalysis, she is the founder of the ongoing educational initiative, ColorMePhD, which creates free coloring activities to explain current research in STEM to aspiring scientists and engineers.

POSTER ABSTRACTS

1. Autothermal Reactor Design and Kinetic Study of High-Temperature Homogeneous Oxidative Dehydrogenation of Ethane

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Steam cracking is widely employed in industry to produce ethylene, with naphtha or ethane as feedstock. Due to its endothermic nature, it requires elevated temperatures, typically in excess of 850 °C. A surge in ethylene production of approximately 6.2% was reported between 2021 and 2023, and the global market is projected to grow at a compound annual growth rate of about 7%, driven by its use in producing a variety of important products, including polyethylene, ethylene oxide, vinyl chloride, and others.

Albeit, efforts have been made to move towards producing ethylene by alternate methods, most notably ethane partial oxidation or oxidative dehydrogenation of ethane (ODHE) where most studies have focused on catalytic chemistry; however, these methods have not yet been commercially implemented. Nevertheless, limited work has addressed the influence of homogeneous chemistry, which can play a pivotal role even in catalytic systems under high-temperature conditions and may dominate under certain process regimes. Therefore, it is essential to independently corroborate such behavior. Considering its strong performance, homogeneous chemistry offers a more holistic advantage by simplifying overall modeling and facilitating process scale-up, especially when compared to heterogeneous or hybrid systems under specific conditions.

The present work aims to develop a global kinetic model for homogeneous (non-catalytic) ODHE based on 7 reactions and 8 species, with the objective of simplifying the interpretation of reaction pathways, reactor bifurcation, and potential scale-up analysis [1]. From a kinetic modeling perspective, previous studies have primarily focused on microkinetic models involving numerous species and reaction steps. Model predictions are compared with both literature data and experimental results to validate the approach and kinetic parameters, and to evaluate conversion and product distribution in terms of selectivity and yield under varying feed ratios, space time, and temperature conditions. Additionally, thermodynamics and the effects of characteristic time scales in determining isothermal and adiabatic conditions in a laboratory-scale tubular reactor are examined. Reaction pathway analysis, product cofeed experiments, the influence of cracking chemistry, and the overall modeling approach are also discussed.

The process is also characterized by nearly CO_2-free production. In traditional steam cracking, approximately 70% of the ethylene production cost is attributed to energy requirements. By utilizing exothermic heat to enable autothermal reactor operation (without external heat input) under a lumped thermal reactor configuration by leveraging thermal back-mixing and considering industrial constraints, millisecond-order space times are desirable to meet reactor volume limitations. Under these conditions, an ethylene yield of 45–48%, with ~58% conversion and ~83% selectivity, is predicted [2,3].

References:

[1] Imam SA, Bollini P, Balakotaiah V. A global kinetic model for high temperature homogeneous oxidative dehydrogenation of ethane. AIChE J. 2026;e70262. doi:10.1002/aic.70262
[2] Imam SA, Bollini P, Balakotaiah V. Design and analysis of a novel reactor for homogeneous oxidative dehydrogenation of ethane to ethylene. AIChE J. (In Review)
[3] Balakotaiah V, Imam SA, Bollini P, Pandit DM. Method and reactor for homogeneous oxidative dehydrogenation of ethane to ethylene. 2025; U.S. Patent Application Number # 63/893,329

2. Informing Thermo(electro)chemical Catalysis Through Electrochemical Corrosion Principles

Raul A. Marquez, Alyssa K. Uvodich, and Joaquin Resasco*
McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712
*resasco@utexas.edu

Corrosion science has historically been pivotal for understanding how materials behave under dynamic environments. Recent advances in catalysis have drawn on core concepts from corrosion science to inform mechanisms; a clear example is the use of mixed potential theory and galvanic coupling to explain spontaneous polarization at metal-liquid interfaces. Herein, I describe how corrosion measurements can capture the dynamics of thermocatalytic reactions that undergo galvanic coupling. Using aerobic alcohol oxidation driven by Pd corrosion as a probe system, we extract rate scaling trends, identify impurities, and diagnose inactivation using potentiometry, potentiodynamic polarization, polarization resistance, and electrochemical frequency modulation. Taken together, these techniques underscore the value of corrosion science principles for studying catalysts under dynamic environments.

3. Autothermal Reactor Design for Direct Natural Gas Conversion to Ethylene

Dhagash M. Pandit, Praveen Bollini, Vemuri Balakotaiah*
William A. Brookshire Department of Chemical & Biomolecular Engineering,
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Ethylene is among the highest-volume chemicals and plays a vital role in the petrochemical industry, serving as a key building block for numerous intermediates and polymers. However, its production remains largely dependent on the highly energy-intensive process of ethane steam cracking. Alternative routes such as oxidative dehydrogenation of ethane (ODHE) and oxidative coupling of methane (OCM) have been widely explored as lower-energy pathways to ethylene, but their commercialization has been hindered by challenges in heat management.

In this work, we demonstrate the feasibility of conducting these partial oxidation reactions in an autothermal reactor through a comprehensive bifurcation analysis. We use a multi-scale reduced order model that accounts for pore diffusion to analyze the ignition-extinction behavior during ODHE in a monolith reactor coated with a MoVTeNbOx (M1) catalyst. Our modeling results indicate that metallic monoliths with intermediate length, high substrate conductivity and high cell density are optimal to approach the so called "homogeneous lumped thermal reactor (LTR) limit" which leads to the best reactor performance (92% ethylene selectivity at 25% ethane conversion).

We compare OCM (La2O3/CaO-catalyst) and ODHE (M1-catalyst) from a kinetic perspective, highlighting the impact of species back-mixing and operating temperature on ethylene formation. The presence of oxygen gradient with uniform temperature improves ethylene selectivity in ODHE, whereas lower oxygen concentrations favor ethylene production in OCM. It is also shown that operation in external mass transfer regime can improve the ethylene yield in OCM because of the kinetic effects. Cofeeding ethane along with methane can improve ethylene selectivity up to 25% with appropriate amount of oxygen for which direct natural (shale) gas can be utilized. Two different configurations of shallow bed reactor are proposed to carry out such conversion. Our modelling results provide critical insights to design a CO2 (thermal) free reactor with high throughput, thereby aiding the scale-up of ODHE and OCM to commercial level.

References

1. Pandit, D. M., Bollini, P., & Balakotaiah, V. (2025). Optimization of monolith reactor design for autothermal oxidative dehydrogenation of ethane over a MoVTeNbOx catalyst. Chemical Engineering Journal, 509, 161266.

2. Pandit, D. M., Bollini, P., & Balakotaiah, V. (2025). Design and Optimization of a Novel Monolith Reactor for the Conversion of Natural Gas to Ethylene by Oxidative Coupling. Industrial & Engineering Chemistry Research, 64(50), 23979-23991

4. Au-Pd Single Atom Alloy Catalysts for Efficient Electrochemical CO_2 Reduction to CO

Jiwon Kim and Joaquin Resasco*
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Electrochemical carbon dioxide reduction (CO2RR) is a promising technology for converting CO_2 into valuable chemical products such as carbon monoxide (CO), formate, ethylene, and ethanol. Although multi-carbon products have significant value, their selective production remains challenging and less economically viable due to the complex reaction pathways involved in their generation. Monometallic Au and Ag are well known to be highly selective for CO_2 reduction to CO. However, their activity is limited due to sluggish CO_2 activation, requiring large overpotential to achieve appreciable reaction rates. In contrast, more reactive Pt-group metals facilitate CO_2 activation and subsequent formation of surfacebound CO at low overpotential but also promote the competing hydrogen evolution reaction (HER).

In this work, we design Au-Pd alloy catalysts as single-atom alloys to enhance CO_2 reduction performance toward CO. We find that introducing small amounts of Pd increases CO formation rates by promoting CO_2 activation, whereas further increases in Pd content reduce activity toward the desired product and leads to increased rates of HER. By electrochemically quantifying surface Pd and Au sites and normalizing catalytic rates accordingly, we reveal intrinsic activity trends across different Pd loadings. Using kinetic analysis and density functional theory (DFT) calculations, we correlate these trends with Pd active site motifs on the catalyst surface, where isolated Pd sites enhance CO_2 reduction activity while Pd ensembles favor hydrogen formation. These findings highlight that atomic-level tuning of active site motifs can improve efficiency and selectivity in CO_2-to-CO conversion, providing mechanistic insight for the rational design of more efficient CO_2RR electrocatalysts.

5. Decoupling Photon-Driven CO Desorption from Photothermal Heating on Pt Catalysts

Kenneth L. Kusima[1,2,3], Omar Abdelrahaman[1,2], Philip Christopher[1,4], and Lars C. Grabow[1,2,3]*
1. Center for Programmable Energy Catalysis (CPEC) University of Minnesota
2. William A. Brookshire Department of Chemical and Biomolecular Engineering University of Houston
3. Texas Center for Superconductivity (TcSUH) University of Houston
4. Department of Chemical Engineering University of California Santa Barbara
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Separating photochemical desorption from photothermal heating is a central challenge in light-driven catalysis. Using CO temperature-programmed desorption (TPD) from Pt/Al_2O_3 under visible illumination (440 nm), we rigorously compare two kinetic frameworks: (i) an additive photodesorption model with a parallel photochemical channel, and (ii) a heating-only model mapping photon absorption to an effective local temperature. Although both reproduce experimental TPD traces with equivalent fidelity ($R^2 = 0.991$), they diverge sharply in physical interpretability.

The isolated photodesorption rate scales linearly with photon flux and exhibits an Arrhenius barrier of ~20.7 kJ/mol, 6-7× lower than the dark thermal baseline, evidence of a mechanistically distinct channel. The heating-only model, by contrast, predicts superlinear intensity sensitivities (degree of rate control ≈ 7) and physically implausible effective temperatures exceeding 1,155°C at moderate flux. These results demonstrate that goodness-of-fit alone is insufficient for mechanistic assignment and establish deployable photokinetic descriptors such as apparent quantum efficiency and reduced photochemical barrier - for microkinetic modeling of photo-assisted catalytic cycles on metal surfaces.

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6. Tuning surface species on functionalized zeolites for propylene/propane separation

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The separation of C_3H_6 and C_3H_8 remains challenging due to their similar properties. Conventional zeolites lack tunability in pore environments, limiting control over separation performance. Herein, we propose a strategy to anchor the organic moieties onto Brønsted acidic aluminosilicates via strong acid-base interactions, enabling tunable surface functionality. Organic modifiers with different terminal functional groups (-COOH, -OH, $-NH_2$ and $-CH_3$) were introduced to modulate the electrostatic interactions within the pores, resulting in different adsorption behavior between C_3H_6 and C_3H_8.

Modification with n-propylamine, monoethanolamine, and ethylenediamine generates a single surface species, while glycine uniquely leads to multiple surface species, including glycinium, zwitterion, and diketopiperazine (DKP). The distribution of glycinium and zwitterion depends on the Si/Al ratio of the zeolite framework, and these species follow different pathways for DKP formation. This behavior demonstrates that surface speciation can be controlled to regulate adsorption interactions for targeted separation.

Glycine-derived species exhibit significantly stronger interactions with C3H6, resulting in a sixfold higher adsorption capacity for C_3H_6 compared to C_3H_8 at 308 K with a selectivity of 18 from single-component adsorption. Surface hydroxyl groups in BEA zeolites preferentially interact with C_3H_6, as evidenced by a higher heat of adsorption (-39kJ/mol) compared to C_3H_8 (-20 kJ/mol). The role of confinement is further supported by the reduced heat of adsorption (−10 kJ/mol) observed in FAU-based zeolites with larger pore sizes. This study provides an effective strategy for designing tunable zeolite systems with organic molecules for C_3H_6/C_3H_8 separation.

7. Interfacial engineering of electrochemical carbon dioxide electrolyzers for practical and stable operation

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Electrochemical carbon dioxide reduction reaction (CO2RR) can enable decentralized, energy-efficient chemical manufacturing by converting waste CO2 into value-added fuels and chemicals, reducing dependence on traditional supply chains. In this poster, I will highlight my doctoral research on the design of porous solid electrolyte (PSE) reactors, which leverage ionic transport and molecular transformations to deliver electrolyte-free liquid products with high carbon efficiency. I will also discuss engineering strategies to mitigate salt formation in membrane-electrode assemblies (MEAs) in order to extend their operational stability.

