SOUTHWEST CATALYSIS SOCIETY

2025 SPRING SYMPOSIUM

Friday, May 2, 2025

Rice University

Grand Hall of the

Ley Student Center

Houston, TX

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RICE ENGINEERING AND COMPUTING
Department of Chemical and Biomolecular Engineering

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The SWCS officers and I welcome you to the 2025 Southwest Catalysis Society Spring Symposium, Friday, May 2, 2025, at Rice University.

We are delighted to present six invited speakers and 66 poster presentations at this year's symposium. The 2025 SWCS Excellence in Applied Catalysis Award will be presented. Furthermore, meritorious posters presented by students and postdocs will be identified with Best Poster Awards. See Page 5 for an outline of the Program.

The 2025 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 6 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).

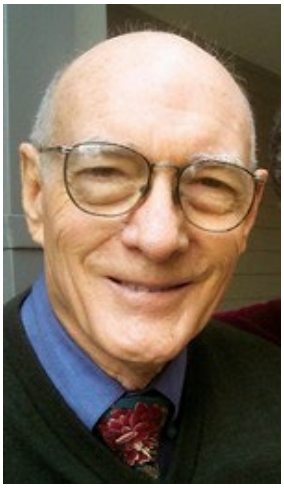
We hope you enjoy the Symposium!

Tom Senftle

SWCS Chair
Associate Professor
William Marsh Rice Chair
Department of Chemical and Biomolecular Engineering
Rice University

A Brief History of the Southwest Catalysis Society

As recounted by Joe W. Hightower, Professor Emeritus, Rice University (April 2009)
B.S. '59 - Harding University; M.S. '61 and Ph.D. '63 - The Johns Hopkins University



I came to Rice University from the Mellon Institute in Pittsburgh during the summer of 1967 and immediately set out to meet catalyst people in the area. We announced an organizational meeting to be held at Rice, Fall 1967. There were 63 people as charter members of what was to become the Southwest Catalysis Club. Jim Richardson (Esso Research and Engineering, now University of Houston) drafted the Bylaws and was elected Vice President, Jack Lunsford (Texas A&M University) was Secretary, Paul Conn (Shell Oil) was the Treasurer, and I served as the first elected President. The officers held the first all-day Spring Symposium in May 1968 in the Grand Hall at Rice, and the SWCS was off and running (42 years and counting!). [As a note, I did my PhD thesis research with Professor Paul Emmett at Johns Hopkins, which involved isotopic tracer studies of secondary reactions that occur during catalytic cracking of petroleum products.]

At the time we started, there were about half a dozen "Catalysis Clubs" scattered around the country: Chicago, Pittsburgh, New York, Philadelphia, California, and perhaps one more. I knew people in all these "Clubs" through groups like the Gordon Research Conferences on Catalysis, and they all encouraged us to start a club in the SW. Why 5 states? Texas was obvious. Arkansas was included because of Sam Siegel (Chemist at UArk); Louisiana, because of several researchers at Esso in Baton Rouge; Oklahoma, because of several Phillips researchers in Bartlesville; and New Mexico, because of people at University of New Mexico and at Sandia National Labs in Albuquerque. In spite of the long distances, people from all these places attended some of the early meetings held twice a year, which sometimes had attendance near 200. Most of the early meetings were held at Rice or in the Auditorium at the Shell-Westhollow labs. In later years, the meeting was held in nearby places like Austin, College Station, and New Orleans.

What was going on that made the late 60s an optimal time to establish the SWCS? I think the biggest factor was Shell downsizing its labs in Emeryville, CA and moving most its catalysis people to a new research facility at Westhollow. At the same time, Esso was increasing its applied catalysis work both in Baytown 30 miles east of the city and in Baton Rouge. For several years, Phillips Petroleum had been accumulating an amazing number of patents in catalysis at their laboratories in Bartlesville. Bob Eischens came from New York and was applying his pioneering infrared studies at Texaco in Port Arthur. Celanese had several catalysis people doing research near Corpus Christi. Many of you may recall that Texas City was devastated by the largest US chemical plant explosion of an ammonium nitrate ship in the mid-40s. After the explosion, Monsanto rebuilt its facilities there, where workers were doing research on improving catalytic processes for styrene and acrylonitrile manufacture. Petrotex Chemical in Pasadena, another suburb on Houston's ship channel, was optimizing its butadiene and C4 olefins production through catalytic processes.