8. Functional Group Effects in Oxygenate–Hydrocarbon Co-Processing over H-ZSM-5

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The co-processing of oxygenated bio-derived feeds with conventional hydrocarbons in fluid catalytic cracking (FCC) units presents opportunities for renewable carbon integration. However, bio-derived feeds introduce challenges associated with oxygenates reactivity, catalyst stability, and variability in feedstock composition. Developing a fundamental understanding of how specific oxygenate functionalities influence hydrocarbon conversion and product selectivity is critical for their effective implementation. Here, we investigated the impact of common oxygenate functionality on n-hexane cracking over H-ZSM-5 (Si/Al = 140) under FCC-relevant conditions (500 °C). Oxygenates were selected based on functional group chemistry to probe differences in adsorption strength, reaction intermediates, and deoxygenation pathways. At low partial pressures (<9 kPa), ethanol and diethyl ether exhibited minimal impact on n-hexane cracking catalytic activity and stability, while also readily undergoing selective dehydration to ethylene. At elevated partial pressures (>9 kPa), ethanol competitively adsorbed with hexane and reduced its surface coverage resulting in a loss of cracking activity. In contrast, methanol resulted in a broader product distribution, including methane, propylene, C5+ species, and aromatics, consistent with methanol-to-olefin pathways and an apparent increase in overall n-hexane conversion. These findings demonstrate the complex interactions between oxygenates and hydrocarbons on acidic zeolite catalysts, providing insights for catalyst design in FCC co-processing applications.

9. Generalizing Cation Effects on the Hydrogen Evolution Reaction

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Electrochemical water splitting offers a promising pathway for storing intermittent renewable energy in chemical bonds. While most studies focus on engineering catalyst active sites, the microenvironment around the active sites – particularly electrolyte cations – also plays are critical role in governing reactivity[1,3]. However, the mechanism through which cations influence electrocatalysis is still a topic of intense debate. Among the proposed mechanisms, two more widely discussed perspectives suggest that cations either modify adsorbate binding energies or alter interfacial water structure. While these frameworks capture important aspects, they do not fully explain all experimental observations, motivating the development of more general models.

To date, most studies of cation effects have focused on alkali metal cations, with comparatively limited exploration of organic cations in aqueous medium[4]. Here, we investigate the effect of organic tetraalkylammonium cations on the alkaline hydrogen evolution reaction (HER). Unlike alkali metal cations, these organic cations enable systematic tuning of properties such as size and hydrophobicity via alkyl chain length, as well as targeted functionalization to decouple the roles of interfacial water structure and electric fields. Additionally, they minimize Lewis acid–base interactions, which are often invoked for alkali metal cation effects but are weak or absent for tetraalkylammonium cations.

Rotating disk electrode measurements reveal that HER activity increases with organic cation size for reactive metals (Pt, Pd, Ir, Ni), while the trend reverses for noble metals (Au, Ag, Cu). Molecular dynamics simulations further elucidate the spatial distribution of these organic cations within the electric double layer and its impact on local electric fields. Together, these experimental and computational insights support a distinct framework for understanding cation effects, in which cations modulate the local electric field experienced by adsorbates and transition states at the catalyst surface, thereby altering reaction free energy barriers and enabling a more general description of cation effects.

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10. Tuning Gallium–Zeolite Interactions for Selective Aromatic Production from Ethanol and Ethylene

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Sustainable aviation fuel (SAF) produced via Hydroprocessed esters and fatty acids is deficient in aromatic content (~5%), requiring blending with fossil-derived BTX to meet ASTM D7566 specifications. Ethanol Dehydroaromatization over Ga/H-ZSM-5 offers a renewable single-step route to jet-range aromatics, yet the underlying reaction network and the specific catalytic role of Ga remain poorly resolved.

We report that complete ethanol conversion is a necessary condition for aromatic and C5+ formation. Time-on-stream deactivation experiments show that aromatic selectivity collapses to zero at the precise moment measurable ethanol and diethyl ether (DEE) appear in the effluent. DEE cofeed experiments rule out DEE as an inhibitor, establishing a mechanistic distinction from methanol-to-hydrocarbons: unlike DME, DEE cannot re-enter the hydrocarbon pool, imposing a stricter conversion threshold. Ethylene cofeed studies reveal an aromatic selectivity volcano with ethylene partial pressure and a crossover from net ethylene production to consumption- kinetically decoupling the ethanol dehydration step from the downstream oligomerization-aromatization network.

Iso-conversion ethylene dehydroaromatization experiments across Ga/Al = 0–2 demonstrate that Ga selectively promotes C4 to aromatics conversion while leaving C2–C3 and C5–C8 selectivities unchanged- localizing Ga's function to C4 dehydrogenation/cyclization. Dual normalization of ethylene consumption rates by Brønsted acid sites (H+) and surface Ga3+ (XPS) quantifies the active vs. spectator Ga fraction: rates per H+ saturate at Ga/Al ≈ 0.5 while rates per surface Ga3+ collapse 20-fold, revealing that most surface Ga at high loadings is catalytically inactive.

Liquid-phase ion exchange (LIE) with centrifugal washing outperforms IWI, SSIE, and WI (constant nominal Ga/Al ratio of 1) in both aromatic selectivity and stability. XPS/SEM-EDS analysis shows LIE uniquely induces mild surface dealumination, producing the lowest surface Ga enrichment ratio (2.69 vs. 4.8–8.6) and highest bulk Ga incorporation. In-situ FTIR under H2 flow reveals four GaHx bands (2017, 2040, 2065, 2089 cm−1) at Si/Al = 11.5- extending prior speciation studies into the paired-Al-site regime.

11. Designing Crystallization Pathways for Small-pore Zeolites through the use of Cooperative Structure-directing Agents

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Zeolites are crystalline aluminosilicates with a variety of porous networks that are indispensable for diverse industrial applications. Zeolite synthesis relies on the use of inorganic and/or organic structure-directing agents (SDAs) to stabilize the porous networks and tailor their physicochemical properties. In this presentation, we will discuss how the use of two more SDAs synergistically enhance the efficiency of zeolite crystallization. Our studies include organic-free syntheses of zeolite CHA wherein we show that partial substitution of K+ with other monovalent cations (Na+, Cs+) or divalent cations (Ca2+, Mg2+, Sr2+) can reduce the time of synthesis by an order of magnitude while significantly lowering the temperature compared to conventional syntheses. Furthermore, recent studies have shown that the judicious use of multiple SDAs can have significant effects on and the number and distribution of aluminum site.

Here we will also discuss how this approach has been applied to syntheses of zeolites SSZ-39 (AEI framework) and SSZ-13 (CHA) using combinations of inorganics and organics. Our findings reveal a clear distinction between cooperative and competitive interactions between inorganic SDAs when using structurally similar but chemically distinct OSDAs. Moreover, the identity and concentration of inorganic SDAs are also shown to play a critical role in influencing the crystallization mechanism, tailoring properties such as crystal morphology and defect density, and controlling the stability of metastable phases. Collectively, these observations suggest that the rational optimization of structure-directing agent pairings enables the design of more efficient synthesis strategies, offering novel pathways toward the precise control of zeolite crystallization and their properties for diverse industrial applications.

12. Density functional theory study on tuning metal–support interactions to design sintering resistant metal–oxide catalysts

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Heterogeneous catalysis plays a central role in fuel processing, emissions control, and chemical manufacturing, all of which are critical to modern energy infrastructure. However, catalyst deactivation and poor long-term catalyst stability remain major bottlenecks in achieving sustainable and economically viable processes, in which sintering is one of the major processes. Sintering occurs primarily via Ostwald ripening (OR) and particle migration–coalescence (PMC), which are governed by atomic binding energy and metal–support adhesion energy respectively. These mechanisms are intrinsically linked through metal–support interactions (MSI) and this interplay leads to a volcano-type relationship in sintering resistance, where both weak and excessively strong interactions accelerate catalyst deactivation and optimal stability is achieved at an intermediate regime.1 In this work, atomistic models of metal–oxide interfaces are developed and adhesion energies of transition metals (e.g., Fe, Cu, Au, Pd, Ag, Pt) on oxide supports such as MgO, Al_2O_3, TiO_2, CeO_2, SiO_2, and ZrO_2 are systematically computed using Density Functional Theory (DFT). A systematic dopant method, incorporating transition metal inclusion into supports, alloying within metal clusters, and surface enhancement is utilized to adjust MSI and get optimal adhesion properties. Computed adhesion energies are further correlated with fundamental material descriptors, including oxophilicity and alloy formation energies to establish predictive relationships. This approach enables the rational identification and design of catalyst systems with enhanced resistance to sintering under realistic operating conditions.

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13. Humidity-Driven Direct Air Capture (DAC) with Mixed Metal Hydroxides

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The Moisture Swing Adsorption (MSA) presents an opportunity for effecting Direct Air Capture (DAC) at a single temperature and is characterized by low energy consumption and operational simplicity. In this approach, sorbents adsorb CO_2 under dry conditions and subsequently release it at elevated relative humidity levels. Over the past decade, MSA-DAC has been predominantly demonstrated using polymeric ion-exchange resins that incorporate carbonate anions, which capture CO_2 as bicarbonate under dry conditions and release it in humid conditions. Although inorganic DAC sorbents have shown proven performance in temperature- and pressure-swing systems, their application in moisture-swing adsorption remains largely unexplored. In this study, we investigate our robust, earth-abundant porous nickel hydroxides for moisture-swing DAC applications using dynamic breakthrough experiments coupled with in situ FTIR spectroscopy. These materials exhibit stable cyclic working capacities of 0.25–0.30 mmol/g under dry CO_2 adsorption and humid argon regeneration, comparable to adsorption capacities reported for moisture-swing systems. FTIR analysis shows that reversible CO_2 capture is associated with kinetically labile bicarbonate species, while monodentate and bidentate carbonate species remain strongly bound at room temperature, limiting full regeneration. Cyclic performance is further constrained by incomplete water desorption. To the best of our knowledge, this work represents the first demonstration of cyclic MSA-DAC on a purely inorganic hydroxide platform, supported by direct spectroscopic evidence of bicarbonate–carbonate speciation. These findings establish a mechanistic framework for inorganic moisture-swing systems, highlighting the roles of hydroxyl density, water removal, and carbonate binding strength in governing reversibility.

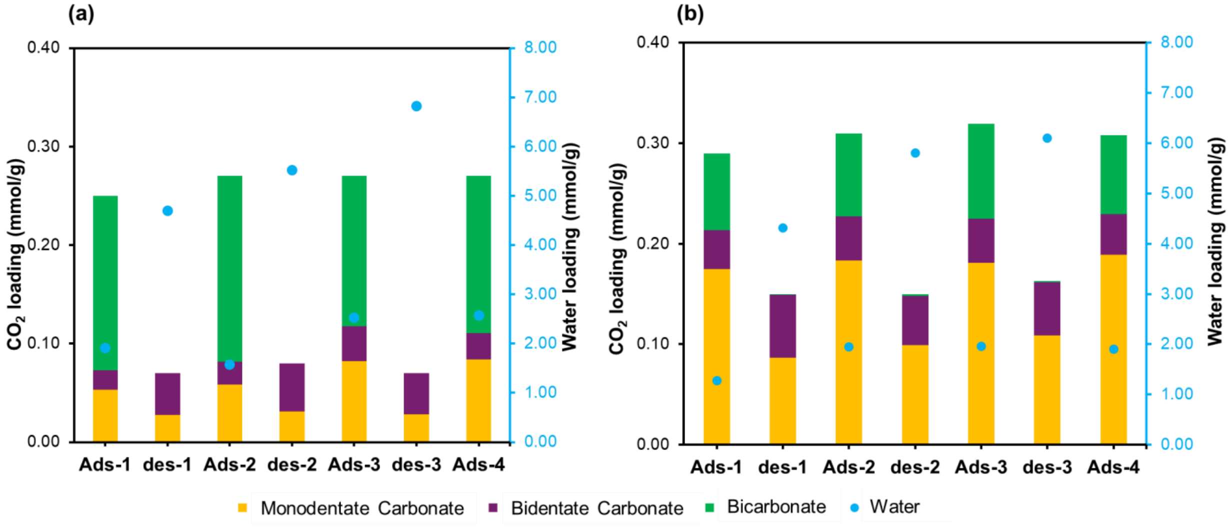

Figure 1: Cyclic moisture-swing adsorption on (a) α-Ni(OH)$_2$ and (b) α-NiCe$_{0.1}$(OH)$_x$, showing CO$_2$ uptake and surface species distribution after each adsorption (Ads) and desorption (des) step. Stacked bars represent CO$_2$ uptake resolved into monodentate carbonate, bidentate carbonate, and bicarbonate species from FTIR analysis, and points indicate water loading.

14. Standard Potentials of Initial Electron Transfer Steps in Redox Degradation Mechanisms of Per- and Polyfluoroalkyl Substances

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Per- and polyfluoroalkyl substances (PFAS) are persistent environmental contaminants that resist thermal, chemical, and biological degradation, thereby posing a significant challenge for effective remediation technologies. Emerging treatment approaches rely on redox-driven activation. Therefore, quantitative knowledge of PFAS redox thermodynamics is essential for assessing the feasibility of degradation. Here, density functional theory calculations were performed to determine aqueous-phase standard oxidation and reduction potentials for 19 environmentally relevant PFAS, including perfluorocarboxylates (C4-C9), perfluorosulfonates (C4-C9), fluorotelomer acids and sulfonamides, and polyfluoroether, GenX. Across all classes, degradation is governed by the initial electron-transfer step, which sets the thermodynamic threshold for activation. At the same time, subsequent bond-cleavage reactions are exergonic and have low activation barriers. PFCAs oxidize at narrowly distributed potentials (2.47–2.52 V vs SHE), followed by spontaneous decarboxylation. In contrast, reductive initiation of PFCAs and PFSAs requires highly negative potentials (−2.5 to −2.7 V vs SHE) to access radical dianions. Partial fluorination lowers oxidation thresholds for fluorotelomer carboxylates (1.66–1.96 V vs SHE), and sulfonamide substitution reduces both oxidative and reductive barriers relative to sulfonates. GenX follows PFCA-like oxidative initiation but preferentially undergoes reductive ether cleavage. Alignment of PFAS redox potentials with photocatalyst band edges reveals that oxidative initiation is broadly accessible on common metal oxides, whereas direct photoreduction is restricted to highly reducing materials. These results provide a quantitative framework for assessing the thermodynamic feasibility of redox-initiated PFAS degradation pathways and for designing photocatalytic and electrochemical treatments.

15. Quantitative Interpretation of Propane Dehydrogenation Kinetics Over Spatially Non-Isothermal Joule-Heated Platinum-Carbon Felts

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Joule heating or resistive heating is one of the electrification technologies that shows a potential for scale-up without compromising with efficiency and addresses the on-going rise in CO2 emissions. One of the reasons for improved performance of the joule heated reactor compared to conventional heating reactors is proposed to be due to the electron flow through catalyst layer resulting in changes in active sites and the reaction mechanism. However, it is important to understand that the temperature gradients encountered within the joule heated catalyst structure may contribute to significant differences in observed performance compared to conventional heated reactors under similar reaction feed conditions. Certain commonly employed substrates like carbon fibers which exhibit high heating and cooling rates, can also have large temperature gradients rendering quantitative interpretation of reactor performance exceedingly challenging.

In this study we present an analysis of lab-scale propane dehydrogenation data obtained over 5 wt% Platinum loaded carbon felt being used as both heating substrate and catalyst support. During the reaction, the temperature maps of the surface of carbon felt for different power settings under joule heating were analyzed using an infrared camera. The corresponding radial gradients were obtained using energy balance calculations and from the overall temperature distribution corresponding to both spatial and radial domains, it was observed that the thermal gradients were observed to be greater than 150°C within the volume of carbon felt at different power settings. These gradients were hence included in the kinetic analysis of propane dehydrogenation chemistry with both gas-phase thermal reaction rates and catalytic rates along with deactivation information to understand the overall performance. The rate expressions were validated using conventional heating experiments specific to the Pt-CF catalyst under similar reaction feed conditions, from which the kinetic parameters were obtained. We observed that ignoring gas-phase contribution can lead to underestimating the rates by 2 orders of magnitude when compared with the experimental rates measured at power settings. Also, for the case, when the rates were calculated at Tavg considering both gas-phase and catalytic contributions, the estimated rates were 3-5 times lower. However, when considering the radial and spatial thermal gradients, the rates are predicted to be in the same order of magnitude, and closer to the experimental values compared to the other cases. This study highlights that the temperature being the salient factor for determining the performance of joule heated reactors, and not necessarily the electron density changes, for propane dehydrogenation over Pt-carbon catalysts.

16. Tuning the acid site strength of Nb2O5 to probe the effect of acid strength has on Vinyl Acetate Catalysis

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Vinyl acetate (VAM) is a key industrial intermediate typically used in the polymer industry to produce materials such as polyvinyl alcohol (PVA), polyacrylonitrile (PAN), and vinyl acetate-ethylene copolymer emulsions (VAE).[1-3] VAM is synthesized through an acetoxylation of ethylene process by which a gaseous mixture of ethylene, acetic acid, and oxygen react over a PdAu based catalyst.[4-6] The role of surface acidity on VAM catalysis was recently studied, and it was found that acid sites in aluminosilicates improved the activity and selectivity of the process by generating more active sites.[7]

Niobium oxide (Nb_2O_5) is a well known acidic solid material. Niobic acid ($Nb_2O_5 \bullet nH_2O$) contains both Lewis and Bronsted acid sites. The metal oxide contains NbO_6 octahedra and NbO_4 tetrahedra that act as the Lewis acid sites while the highly polarized Nb-O bonds function as sites for OH groups that act as Bronsted acid sites.[8] Additionally, the surface acidity of Nb_2O_5 can be tuned by calcining niobic acid to generate other Nb_2O_5 polymorphs that have reduced surface acid site concentration.9

In this work, we supported PdAu particles on different polymorphs of Nb_2O_5 to probe the effect of acid sites on VAM catalyst performance. We show that there is a volcano-like relationship between catalyst activity and Nb_2O_5 surface acidity.

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17. Isopotential Electron Titration for Quantifying the Charge Transfer of Catalytic Chemistries

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Isopotential Electron Titration (IET) is a rapid, non-destructive technique to quantify charge transfer between a surface and adsorbate in-situ. The extent of charge transfer, a normalized molar quantity of electrons transferred between adsorbate and surface, can be used to identify optimal reaction pathways for catalytic chemistries. However, measuring the extent of charge transfer in a system that contains an ensemble of different adsorbates on a surface is elusive. This is due to each moiety simultaneously generating charges that are experimentally indistinguishable from the individual charges of other moieties, posing a barrier to gaining fundamental insight from macroscopic observables. To overcome this challenge, a model was developed using the experimentally measured extents of charge transfer of hydrogen and oxygen to understand a water synthesis surface reaction. Results showed that hydrogen reversibly donated 0.19% |e|/H upon adsorption, whereas oxygen reversibly withdrew 0.11% |e|/O upon adsorption.1 Using these inputs, along with the activity and composition of the bulk through a residence time distribution, the model consistently predicted the transient behavior of the water synthesis reaction in line with experimental results. The analysis elucidated that charge transfer contributions from hydrogen and oxygen adsorption are attributed to over 99% of the total charge transfer. These contributions vastly outweighed the charge contribution from the formation and consumption of the hydroxyl intermediate, as well as the formation and desorption of the product, water. These findings reveal that measurable charge transfer is dominated by species exhibiting non-zero net coverage changes over the reaction cycle, while intermediates and products with closed catalytic cycles contribute negligibly to the macroscopic signal. This framework provides a quantitative basis for interpreting IET measurements in complex reaction networks and suggests that future applications should target chemistries where key surface species undergo substantial net coverage changes. In this way, IET can be extended as a predictive tool to deconvolute charge transfer contributions and identify rate-determining steps across a broad range of catalytic systems.

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18. Circumventing Methane Activation Barriers through Plasma-Assisted Catalysis

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The adoption of plasma-assisted catalysis holds the promise to improve the efficiency and yield of many important energy generating reactions The benefits are particularly pronounced when the reactants involve molecules with strong chemical bonds such as N2, CO2, or methane (CH4). In this study, we employ density functional theory (DFT) and descriptor-based microkinetic modelling to investigate the impact of plasma activation on partial oxidation of methane (POM) over metal (211) surfaces. Simulations were conducted under both thermal and plasma-assisted conditions. The inclusion of pre-activated reactants and hydrocarbon radicals in the plasma case enables the reaction to proceed at significantly lower temperatures compared to the purely thermal pathway. Furthermore, plasma activation facilitates the bypassing of the rate-limiting methane activation step and allows for selective product formation on certain monometallic catalysts. Our results suggest that plasma catalysis could be widely applicable to other methane upgrading reactions, such as methane dry reforming and steam reforming.

19. Beyond Thermal Limits of Chemical Catalysis: Photon-Driven Formic Acid Dehydrogenation.

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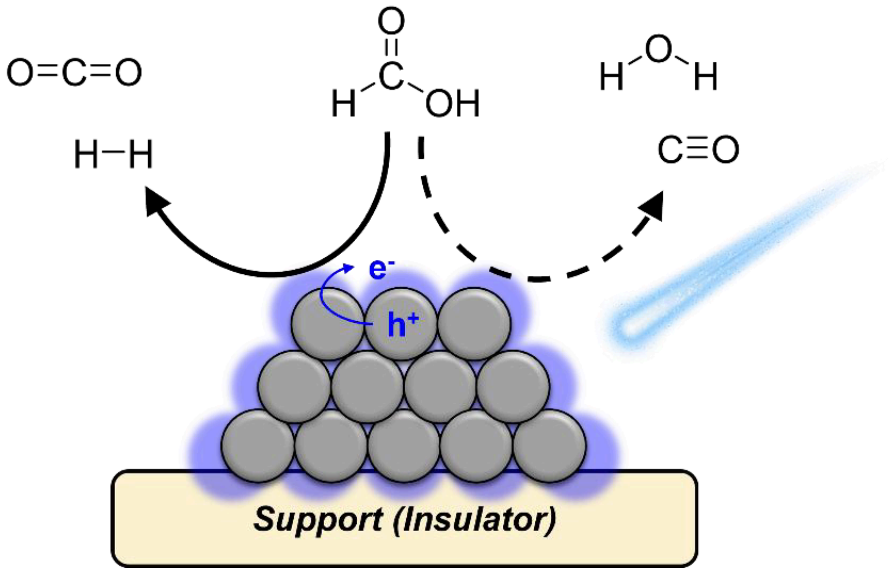
The dehydrogenation of liquid organic hydrogen carriers (LOHC) on catalytic surfaces face significant kinetic barriers, exacerbated by the accumulation of surface spectator species, limiting their utility for on-demand hydrogen delivery. While thermo-, electro-, and photo-catalytic approaches have been demonstrated for the selective dehydrogenation of liquid organic hydrogen carriers, the cooperative use of multiple energetic stimuli remains under-utilized. Using precious metal catalytic surfaces that facilitate the thermal dehydrogenation of formic acid, we investigated the ability of visible light to selectively promote the rate of catalytic turnover through electronic excitation of kinetically relevant intermediates. Over Pt nanoparticles supported on silica, a continuous wave of 450 nm light significantly accelerated the overall catalytic rate of formic acid decomposition. The rate enhancement was selective towards the desired dehydrogenation, with the rate of turnover being more than 95% selective to formic acid dehydrogenation over dehydration. Visible photon fluxes were found to promote the reaction in a wavelength-dependent manner. Using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), we quantified surface coverages of kinetically relevant intermediates and observed that the photo-induced enhancement correlates with the removal of adsorbed carbon monoxide. These findings indicate that visible light selectively accelerates catalytic turnover by electronically exciting and desorbing inhibitory intermediates, enabling more efficient dehydrogenation under mild conditions. The rate of formic acid photolysis was found to be insensitive to temperature, resulting in negligible apparent activation energy (Ea,app ~ 0 kJ/mol) consistent with a non-thermal catalytic process. The difference in the rate of dehydrogenation over dark (thermal only) and illuminated surfaces demonstrates the selective acceleration of chemical catalysis through photolysis, by targeting kinetically relevant intermediates that are responsive to light.



20. Computational Design and Discovery of High-Entropy MXene for Stabilizing Confined Pt Nanolayer

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High-entropy MXenes (HE-MXenes) are an emerging class of two-dimensional materials with tunable local chemical environments, yet their catalytic potential remains largely unexplored. Motivated by prior studies showing that thin Pt nanolayers can be stabilized on Mo_2TiC_2 MXene, this work investigates whether HE-MXenes can serve as supports for confined Pt nanolayers. We developed a high-throughput DFT workflow that combines special quasirandom structure generation with a three-step screening process based on convergence behavior, geometric stability, and interfacial adhesion. This screening identifies a limited set of stable candidates and reveals that Mo, Nb, Ta, and W dominate the most promising compositions, highlighting the important role of group 5/6 metals in stabilizing confined Pt layers. Further adsorption and transition-state calculations show that Pt/HE-MXene interfaces form edge-like active ensembles. H_2 dissociation remains facile but exhibits moderately higher barriers than Pt(111), consistent with selective passivized catalysis (SPC), in which support interactions tune Pt reactivity without suppressing catalytic activity. Recent calculations also indicate that sequential C_2H_6 dehydrogenation on Pt/Mo-Nb-Ta-W is kinetically feasible. Overall, this study establishes HE-MXenes as promising platforms for stabilizing and tuning confined Pt nanolayers for catalytic applications.