In addition, catalysis groups were springing up at several universities, including surface science by the late John Mike White at the University of Texas, Jack Lunsford's and Wayne Goodman's highly productive groups at Texas A&M, Richard Gonzales at Tulane, Jim Richardson at U of H, Kerry Dooley at LSU, Tom Leland and me at Rice, and groups at other universities in the 5-state area. What was lacking? There was no formal mechanism for these diverse groups to exchange information or get advice in the southwest. The time was ripe for an organization where catalysis could be openly discussed. Although much catalysis research is proprietary, enough was sufficiently open to create a stimulating environment for sharing mutual interests, many focusing on new ultra-high vacuum analytical equipment that was being rapidly developed.

The first thing we did was to organize an NSF-supported workshop at Rice which (not surprisingly) concluded that more funding was needed for research on catalysts for fuels, environmental protection (cat converters), chemicals, etc. At that time, demand was also great for new employees with catalysis training, but the supply was quite limited. This provided an occasion for the development of short courses to train industrial employees in heterogeneous catalysis. Several courses were started around the country. One of the most successful was started at Rice and has continued for more than 30 years through the University of Houston. It

can be said, then, that **SWCS was instrumental in starting these heterogeneous catalysis short courses.**

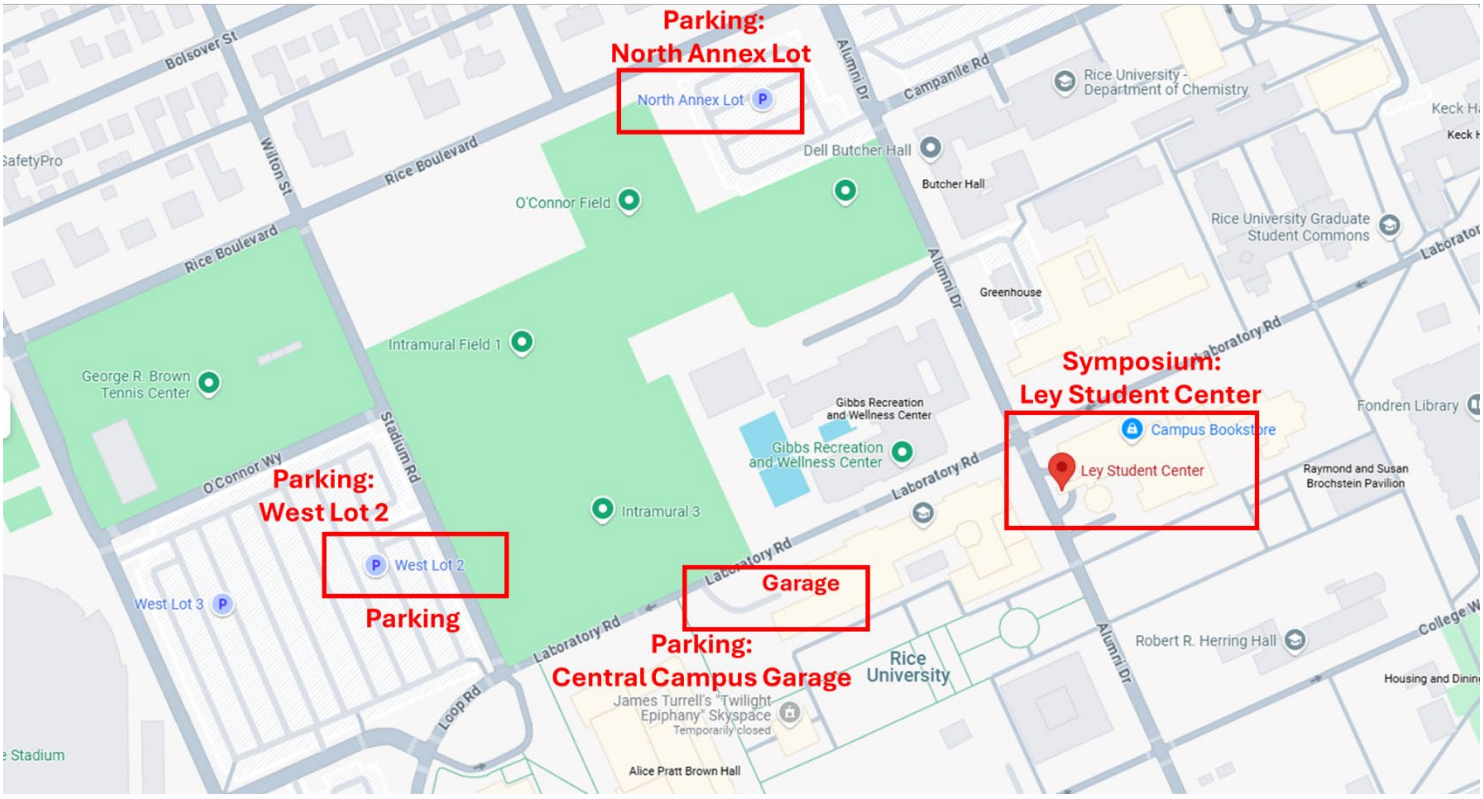
The "Club" was soon invited to join the other half dozen Clubs as a part of the growing North American Catalysis Society. Being the new kid on the block, our Club was asked to host its first biennial North American Meeting (NAM-2) in February 1971, which was held at the Astrodome Hotel in Houston. Jim Richardson and I were Associate and General Chair of the meeting, while Paul Venuto (Mobil Research/Development and a colleague of the late Heinz Heinemann) was in charge of the Program. At that meeting the late Dr. R. J. Kokes (one of my professors at Johns Hopkins) and Dr. H. S. Bloch (Universal Oil Products) were recipients, respectively, of the first Paul H. Emmett and Eugene J. Houdry Awards in fundamental and applied catalysis.