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21. Role of S in the Formation Fe Nanoclusters

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Understanding catalyst behavior under reaction conditions is essential for controlling activity, selectivity, and stability in catalytic processes. In floating catalyst chemical vapor deposition (FC-CVD) reactors for carbon nanotube (CNT) synthesis, sulfur is widely used as a promoter; however, its mechanistic role in governing catalyst structure and surface chemistry remains poorly understood. The study provides insight into the morphology of iron-based catalysts when CNT growth is occurring. To understand their composition, energetics, and dynamics, grand canonical Monte Carlo (GCMC) modeling, and density functional theory (DFT) calculations were employed. By constructing surface phase diagrams as functions of temperature and gas-phase composition, we quantify how sulfur and carbon compete for adsorption sites under realistic reaction conditions. Our results reveal a dynamic trade-off between sulfur and carbon adsorption. Sulfur preferentially occupies surface sites at early stage, stabilizing catalyst particles and limiting excessive carbon binding. As carbon concentration increases, carbon progressively displaces sulfur, enabling carbon incorporation necessary for CNT growth. This competitive adsorption behavior is strongly influenced by temperature, surface structure, and local composition, highlighting the importance of reaction conditions in governing catalyst surface evolution. These findings suggest that sulfur acts as a transient regulator of catalyst surface chemistry, balancing catalyst stability and reactivity through competitive adsorption with carbon. This work provides a general framework for understanding promoter effects in catalytic systems and offers insights for optimizing reaction conditions to control catalyst performance and product quality.

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22. Facilitating Electrocatalytic Epoxidation via Potentiodynamic Control

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Electrochemical alkene epoxidation is a promising alternative to current oxidation methods, which often use environmentally unfriendly oxidants that also generate significant chemical waste. These electrochemical processes facilitate renewable electrons and water as the oxygen source to produce epoxides at ambient conditions. Here, the electrochemical epoxidation of hexene on Gold (Au) was proposed to follow a Langmuir-Hinshelwood mechanism, consistent with first-order dependence on Hexene (0.01 – 0.5 M) and zeroth-order dependence on water concentration (1 -15 M). The importance of competing kinetic timescales was demonstrated through a potentiodynamic strategy, in which a triangular potential oscillation waveform was systematically modulated between -0.6 and 1.1 $V_{Fc/Fc+}$ (Fig. 1A) across a frequency range of 10^{-3} – 10^{-1} Hz. Potentiodynamic operation accelerated the rate of electrochemical epoxidation across a range of hexene concentrations in solution (Fig. 1B). The rate enhancement is proposed to result from a decreased oxygen surface coverage, which in turn increased the fractional coverage of Hexene, allowing atomic oxygen to attack its carbon double bond. In addition to reaction kinetics, epoxidation was hindered by hexene diffusion in solution, thereby constraining its fractional coverage on the Au surface. Epoxidation rates increased with electrolyte flow rate across the surface as a result of enhanced hexene diffusion, until the availability of surface atomic oxygen became limiting. Ultimately, over an order of magnitude enhancement in the rate of epoxidation was achieved through potentiodynamic operation without sacrificing Faradaic efficiency, reaching up to 20% at 0.5 M Hexene.

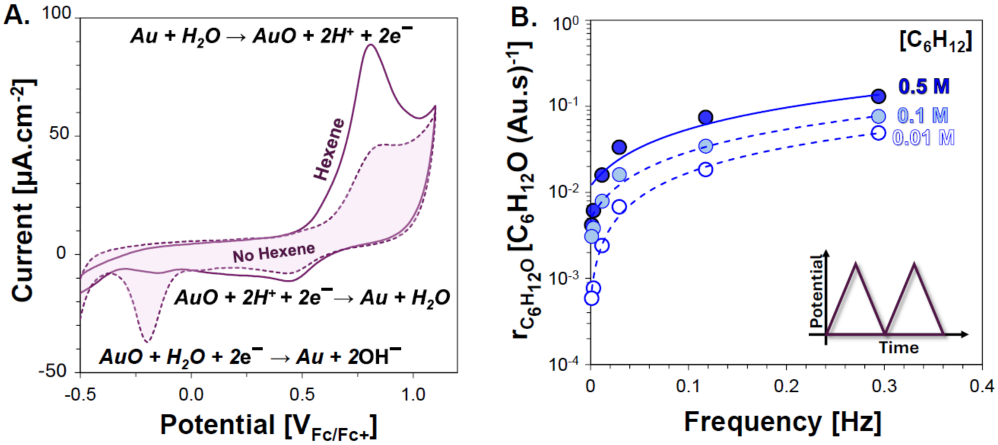

Figure 1. Electrochemical Alkene Epoxidation A. Cyclic voltammetry of Au foil at 10 mV s^{-1} between -0.6 and 1.1 $V_{Fc/Fc+}$ in the presence (solid) and absence (dashed) of 0.5 M Hexene, respectively B. Epoxidation rate as a function of potentiodynamic frequency (10^{-3} – 10^{-1} Hz) at 0.01, 0.1, 0.5 M Hexene, all experiments are in 0.1 M $TBAClO_4$, 10 M H_2O in Acetonitrile.

23. Flow-Enabled Solar Nitrogen Upgrading Using an Unassisted Photoelectrochemical Reactor

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Photoelectrochemical (PEC) systems offer a promising pathway for solar-driven chemical synthesis by directly coupling photovoltaic energy conversion with electrochemical catalysis. While PEC technologies have been widely explored for hydrogen production, their application to selective chemical upgrading remains limited, with most systems operating in batch configurations or requiring external electrical bias. Here, we report a membrane-separated laminar flow reactor enabling the selective formation of ammonia, hydrazine, and hydroxylamine via coupled NO_2RR and OER. Using a commercial Rh and Ru catalyst under applied bias, precise control of reactant flow rates (0.5–9 mL min^{-1}; 92–5 s residence time) yields single-pass nitrite conversion from 10% to 82%, with selectivities up to 84% ammonia, 9.2% hydrazine, and 3.2% hydroxylamine. Integration with a monolithic perovskite/silicon tandem (Voc = 1.87 V) enables unassisted operation for 2 h at residence times below 15 s, achieving single-pass conversion of 8–76% and solar-to-product efficiencies of 4.87% (NH_3), 0.62% (N_2H_4), and 0.29% (NH_2OH). Continuous-flow, solar-driven chemical synthesis offers a transformative route for coupling renewable energy with scalable manufacturing of upgraded chemicals. As photoelectrochemical technologies continue to advance, the integration of selective synthesis reactions such as nitrogen upgrading into bias-free platforms is poised to unlock new pathways for sustainable and decentralized chemical production.

24. Reaction pathways and intermediates for CO_2 methanation over Ni-Ce mixed metal oxides

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The methanation of CO_2 is receiving increasing recent attention in light of the need for viable strategies for capturing and converting CO_2 from dilute sources. In this context, Ni-Ce mixed metal oxides have emerged as a single-component dual-function material for the direct air capture and conversion of CO_2 to methane. Although these materials clearly outperform other sorbent-catalyst systems for the capture and conversion of CO_2, the nature of the active sites involved in CO_2 conversion, as well as the identities of reaction intermediates mediating methanation turnovers, especially at low pressures, remain unclear. More specifically, proposed mechanisms primarily fall into two categories: unassisted activation routes in which CO_2 dissociates unimolecularly to form CO*[1] followed by subsequent hydrogenation steps, and H-assisted routes involving formate or carboxyl species.[2] In this study, we use kinetic, in situ spectroscopic, and isotopic measurements to provide evidence for the participation of H-assisted CO_2 activation routes in the presence of Ceria, unlike in the Ni/SiO_2 catalyst. In-situ FTIR reveals the presence of bidentate carbonates, bidentate formates, and formyl species on the surface under CO_2 methanation conditions. To understand the role of these formate species, the formate adlayers formed under methanation conditions were subjected to either Ar or H_2 flow. Formate decomposition rates are insensitive to the presence of H_2, indicating that they are likely spectator species under the conditions used. Zero-order kinetics in CO_2 and fractional order (0.2 to 0.5) kinetics in H_2 can be rationalized to be resulting from kinetically relevant H addition to CO* occurring on surfaces covered with carbonyls

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25. One-Pot Catalytic Transfer Hydrogenolysis of PET and Co-Upgrading of Ethanol over Tunable ZrO_2-Supported Cu Catalysts

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Catalytic transfer hydrogenolysis (CTH) has emerged as a promising H_2-free strategy for upcycling polyethylene terephthalate (PET) into platform chemicals and sustainable fuel components. This reaction typically uses methanol as the solvent and H_2 donor, but its production is energy-intensive, and its decomposition produces CO, a harmful by-product that also makes this system carbon-inefficient. We demonstrate ethanol-assisted CTH of diethyl terephthalate (DET, produced from the in situ ethanolysis of PET) to p-xylene over zirconia-supported Cu catalysts (Cu/m-ZrO_2 and Cu/t-$ZnZrO_x$), achieving a sustainable, carbon-efficient CTH strategy that upcycles waste PET and co-upgrades ethanol into highervalue oxygenates. Ethanol can be dehydrogenated to acetaldehyde using Cu on a reducible metal oxide (MOx) support, such as ZrO_2, which creates Cu-M interfacial sites that are active for alcohol dehydrogenation and substrate hydrogenolysis. Acetaldehyde then reacts via aldol condensation (AC) to form C4+ unsaturated carbonyls, which are subsequently re-hydrogenated to form C_{4+} alcohols (Guerbet coupling) or dehydrogenative coupling (DHC) to form ethyl acetate. We show that (1) ethanol dehydrogenates on the Cu metal sites with oxygen vacancies ([O]) at the Cu-Zr interface enhancing dehydrogenation by anchoring ethoxy species, (2) acetaldehyde couples over acid-base sites in ZrO_2 and its selectivity can be tuned by the phase of ZrO_2 and Zn incorporation, and (3) C-O hydrogenolysis occurs on both Cu and Cu-Zr interfacial sites where [O] favorably adsorbs the ester. We then show that Cu/t$ZnZrO_x$, which has a 3x higher DHC rate, results in >2x higher CTH rates, enabled by a higher in situ H_2 partial pressure, compared to Cu/m-ZrO_2 that is comparably active for ethanol dehydrogenation and highly selective for Guerbet coupling. Finally, we show that the DET hydrogenolysis rate increases with H_2 partial pressure and is not inherently coupled to the ethanol dehydrogenation rate, suggesting that H is transferred indirectly via the gas phase.

26. Dynamic behavior of molecular Pd-acetate trimers and dimers in heterogeneous vinyl acetate synthesis

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Vinyl acetate monomer (VAM) is a crucial intermediate in the production of various polymers. While molecular Pd-acetate trimers and dimers, such as Pd3(OAc)6 and K2Pd2(OAc)6, are known to form on potassium acetate (KOAc)-promoted PdAu catalysts during heterogeneous VAM synthesis, their mechanistic role remains unclear. Here, we study the dynamics of different Pd-acetate species by utilizing in situ and operando crystallographic and spectroscopic characterizations combined with computational modeling on monometallic Pd model catalysts. The promoter-free catalyst expectedly shows low catalytic activity and VAM selectivity, corresponding to the complete reduction of Pdn(OAc)2n species to form Pd0 and PdCx nanoparticles. Conversely, noticeable quantities of KnPd2(OAc)n+4 species remain on the KOAc-promoted catalyst, leading to smaller nanoparticle formation with 10 times the activity and double the selectivity for VAM. This study reveals that molecular Pd-acetate trimers and dimers are significant indicators of catalytic performance and highlights their structurally dynamic nature in heterogeneous vinyl acetate chemistry.

27. Achieving Zeolitic Confinement through Ion-Exchange for the Selective Hydrogenation of Phenylacetylene

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Metal – zeolite composite catalysts have been demonstrated as useful for a variety of chemistries by providing activity and/or selectivity as a result of metal confinement in zeolitic cages. The synthesis of these materials typically follow one of three methods: (i) ligand protected hydrothermal synthesis (LPHT), (ii) ion-exchange (IE), or (iii) incipient wetness impregnation (IWI). LPHT, despite long synthesis times and limited scalability, is generally preferred over IE and IWI because they offer limited control over metal siting, often resulting in surface deposition that negates the advantages of zeolitic confinement. Here, we show how parameters such as metal precursor identity, solution pH, and zeolite acidity impact metal siting within the zeolite during the IE of palladium (Pd) with H-ZSM-5. Specifically, we maximize the degree of Pd confinement utilizing low pH exchange solutions (to prevent strong electrostatic adsorption with terminal silanol groups) and passivating surface acid sites. Catalysts with the highest degree of confinement show superior performance in the hydrogenation of phenylacetylene to styrene compared to unconfined and partially confined controls. The zeolitic confinement is hypothesized to prevent the over hydrogenation of styrene to ethyl-benzene through a destabilization/size exclusion of the transition-state associated with the secondary hydrogenation step.

28. Quantitative Analysis of Clustering and Layering Formalism for Water Adsorption on Extended (Hydr)oxide Surface

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Water plays a critical role as a co-adsorbate on catalyst surfaces, where it can enhance adsorption via cooperative interactions or suppress it through competitive site occupation, depending on the sorbent system. Despite extensive use of isotherm frameworks, the mechanism of water adsorption on hydroxylated metal oxide catalysts remains unclear, particularly whether it follows classical multilayer formation or cluster-based assembly driven by intermolecular interactions. In this study, water adsorption on metal hydroxide catalyst surface α-Ni(OH)$_2$ was analyzed at 25, 50, and 75 °C using three isotherm models: BET, Anderson and the cluster-based ζ isotherm. Classical multilayer models BET and Anderson failed to describe adsorption across the full relative pressure range and diverged near saturation due to their assumption of independent adsorption sites, considering only vertical interactions while neglecting lateral adsorbate–adsorbate interactions. At high relative pressure, closely

packed water molecules exhibited significant intermolecular interactions, which were not captured by these models. In contrast, the ζ isotherm treated a site–adsorbate ensemble as an active site and incorporated three-dimensional interactions, enabling reasonable prediction over the full pressure range. Additionally, the porous structure of α-Ni(OH)$_2$ imposed physical limits on multilayer growth, making classical predictions unrealistic at high pressure. The model also indicated a finite maximum cluster size and allowed quantification of cluster size distributions. The overall adsorption was governed by intermolecular interaction-driven cluster formation rather than classical multilayer stacking, with implications for catalytic and separation systems.

29. Unraveling the Role of Gallium Speciation in Zeolites for Methanol-to-Hydrocarbon Tandem Catalysis

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The growing demand for light olefins necessitates the development of more efficient and sustainable catalytic processes. Zeolites, with their tunable acidity and shape selectivity, are widely used in hydrocarbon upgrading, where aluminum associated Brønsted acids typically serve as the active sites. However, incorporating less acidic heteroatoms has emerged as a strategy to tune their activity and influence reaction pathways. In this presentation, we discuss our recent work showing how combining gallosilicates and aluminosilicates with distinct zeolite pore topologies (e.g., MWW, CHA, MFI) in a dual-bed reactor enhances production of olefins in the methanol-to-hydrocarbons (MTH) reaction. This configuration uses the less acidic Ga-zeolite upstream as a highly effective dehydration catalyst to convert alcohols to intermediates for downstream upgrading using the Al-zeolite. Here we will discuss recent efforts to elucidate the judicious pairing of zeolites on the basis of Ga speciation and its impact on catalytic performance. To this end, we have used different methods to control gallium speciation via direct synthesis and post-synthesis treatment wherein we assess their performance in tandem MTH reactions with a fixed Al-zeolite (ZSM-5) downstream to establish more robust structure-performance relationships. We have shown that higher Ga loadings promote extra-framework Ga species that suppress C–C coupling, leading to preferential formation of dimethyl ether (DME), while lower Ga loadings with reduced extra-framework Ga promote hydrocarbon production akin to Al-based zeolites. Additionally, we examined the influence of gallium oxide species deposited on siliceous zeolites and mesoporous silicates (benchmark materials). We observed exclusive DME formation over a broad range of Ga loadings, confirming their inability to facilitate hydrocarbon formation. By systematically controlling gallium speciation, this work provides new insights into how different Ga sites influence catalytic pathways in MTH chemistry. Understanding these relationships improves the design of multifunctional zeolites with precisely tailored properties, achieving more versatile and efficient catalysts.

30. Catalytic upcycling of PET to p-xylene through methanol-mediated transfer hydrogenolysis on MO_Xsupported Cu and Ru catalysts

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Polyethylene terephthalate (PET) constitutes approximately 10.6% of global plastic waste. Modern methods of plastic waste management, such as incineration and landfilling, pose serious environmental and health hazards. Methanol-mediated catalytic transfer hydrogenolysis (CTH) offers a sustainable and safer chemical upcycling alternative to hydrogenolysis using high-pressure gaseous H_2. In this process, methanol acts as both a depolymerization agent and a hydrogen donor to convert PET-derived dimethyl terephthalate (DMT) into p-xylene, facilitating a circular plastic economy. To this end, catalysts require active sites for both the decomposition of methanol to H_2 and the removal of ester groups from the PET monomer, dimethyl terephthalate (DMT), to selectively produce p-xylene. We evaluated Cu- and Ru-based catalysts, particularly on ZrO_2-based supports, in a one-pot batch reactor system, identifying Cu/ZrO_2 and $Ru/ZnZrO_x$ catalysts as the most selective and active for the CTH of DMT to p-xylene. Our findings indicate a direct correlation between methanol decomposition rates and p-xylene yields. While incorporating Zn in $Ru/ZnZrO_x$ catalysts tailored selectivity toward methanol decomposition to H_2 by suppressing CO methanation, increasing the Zn content in $Cu/ZnZrO_x$ catalysts significantly decreased CTH rates. To investigate the role of Cu/Zr interfacial sites and the importance of Cu and Zr proximity, we employed ballmilling and thermal treatment of Cu/SiO_2 and ZrO_2 together. This was found to significantly increase CTH activity, demonstrating that the synergy between Cu and Zr at the interface is the primary driver of CTH activity, rather than the individual components. Altogether, the results show that modifying the interfacial Cu/Zr sites through thermo-mechanochemical methods or by introducing dopants such as Zn can significantly alter CTH rates.

31. Selective Passivized Catalysis via Bismuth Incorporation in Platinum Nanoparticles: A Computational Investigation for Short Alkane Conversion

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Platinum-based catalysts play a central role in converting short alkanes from abundant shale gas reserves into value-added chemicals and fuels. However, unmodified Pt surfaces often exhibit excessively high C–H bond activation activity, leading to deep dehydrogenation, rapid coke deposition, and poor selectivity toward desired products. Selective Passivized Catalysis (SPC), recently developed in our group, provides a rational design strategy in which a fraction of overly reactive Pt sites is intentionally attenuated or blocked to suppress undesired pathways while preserving sites responsible for selective C–H activation. Bismuth (Bi) has emerged as a particularly effective post-transition-metal promoter within this framework, yet the atomic- scale mechanisms by which Bi modifies Pt surface reactivity remain poorly understood.

In this work, density functional theory (DFT) is systematically employed to investigate how Bi incorporation alters the electronic and geometric structure of Pt nanoparticle surfaces and the resulting impact on catalytic behavior. Three surface models are examined to represent distinct incorporation modes: clean Pt(111) slabs as the unmodified baseline, Bi-adatom-decorated Pt(111) surfaces representing partial selective passivization, and Pt3Bi intermetallic slabs representing full alloying. H_2 binding energies and dissociation barriers, calculated using the climbing-image nudged elastic band (CI-NEB) method, are used as probes of surface reactivity across these models. Preliminary results reveal systematic trends in H_2 binding strength and dissociation barriers as a function of Bi incorporation mode, providing quantitative evidence for the ensemble and electronic effects underlying SPC. These findings establish a computational framework for understanding how Bi promoters tune Pt surface reactivity and guide the rational design of passivized Pt–Bi catalysts for selective short- alkane conversion.

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32. Silanols as Active Sites for Oxidative Dehydrogenation of Propane in Zeolite Catalyst

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The identity of the active site in boron-containing zeolite catalysts for the oxidative dehydrogenation of propane (ODHP) remains actively debated. Proposed active centers range from B–O–B oligomers to isolated boron species with specific hydroxyl configurations, yet the key descriptors governing catalytic performance have not been established. In this work, we challenge the prevailing boron-centric view and present evidence that silanol species are the primary active sites for ODHP in zeolite catalysts.

We synthesized a series of boron-incorporated CHA zeolites with a controlled range of framework and extra-framework boron species, characterized by ^{11}B and ^{1}H MAS NMR and FTIR. Despite measurable ODHP activity across all samples, no correlation between boron speciation and catalytic performance was found. Hydrothermal treatment was then used to partially or fully remove boron from the framework. Counter-intuitively, steam-treated and fully deboronated samples exhibited higher activity than their boron-containing counterparts while retaining high olefin selectivity—directly implicating silanol species, generated upon boron removal, as the catalytically relevant sites.

To establish the generality of this finding, we extended the study across multiple zeolite frameworks (MFI, MWW, MTF, AFI, and mesoporous silica) and found no correlation between pore topology and ODHP performance, ruling out confinement effects as a dominant factor. Finally, fully siliceous AFI zeolites synthesized under varying conditions demonstrated a direct correlation between silanol nest density—quantified by ^{1}H NMR and FTIR—and catalytic activity. These results collectively identify silanol nest density as the key performance descriptor for ODHP in zeolites, offering a new design principle for selective propane dehydrogenation catalysts.

33. Development of Carbon-Supported Platinum Catalysts for Joule-Heated Propane Dehydrogenation

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Propylene is an essential industrial chemical used in the production of polypropylene, acrylic acid, acrylonitrile, and propylene oxide. Conventional production routes, including steam cracking and fluid catalytic cracking, are increasingly inadequate to meet growing demand. In view of this, propane dehydrogenation (PDH) has emerged as a significant on-purpose route for propylene production, given the growing availability of shale-gas-derived propane. Because propane dehydrogenation is highly endothermic, heat delivery is a critical factor in reactor performance. Electrified heating concepts, including induction, microwave, and joule heating, have therefore attracted peak interest with joule heating offering a particularly direct route for heat generation within conductive materials. In such systems, catalyst performance depends not only on the active metal but also on the properties and morphology of the support and the strength of the metal-support interaction. Carbon-based materials are compelling in this scheme as they offer tunable surface properties, high electrical resistivity, high thermal conductivity, and potential compatibility with joule-heated reactor designs. Recent studies on platinum deposition onto carbon felt often rely on specialized and intricate fabrication techniques such as electrodeposition or rapid-heating methods. In contrast, this work explores a facile liquid-phase synthesis route for depositing platinum on carbon felt for propane dehydrogenation, while establishing a basis for future comparison with other preparation methods. Among the conditions examined, an intermediate formic acid concentration during liquid-phase synthesis improved platinum dispersion relative to conventional impregnation, whereas both lower and higher concentrations led to less favorable platinum distributions. Analogous results show a strong dependence of catalytic activity on synthesis route and resulting catalyst structure. Overall, this work establishes a framework for the development of carbon supported platinum catalysts for propane dehydrogenation and provides preliminary synthesis-structure-performance insights relevant to the design of catalysts for joule-heated reactor systems.

34. Beyond ‘Closer is Better’: Quantifying Proximity Effects in Tandem CO_2 Hydrogenation

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Tandem conversions underpin both conventional and emerging processes and are often treated as sequential reactions guided by the qualitative proximity-criterion “closer is better”. We quantitatively investigate these proximity effects for CH3OH-mediated tandem CO2 hydrogenation (TCH) over oxide/zeolite catalysts by analyzing reaction pathways, thermodynamics, and transport processes across length-scales. We reveal molecular-scale nuances that influence rates and product selectivity. Specifically, CH3OH decomposition to HCHO and CO on redox sites influences the hydrocarbon-pool mechanism in the zeolite micropores through Prin’s condensation and carbonylation pathways, respectively. These intermediates promote aromatic formation, altering product selectivity with decreasing active site distance. At the reactor-scale, we propose a transport resistance model by incorporating intrapellet and zeolite intrapore diffusion at different proximities. This model quantitatively predicts observed rate enhancements with proximity. Finally, we link transport effects to process-level metrics (e.g., net profit and CO2 emissions) and show that optimal proximity and diffusion characteristics maximize aromatic yield, improve process profitability, and reduce carbon intensity. This work moves beyond qualitative proximity arguments by establishing a quantitative framework that enables rational catalyst design and benchmarking of tandem catalytic systems for CO_2 conversion.

35. Combating Climate Change: Upgrading CO_2 into Ethanol Using Cu/CeO_{2-x} Catalysts

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To combat climate change, the effective utilization of captured CO_2 by converting it into value-added products is essential. Ethanol, owing to its broad industrial applications and established role as a fuel additive, represents a particularly attractive target. Here, a series of Cu/CeO^{2-x} catalysts are presented that achieve high selectivity (~95%) toward ethanol during CO_2 hydrogenation under reaction conditions of 30 atm, H_2/CO_2 =3, and 240 °C, with a CO_2 conversion of ~5%. The catalysts also demonstrate remarkable stability over 72 hours of continuous operation without significant deactivation. By varying Cu loading and reduction temperature, the densities of Cu(I) species and oxygen vacancies (O_v) can be independently tuned. A synergistic relationship between these sites is observed in terms of turnover frequency (TOF), with values of 0.23 h^{-1} per O_v site and 3.97 h^{-1} per Cu(I) site. Operando FTIR spectroscopy, supported by DFT+U calculations, provides unique kinetic insight into the reaction mechanism, identifying CH_2OH^* and CH_2^* intermediates with an associated kinetic barrier of ~1.0 eV. The integration of mechanistic and computational studies enables deconvolution and independent modification of the surface active sites, opening a pathway toward rational active-site engineering and catalyst optimization.

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36. Pyrene-based Covalent Organic Frameworks with Diacetylene Linkers for the Photodegradation of PFAS

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Poly- and perfluoroalkyl substances (PFAS) are synthetic chemicals used in various applications due to their surfactant properties. Their bioaccumulation and potential health effects have led to increased concern and the implementation of strict regulatory measures.[1] Traditional removal methods, such as adsorption, do not degrade PFAS and require subsequent regeneration and handling of the toxic waste. The catalytic degradation of PFAS via oxidative or reductive processes is an alternative. However, challenges remain in achieving complete mineralization, selectivity, and scalability.[2] Covalent organic frameworks (COFs) are low-cost, tunable materials with photocatalytic activity, making them promising for PFAS degradation in water treatment. However, current studies have mainly focused on non-destructive approaches, such as adsorption.[3] We designed and synthesized a diacetylene-functionalized photoactive Py-DEBD COF framework that has both PFOA adsorption and degradation capacity. In photocatalytic degradation experiments at pH 2, over 99% of PFOA was removed from solution, and 32% defluorination was achieved within 24 h. Short-chain degradation byproducts accumulated early in the reaction, with several reaching peak concentrations before decreasing as photochemical degradation continued. Experimental and computational studies on the photo-degradation mechanism of PFOA on Py-DBED supported a decarboxylation-hydroxylation-elimination-hydrolysis (DHEH) mechanism and pointed to the diacetylene linker as a key site for the formation of adsorbed *OH via water oxidation. The photocatalytic degradation proceeds through a thermodynamically favorable photoinduced oxidative charge-transfer pathway. In the decarboxylation step, a favorable alignment between the oxidation potential of PFOA (1.02 V vs SHE; –5.30 eV vs vacuum) and the valence band edge of Py-DEBD (–5.75 eV vs vacuum at pH 2) enables the photogenerated holes to oxidize adsorbed PFOA efficiently. This is further supported by TD-DFT calculations that indicate that light irradiation promotes charge transfer from PFOA to the diacetylene linker, generating a perfluoroalkyl radical that subsequently reacts with surface-bound *OH. Formation of *OH on the diacetylene linker via water oxidation is also energetically favorable, with a calculated E_0 = 1.27 V vs SHE (–5.55 eV vs vacuum at pH 2). The hydroxylation of the radical to form

$C_7F_{15}OH$ is exergonic (ΔG = –2.67 eV), and is followed by a favorable HF elimination (ΔG = –0.13 eV) to $C_6F_{13}COF$ and hydrolysis to $C_6F_{13}COOH$ (ΔG = –0.45 eV). This study represents the first comprehensive investigation of COFs as both adsorbents and photocatalysts for PFOA degradation, providing a novel approach to addressing PFAS-contaminated water.

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37. Insights into Metal Incorporation and Demetallation Strategies for Zeolite Defect Engineering

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Controlling the synthesis of zeolites to attain desired physicochemical properties is challenging, owing to their complex growth media, which can pose limitations on the selection of synthesis parameters. While organic structure-directing agents (OSDAs) and the incorporation of heteroatoms offer solutions to tailor zeolite properties, their utilization raises concerns regarding economic viability and environmental impact, among others. Here we will present our recent studies using metals as inorganic structure-directing agents (ISDAs) and growth modifiers as alternative methods of controlling zeolite crystallization. Determining the effects of metals on zeolite crystallization is complicated by the elusive addition of heteroatoms, due to the difficulty in characterizing the zeolite growth from diverse precursor species. Our group has pioneered high temperature atomic force microscopy (AFM) that we have used to visualize zeolite surface growth in situ at a near molecular level. We have demonstrated that zeolite crystallization primarily occurs through nonclassical pathways, such as crystallization by particle attachment, with classical layer-by-layer growth via monomer incorporation playing a minor role.

In this presentation, we will showcase the OSDA-free accelerated crystallization of zeolite CHA using binary pairs of inorganic cations. We have shown how their solvated structure and hydrated ionic radii influence crystallization [1]. Conversely, addition of zinc to zeolite growth mixtures is beneficial owing to its ability to stabilize and enhance the catalytic properties [2,3]. We will present our study of Zn-FAU crystallization using in situ AFM to probe the inhibitory effect of metal incorporation. We will also discuss demetallation approaches for various metals in commercially relevant zeolites of different pore sizes, such as *BEA, MFI, and CHA frameworks, to introduce defects for diverse commercial applications.[4]

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38. Mining ZSM-5 Synthesis Data from the Literature Using Open-Source Large Language Models

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Data-driven materials research depends on access to large amounts of reliable synthesis data, but most of this information is still buried in the literature in formats that are difficult to collect and organize at scale. In many papers, synthesis details are reported in heterogenous formats, or inconsistent styles, which makes it challenging to convert them into structured datasets for downstream analysis. In this work, we developed an automated open-source workflow to extract synthesis information directly from published papers. We focused on the hydrothermal synthesis of ZSM-5, an important zeolite catalyst whose physicochemical properties that are highly sensitive to the selection of synthesis conditions. Our workflow combines large-scale document processing, targeted extraction with a compact open-source large language model (LLM), and chemistry-aware post-processing to convert unstructured literature into structured synthesis records. Using this approach, we built a dataset containing 1,659 ZSM-5 synthesis entries, including information such as synthesis temperature, crystallization time, precursor sources, and gel composition. We evaluated the extracted data against a manually curated set of recipes and found strong benchmarking performance across most categories. Analysis of the resulting dataset also revealed synthesis trends that are consistent with established understanding of ZSM-5 crystallization. At the same time, the study highlights how incomplete and inconsistent reporting in literature remains a major challenge for automated data extraction. Overall, this work shows the potential of open-source LLM-based workflows for building synthesis datasets from literature and supporting future data-driven studies of zeolite materials.

39. Controlling Complex Nonclassical Zeolite Crystallization Pathways by Cooperative Structure Direction

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Synthesizing zeolites with controlled morphology, porosity, and composition is essential for adsorption, separations, and catalysis, and practical advances that lower synthesis time and temperature are key to broader industrial deployment. Zeolite crystallization is typically directed by organic and/or inorganic structure-directing agents (SDAs), yet the mechanistic roles of cooperative SDA pairings remain insufficiently understood. Here, we investigate how combining organic and inorganic SDAs can synergistically enhance crystallization efficiency and enable rational control over zeolite formation pathways.

Zeolite β (BEA) is a quintessential example, conventionally requiring elevated temperatures and long crystallization times, which limits mechanistic studies. Moreover, the Si–Na–OSDA compositional space that yields phase-pure BEA is narrow and highly temperature sensitive, complicating reproducible tuning of material properties such as particle size. We show that incorporating inorganic SDAs (K^+ or Li^+) expands the accessible BEA window and markedly improves their crystallization relative to Na^+ systems, enabling highly crystalline nano BEA to be synthesized in just 24 h under seed-free conditions. Time-resolved particle analyses reveal the evolution of distinct particle populations and their subsequent assembly, which is consistent with a nonclassical, particle-attachment-driven growth pathway that provides a mechanistic basis to accelerate synthesis

while controlling crystallinity and size.

To further elucidate nonclassical growth in zeolite formation, we employ high-temperature in situ atomic force microscopy (AFM) developed in our group to directly visualize crystallization at near-molecular resolution. Using CHA as a model system, we observe growth dominated by particle attachment and demonstrate how crystallization dynamics change under cooperative SDA pairings conditions. Collectively, these results highlight how rational optimization of cooperative SDA pairings can steer crystallization pathways, offering new routes to faster syntheses and improved control of zeolite microstructure for diverse industrial applications.

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40. Confinement-Enhanced Ethane Dehydrogenation on Pt Nanolayer/Mo$_2$TiC$_2$ MXene Catalysts: A DFT Study

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The performance of heterogeneous catalysts is typically evaluated by activity, selectivity, and stability; however, in the dehydrogenation of light alkanes, rapid deactivation due to metal sintering and carbonaceous coke deposition remains a major limitation for industrial applications. To address these challenges, this work investigates a novel catalytic architecture consisting of an atomically thin platinum (Pt) nanolayer confined within a two-dimensional Mo$_2$TiC$_2$ MXene support. This system has experimentally demonstrated enhanced stability and high ethylene selectivity at 550℃. Density Functional Theory is employed in this work to elucidate the structure-property relationships and reaction kinetics governing ethane (C_2H_6) dehydrogenation on the Pt/Mo$_2$TiC$_2$ catalyst. Sequential C–H bond activation pathways were analyzed to identify transition states and energy barriers for ethane-to-ethylene conversion. The results indicate that the unique coordination environment of the MXene-confined Pt nanolayer promotes catalytic activity by enabling more favorable dissociative adsorption compared to conventional Pt (111) surfaces. In addition, Pt–Pt interactions were examined to understand nucleation behavior within the confined interlayer spaces of the MXene support. The findings showed that Pt atom diffusion and interaction energies strongly influence early- stage aggregation and cluster formation, with spatial confinement playing a key role in regulating these processes. Thus, this work links theoretical insights with experimental observations and establishes a mechanistic framework for designing next-generation, deactivation-resistant catalysts through controlled metal-support interactions and nanoscale confinement for alkane upgrading applications.

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41. Developing Effective Heterogeneous Catalysts for the Anionic Oxy-Cope Rearrangement in the Chemical Synthesis of Nootkatone

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(+)-Nootkatone is a high-value sesquiterpenoid ketone widely recognized as a grapefruit flavoring and fragrance agent, registered by the U.S. EPA as a safe and effective broad-spectrum insect repellent with demonstrated efficacy against ticks, mosquitoes, fleas, lice, and termites. Despite its commercial promise, existing production routes remain economically unviable for the insecticide market due to prohibitively low yields and high costs, necessitating the development of alternative synthetic strategies. A patented 8-step chemical synthesis developed at Louisiana State University (LSU) offers a compelling route to nootkatone, but its commercial viability is severely constrained by a key anionic oxy-Cope (AOC) rearrangement step, which alone accounts for more than 50% of the total synthesis cost. This [3,3]-sigmatropic transformation conventionally requires hazardous and costly reagents such as KH or KHMDS paired with 18-crown-6 ether, to generate the alkoxide intermediate necessary for efficient rearrangement, posing serious challenges to safety, scalability, and cost. Herein, we report the development of heterogeneous base catalysts as practical replacements, wherein cesium salts (CsF and Cs_2CO_3) deposited on high-surface-area supports —including La/Al_2O_3, Al_2O_3, mesoporous MP-HMS-C8 silica, and MgO — via incipient wetness impregnation were systematically screened under varied reaction conditions. CsF/MgO emerged as the most active system, with its superior performance attributed to a synergy between the intrinsic basicity of MgO and the high cesium ion mobility of CsF, collectively enabling efficient rearrangement at 120°C in DMSO. These findings represent a significant advancement toward a safer, scalable, and economically viable platform for the key AOC step, enabled by reusable heterogeneous catalysts, with direct implications for commercial synthesis.

42. Kinetics of the oxygen evolution reaction over iridium oxide catalysts determined via temperature-dependent methods

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The electrochemical oxidation of water via the oxygen evolution reaction (OER) balances charge and supplies protons for important reactions like hydrogen generation, carbon dioxide reduction, and ammonia synthesis. Iridium oxide remains the only material both active and stable for the OER in acidic electrolyte, but its high cost (~5x that of platinum) drives efforts to design materials that maximize activity at lower mass loading. Although many strategies enhance the mass activity of iridium-based catalysts, their effects on intrinsic activity remain poorly understood because of challenges in identifying and quantifying active sites under reaction conditions. As a result, conventional turnover frequency metrics are often reliable.

To address this limitation, we measure intrinsic activity metrics that are independent of active site density, specifically the transfer coefficient and the enthalpy of activation. Rather than requiring precise counts of active sites, the transfer coefficient and enthalpy of activation are derived from how reaction rates respond to changes in thermodynamic driving forces. Additionally, these metrics are comparable across the range of thermodynamic conditions accessible by electrochemistry, among which relative apparent activities vary between different materials.

We measure the OER activity over commercial iridium oxide electrocatalysts using rotating disk electrode experiments in 0.1 M perchloric acid between 298.15-303.15K. The transfer coefficient is obtained from the Tafel slope, the change in order of magnitude of activity with applied overpotential, and the enthalpy of activation is determined via the Eyring equation. We find that there is a disconnect between standard activation barriers and apparent activity at OER overpotentials and show that the transfer coefficient and enthalpy of activation barrier vary significantly, even for similar materials. These findings suggest that optimal iridium oxide catalyst designs combine both low activation barriers and high transfer coefficients to maximize performance sensitivity to applied potential.

43. Precursor Chemistry Governs Iron (Fe) Site Evolution and Crystallization Dynamics in SSZ-13

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Iron-exchanged zeolites are valued for their hydrothermal stability and tunable redox properties, making them effective catalysts for high-temperature reactions such as selective catalytic reduction (SCR) of NO_x, N_2O decomposition, and selective oxidation. Their performance depends on the nature and distribution of iron species, including framework Fe, extra-framework cations, and oligomeric clusters.[1] However, how these species form during synthesis, and how precursor chemistry governs their evolution remains unclear. Here, we investigate how iron precursor identity influences crystallization and Fe speciation in SSZ-13 (CHA) synthesized via interzeolite transformation from FAU. We compare an organometallic precursor (ferrocene) with a conventional inorganic precursor (iron(III) nitrate nonahydrate) to determine their effects on nucleation, phase transformation kinetics, and metal incorporation.

Ferrocene-derived synthesis yields fully crystalline CHA after 48 h, with intermediate FAU–CHA mixtures observed as early as 24 h. In contrast, iron nitrate requires 96 h to achieve comparable crystallinity, indicating that the organometallic precursor accelerates CHA formation by at least a factor of two. Catalytic evaluation of the resulting Fe-CHA materials in NH_3-SCR demonstrates NO_x conversions ≥ 90% under high-temperature conditions, consistent with state-of-the-art Fe-zeolite catalysts. Despite these advantages, one-pot synthesis using ferrocene is limited in achievable iron loading (≤ 1.5 wt.%), constrained by micropore capacity and the onset of metal agglomeration. Consequently, applications requiring higher Fe content such as Fischer–Tropsch synthesis for syngas ($CO + H_2$) upgrading, necessitate post-synthetic approaches such as wetness impregnation. Overall, this work highlights the critical role of precursor chemistry in governing zeolite crystallization kinetics and iron speciation. It further delineates the trade-offs inherent to one-pot metal encapsulation strategies, providing guidance for the rational design of Fe-zeolite catalysts tailored to specific catalytic applications.

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44. Leveraging Carbonaceous Deposits through Selective Passivized Catalysis (SPC)

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Carbonaceous deposits, commonly referred to as “coke,” have traditionally been viewed as detrimental to catalytic performance because they deactivate catalysts by blocking active sites and pores. However, literature increasingly shows that coke can also provide important catalytic benefits through several mechanisms. Through Selective Passivized Catalysis (SPC), carbonaceous species can be intentionally utilized to enhance selectivity, activity, and long-term stability through deliberate pre-treatment or controlled in situ formation. Coke can selectively deactivate highly energetic, non-selective surface sites that would otherwise promote undesirable side reactions such as cracking or transalkylation. In other systems, it can participate directly in reaction pathways, as demonstrated by the “hydrocarbon pool” mechanism in methanol-to-hydrocarbon conversion, where coke precursors serve as reactive intermediates. Carbonaceous species may also evolve into the primary active sites themselves, particularly in oxidative and non-oxidative dehydrogenation reactions. The significance of SPC is especially evident in the non-oxidative coupling of methane (NOCM), a process typically limited by rapid catalyst deactivation from uncontrolled coking. Recent studies show that both ex situ strategies, such as Pt–Bi alloying and geometric confinement on MXenes, and in situ passivization approaches can balance activity and durability, achieving C_2 selectivities above 90% with sustained performance. SPC therefore represents a shift in catalyst design philosophy, moving beyond simply minimizing activation barriers toward optimizing the balance between reactivity and site stability, and offers a promising framework for developing more robust and sustainable catalytic processes.

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45. Facet-dependent Oxygen Chemistry of MgO Catalysts for Oxidative Coupling of Methane

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Oxidative coupling of methane (OCM) is an attractive route for the direct conversion of methane to C2 hydrocarbons, but the surface species governing structure-sensitive OCM over MgO remain poorly understood. Here, we establish structure–performance relationships for MgO catalysts exposing {100}, stepped {100}, and {111} facets. A structurally stable {111}-faceted MgO catalyst consistently outperforms its conventional counterparts over a range of reaction conditions, although its superior performance is transient. Kinetic analysis, operando Raman spectroscopy, and computational calculations indicate that preadsorbed molecular oxygen species on {111} facets promote methane activation, while their consumption during OCM accounts for the transient behavior. Facile oxidative regeneration replenishes these species and restores the initial reactive state, enabling sustained OCM–regeneration cycling. These findings reveal a distinctive catalytic role of MgO{111} surfaces as a dynamic oxygen reservoir during OCM and underscore the advantages of engineering metal oxides with well-defined surface structures.

46. A Practical Reactor Platform for Efficient Amine and Nitrile Process Development

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An optimized reaction platform for amine and nitrile process development is described, enabling efficient evaluation of ammonia-based gas-phase catalytic reactions. The system integrates safe ammonia handling with cost-effective, modular reactor design to provide precise control over reaction conditions. Flow stability across multiple reactor configurations is analyzed through detailed modeling, providing a framework for selecting and configuring reactors to achieve targeted operating regimes. This approach offers a practical template for improving reproducibility and accelerating process development in ammonia-based systems.

47. Selective Passivization of Pt Catalysts for Hydrogen Production

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Methane, the most abundant hydrocarbon in Louisiana shale gas, offers the highest hydrogen-to-carbon ratio among alkanes (4:1), making it an attractive feedstock for clean hydrogen production. However, direct methane-to-hydrogen conversion remains uncommercialized because rapid coking deactivates catalysts, forcing industry to rely on oxidative syngas routes that sacrifice efficiency and generate additional carbon emissions. Achieving long-term stability in non-oxidative pathways has proven particularly resistant to conventional catalyst design strategies. Selective Passivized Catalysis (SPC) addresses this challenge through targeted surface engineering, where unproductive active sites are passivized to suppress coking and side reactions while productive sites are preserved for sustained, highly selective conversion. Here, we extend SPC to the non-oxidative coupling of methane (NOCM) for direct hydrogen generation using two architecturally distinct catalyst platforms: (1) Pt nanolayers confined within the interlayer spacing of $Mo_2TiC_2T_x$ MXene and (2) Pt–Bi bimetallic nanoparticles supported on ZSM-5. Both systems were benchmarked against unpassivized Pt nanoparticles under NOCM conditions (750 °C and 650 °C for the nanolayer and nanoparticle systems, respectively). The unpassivized Pt catalyst deactivated rapidly, whereas both SPC catalysts reached stable methane conversion within 4 minutes on stream (1.9% for Pt/$Mo_2TiC_2T_x$ and 1.4% for Pt–Bi), approaching near-thermodynamic equilibrium values (2.9% and 1.8%, respectively). These results establish SPC as a viable pathway toward direct, cost-effective hydrogen production from Louisiana shale gas.

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(3) Li, Z.; Xiao, Y.; Roy Chowdhury, P.; Wu, Z.; Ma, T.; et al. Nat. Catal. 4 (2021) 882–891.

48. Computational Investigation of Co and Ni Diffusion and Agglomeration on Ceria

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Transition metal nanoparticles (NPs) dispersed on ceria are widely used to catalyze technologically important reactions, including three-way catalysis, water-gas shift, and hydrocarbon reforming. There is ample evidence in the literature that base metals such as Co and Ni exhibit unique, often superior catalytic activity when supported on ceria compared to other oxides, which are broadly attributed to metal-ceria interactions and redox actions made possible by ceria. Understanding the growth and stability of these metal nanoparticles on ceria surfaces is therefore of importance in heterogeneous catalysis. We will present a theoretical study of potential mechanisms of Co and Ni diffusion via small metal species consisting of 1~4 metal atoms on $CeO_2(111)$ based on density functional theory (DFT) calculations. The diffusion of the nanoclusters is found to be markedly more facile than that of the adatom. The implications of the different energies and diffusivities of the nanoclusters to particle size distribution and stability are discussed in the context of mathematical models, which are used to rationalize surface science studies, including STM and XPS, of Co and Ni on model ceria surfaces. We will highlight the differences between the two metals and furthermore discuss factors that enhance or hinder the diffusion of these metals on ceria. Our findings provide fundamental insights into the understanding of ceria-supported Co- and Ni-catalyzed reactions and guidance to improved catalyst design.

49. Programmable Design of Hierarchical Zeolite Catalysts with Compositional Zoning Using Facile Secondary Growth Methodologies

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The design of hierarchical zeolites through post-synthetic modification offers versatile routes to tune their catalytic performance by engineering properties such as morphology and/or aluminum distribution. In this study, we develop secondary growth methods to produce finned and core-shell zeolites with tailored mesoscopic gradients in acid site density and assess their performance in the methanol to hydrocarbon (MTH) reaction. A series of five catalysts were prepared using either ZSM-5 or its catalytically-inactive siliceous isostructure silicalite-1 as seeds. The secondary growth protocols were designed to generate a variety of compositional gradients where the interior (seed) and exterior (fin or core-shell) were catalytically active and/or inactive. We show that catalysts with only active exteriors function as pseudo nanoparticles (fins) or nanosheets (core-shells), whereas catalytically active cores with siliceous (passivated) exteriors enhance mass transport near pores mouths to extend catalyst lifetime. Our findings reveal that Si-rich fins grown on ZSM-5 seeds outperform finned ZSM-5 with homogenous aluminosilicate regions by enhancing mass transport into the catalyst interior and reducing external coking. The superior catalyst in this study was obtained by growing aluminosilicate fins on silicalite-1 seeds, which leads to a population of ultra-small ZSM-5 nanoparticles (<20 nm) that cannot be achieved by conventional one-pot synthesis. Comparisons between finned and core-shell catalysts of similar compositional architectures indicate the former have much higher cumulative turnover numbers and longer lifetimes. We posit these differences are due in part to the introduction of defects during core-shell growth and the generation of high-density pore openings in finned zeolites. The results of this study highlight the benefits of designing high-performance zeolite catalysts through post-synthetic modifications where controlled elemental zoning in hierarchical structures can be used to markedly enhance their catalytic performance.

Here we also discuss how these design principles were extended to one-dimensional zeolites, which exhibit the most severe diffusion limitations. We have demonstrated that secondary growth induces nanoscale surface roughness composed of step-like features that generate short transport pathways (10–50 nm) while reducing intrinsic defects. This leads to increased micropore accessibility and improved catalytic performance, including higher turnover numbers, selectivity, and stability. Collectively, these findings establish secondary growth as a programmable platform for the rational design of hierarchical zeolite catalysts, enabling independent control of morphology and composition to optimize transport and reactivity in diffusion-limited systems.

50. Mechanistic insights into formate dehydrogenation on Pd(111): A density functional theory study

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The dehydrogenation of formate salts offers a promising chemical pathway for the on-demand production of hydrogen. Despite their relatively low hydrogen capacity, formate salts present significant advantages over metal hydrides and liquid organic hydrogen carriers (LOHCs), particularly regarding cost, safety, toxicity, and the ability to operate under mild conditions. Intriguingly, all common metals except Pd are essentially inactive for this reaction. The fundamental reason behind this unique activity of Pd remains poorly understood, fueling ongoing debate in the literature regarding the exact reaction mechanism. To address this knowledge gap, we present a density functional theory (DFT) study investigating the dehydrogenation mechanisms of both formic acid and formate. By explicitly accounting for aqueous interface and charge effects, our findings reveal that formic acid cannot continuously dehydrogenate on a hydrogen-saturated surface, effectively making it a spectator in the solution. Instead, the catalytic cycle is driven by formate anion dehydrogenation operating under a mixed-potential condition, where the catalyst surface must simultaneously balance the oxidation of formate with a corresponding reduction reaction to prevent charge accumulation.

51. Theoretical Insights for Designing Stable Low-Iridium Oxygen Evolution Catalysts

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The global push towards decarbonization has greatly incentivized the advancement of hydrogen production technologies. Coupled with renewable energy, proton exchange membrane (PEM) water electrolyzers are emerging as a promising technology on the path to green hydrogen, offering a minimal footprint. Yet, scaling the Oxygen Evolution Reaction (OER) with stable, cost-effective anodes remains a significant challenge. Iridium oxide (IrO2), despite its catalytic prowess, is limited by scarcity, and promising alternative catalysts like Ruthenium Oxide (RuO2) often fall short of the operational lifetimes required for industrial scalability. As might be expected, doping Ir into RuO_2 can enhance its durability, but the specifics regarding the origin of this enhancement and the extent to which iridium loading can be minimized remain unclear. Our research leveraged Density Functional Theory (DFT) and Monte Carlo

(MC) simulations toinvestigate iridium's role in enhancing the stability of RuO_2.[1] DFT was employed to design stability rules for Ru in coordination with Ir and to derive energetics for an MC algorithm that simulated the Ir dopant distribution, accounting for thermal fluctuations under nanoparticle synthesis conditions. Importantly, we found that the oxophilicity of iridium and the material morphology have significant implications for the amount of iridium needed to stabilize the RuO_2 lattice. This led to the development of a high-performance low-Ir RuO_2-based material that demonstrated remarkable endurance under commercially-relevant conditions. The synthesized catalyst maintained its stability for several thousand hours at a current density of $2\ A/cm^2$ in a PEM electrolyzer, offering a viable pathway towards sustainable and scalable green hydrogen production and highlighting potential design rules for doped low-iridium oxygen evolution materials.

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52. Programmable chemical sensitivities scale with extent of reaction instead of time

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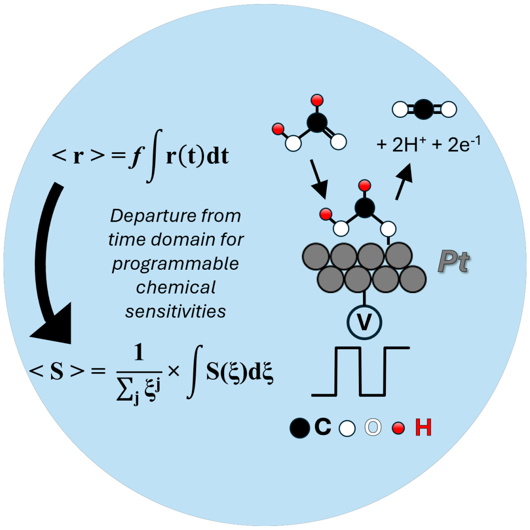
The programmable oscillation of external energetic stimuli to drive a catalytic surface between distinct regimes of kinetic control has emerged as a strategy to surpass steady-state Sabatier limitations, yet experimental probes of the underlying kinetic origins of rate enhancement remain limited. Here, we demonstrate that chemical sensitivities such as apparent reaction orders, activation energies, and the Gibbs free energy, scale with reaction events (extent of reaction) under oscillatory conditions and not time. Using formic acid electro-oxidation on polycrystalline Pt as a model system, an analytical framework demonstrating that transient kinetic parameters are governed by reaction event weighting was developed, rather than time-weighted averages based on duty cycle. Experimentally-observable charge transfer during potentiodynamic oscillations provided a direct and quantitative measure for the extent of reaction, enabling prediction of dynamic chemical sensitivities across a wide range of oscillation timescales (10-3 - 101 Hz) and reaction conditions (285-305 K, 0.05-2.5 M HCOOH). The extent of reaction formalism accurately reconciled experimentally-observed potentiodynamic reaction orders and activation barriers with steady-state behavior. Considering the overall driving force as an extent of reaction weighted average, programmable oscillations were found to significantly reduce the overpotential required to achieve a rate of catalytic turnover equal to potentiostatic operation. Although developed for electrochemical potential oscillations, the extent of reaction weighting framework is universally applicable to any catalytic system driven by programmable energetic stimuli (e.g. electrical, photonic, mechanical).



Scheme 1. Periodic modulation of potential between two energetic states at a Pt surface with frequency (f) tunes the rate (r) of Formic acid electro-oxidation in the time (t) domain. Chemical sensitivities (S) in the rate of turnover depart from the time domain into the extent of reaction (ξ) domain.

53. Controlling Product Selectivity in Catalytic Nitrite Reduction via Isotopic Studies

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Nitrate (NO_3^-) and nitrite (NO_2^-) are pervasive water contaminants originating from both natural processes and anthropogenic activities, including agricultural runoff, wastewater discharge, and industrial waste. Elevated exposure to these contaminants can pose serious human health risks, such as methemoglobinemia and cancer. To mitigate these risks, the U.S. EPA has established the maximum contaminant levels of 10 mg-N/L and 1 mg-N/L for NO_3^- and NO_2^-, respectively. Catalytic reduction using palladium (Pd)-based catalysts has been extensively investigated as an effective strategy for NO_3^-/NO_2^- removal, where ammonium (NH_4^+) and nitrogen gas (N_2) are generally considered the primary end products, with N_2 being preferred for water purification. Due to the analytical challenges associated with direct N_2 quantification, it is commonly assumed that nitrogen not detected as NH_4^+ corresponds to N_2 based on nitrogen mass balance. Here, we demonstrate that this assumption may lead to substantial overestimation of N_2. Using isotope-labeled nitrite ($^{15}NO_2^-$), nitrous oxide ($^{15}N_2O$) is identified as the dominant product upon $^{15}NO_2^-$ depletion, while only trace amount of $^{15}N_2$ is observed. Pd catalysts showed ~70% selectivity to $^{15}N_2O$ under examined conditions. These findings underscore that N_2O formation has been significantly underestimated in catalytic nitrite reduction and can be modulated by controlling reaction conditions, thereby providing a practical strategy to balance environmental remediation of nitrite with the selective production of value-added nitrogen species.

54. Plasmonic Fabry–Pérot Cavities for Enhanced Hydrogen Generation

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Semiconductor-based photocatalysis utilizes natural sunlight or artificial illumination to drive redox reactions, offering promising applications in environmental remediation and photocatalytic hydrogen production. TiO_2 has long been regarded as a promising material for hydrogen production. However, its practical application is hindered by a wide bandgap, which restricts its light absorption range and photocatalytic activity, posing significant challenges to its photocatalytic hydrogen production efficiency. To address these issues, we present the development of a plasmonic metal-insulator-metal (MIM) nanostructure designed to expand the light absorption spectrum and increase amounts of photoactive sites. The MIM structure, Au@TiO_2 NW|Au-NP, is composed of a bottom layer of Au nanoparticles, a middle layer of TiO_2 nanowires synthesized via a hydrothermal process, and a top layer of Au nanoparticles fabricated through a facile photodeposition process under low-watt visible-LED light. Au@TiO_2 NW|Au-NP nanostructure facilitates multiple internal light reflections, significantly enhancing optical localization and charge carrier dynamics. Optical characterization reveals that the structure exhibits broadband absorption from 400 to 1100 nm, with an absorptance exceeding 95%, demonstrating superior light-harvesting capability. Additionally, two-photon-induced photoluminescence (TPI-PL) analysis indicates pronounced broadband near-field amplification, suggesting a reduced dephasing time and efficient hot carrier generation. Finally, Au@TiO_2 NW|Au-NP achieves a photocurrent density of 35 μA cm^{-2}, nearly nine times higher than that of TiO_2 NW|Au-NP. The outstanding photocatalytic activity performance is achieved due to excellent photocurrent-extraction performance and broad plasmonic absorption in UV-Vis-Near IR range. In conclusion, Au@TiO_2 NW|Au-NP nanostructure paves the way for the development of plasmon-enhanced materials for sustainable solar energy conversion and hydrogen production.

55. Computational Insights into PFAS Degradation on Boron Nitride Catalysts

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This study provides insight into the degradation of perfluoroalkyl substances (FPAS) on boron nitride using photocatalysis. BN is a commercially available wide-band-gap semiconductor which has been shown to be more effective at PFCA degradation than other common photocatalysts.1 A key finding is the role that hydrophobicity plays in supporting the degradation of PFOA on BN. Density functional theory (DFT) was used to aid in the understanding of the underlying mechanism for PFAS degradation on BN. Prior work proposed a four-step mechanism for PFOA degradation, as well as showing the importance of the nitrogen-boron replacement defect in facilitating this pathway.[1,2] DFT examined the viability of this defect, as well as the favorability for electron transfer and the density of states of the system.[2,3] Further work has shown that BN is effective in environmentally relevant concentrations and conditions.[4] These results can be used to aid in understanding impact of environmental contaminants on PFAS degradation and aid in designing more effective catalysts for PFAS degradation.

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56. Improved Dry Reforming Activity, Stability, and Selectivity by Tailoring Feed Composition

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Dry reforming of methane (DRM) converts greenhouse gases (CO_2 and CH_4) to syngas (H_2 and CO). Supported Ni catalysts are commonly employed to take advantage of chemical activity and earth abundance. Still, most supported Ni catalysts eventually deactivate either due to coking at lower temperatures (<700°C) or sintering at higher ones. Such deactivation becomes more of a problem at total pressures higher than atmospheric. Great importance has been placed on the development of catalysts to achieve stability (TOS > 100h) and high selectivity (H_2/CO >0.9).

In this work, $Ni/CeO_2/ZrO_2$, $Ni\text{-}Co/CeO_3/La_2O_3$, and other catalysts have been explored for DRM at lower temperatures. The effects of feed ratio (CO_2:CH_4 ratio) and co-feeding of CO and H_2O to the feed were explored in kinetics studies at these temperatures and a range of partial pressures to develop optimal catalytic reaction conditions.

For the Ni/rare earth oxide catalysts, there was little to no coking at standard conditions, an coking/deactivation could be further reduced either by higher (than 1 : 1) CO_2 : CH_4 feed ratios or modest H_2O co-feeding. Kinetics studies showed that increasing CO_2 partial pressure accelerated DRM for redox-capable catalysts, that low CO partial pressures did not inhibit the reaction, and that water addition both suppressed coke formation and stabilized the active Ni phase, water effectively functioning as a promoter of DRM.

57. Maximizing $Cu/ZnO/Al_2O_3$ Catalyst Performance by Unlocking Intrinsic Methanol Selectivity with In-Situ Water Removal

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Manufacturing methanol from CO_2+H_2 has been frequently researched for its promise as a greener alternative to the typical synthesis route from syngas. However, unlike the syngas route, using CO_2 produces water, which inhibits methanol yields and selectivities (1). By co-loading a zeolite sorbent alongside a $Cu/ZnO/Al_2O_3$ (CZA) catalyst, water can be removed in-situ, temporarily enhancing methanol rates. This work aims to model the performance of these sorption-enhanced (SE) reactors and maximize CZA performance by accessing high selectivities, unavailable under steady-state operation, in the absence of water.

Simulations show enhanced methanol and CO formation when water is removed from the reactor, in line with literature observations (2). Removing water from the reactor significantly affects the catalyst performance, but the enhancement is both thermodynamic and kinetic in nature. By tuning the catalyst loading, the thermodynamic and kinetic benefits can be separated and compared. The enhancement of methanol yields via water removal is greater under kinetic control, and there is also a significant selectivity advantage when compared to the thermodynamically controlled regime. In fact, similar integral methanol yields can be attained in both regimes, representing a 20x more efficient catalyst usage under kinetic control.

This work demonstrates the utility of SE reactors for enhancing CZA performance for CO_2 hydrogenation, compared with typical steady-state operation in packed-bed reactors. Methanol formation suffers from kinetic and thermodynamic limitations that are alleviated when water is removed. This work highlights SE’s ability to unlock the innate methanol selectivity of CZA catalysts, which is inaccessible under steady-state operation due to water’s presence. However, it requires careful tuning of the catalyst loading to guarantee kinetic control.

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