In 1985, the Southwest Catalysis Society was again called on to host a five-day 9th North American Meeting (NAM-9) at Houston's Adam's Mark Hotel. This time, Jack Lunsford and Lynn Slaugh were General and Vice Chair; I was Technical Program Chair. Most recently, the SWCS members organized the spectacular North American Meeting at Houston's downtown Hilton Americas Hotel in 2007, attended by over 1000 delegates from all over the world, “Celebrating Catalysis Texas Style.” Kudos again to SWCS officers Kerry Dooley, Brendan Murray, Scott Mitchell, Michael Reynolds, Yun-Feng Chang, Michael Wong, and many, many others! All told, the SWCS has hosted 3 national events now: 1971 (NAM-2), 1985 (NAM-9) and 2007 (NAM-20).

2025 PROGRAM

All talks & posters will be held in the Grand Hall at the Ley Student Center

8:30 AM	**Grand Hall Opens**
8:45-9:25 AM	**Registration and Poster Setup**
9:25 AM	**Welcoming Remarks – Tom Senftle, Chair**
9:30 AM	**Michael Reynolds**, Shell *Flipping for Hydrogen and Soaring on Soybeans*
10:15 AM	**David Flaherty**, Georgia Tech *Binuclear Cobalt Complexes Activate C-H Bonds during Ethane Ammoxidation in Aluminosilicates*
11:00 AM	**Coffee Break**
11:15 AM	**Julie Zhu**, Scientific Design *Ethylene Oxide (EO) Catalysis and Its Industrial Application*
12:00 PM	**Lunch Break and Poster Session**
1:50 PM	**Applied Catalysis Award, presented by Joaquin Resasco** **Jeffrey D. Rimer**, University of Houston **Winner, 2025 SWCS Excellence in Applied Catalysis Award** *Navigating the Boundaries between Fundamental and Applied Research in Zeolite Catalysis*
2:45 PM	**Simon Bare**, SSRL *Adventures in the Applications of Operando X-ray Absorption Spectroscopy to Catalyst Characterization at SSRL*
3:30 PM	**Coffee Break**
3:45 PM	**Javier Guzman**, ExxonMobil *ExxonMobil Global Outlook: Our view to 2050*
4:30 PM	**Presentation of Poster Awards**
4:45 PM	**Closing Remarks**
5:00 PM	**Happy Hour at Valhalla**



Symposium location:

Rice University

Grand Hall – Ley Student Center

Parking location:

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

https://parking.rice.edu/parking-facilities-and-rates

The parking lots closest to the Ley Student Center are the Central Campus Garage, the North Annex Lot (NOT the North Lot), and West Lot 2.

An interactive map of Rice University can be found here:

https://www.rice.edu/campus-maps

Flipping for Hydrogen and Soaring on Soybeans

Michael Reynolds
Senior Principal Science Expert – Catalysis, Shell Catalysts and Technologies, Shell USA, Inc.

An increasing global energy demand coupled with the societal need for sustainable fuels has led to a renaissance in catalyst development and fuel refining. Alternative energy sources such as hydrogen and bioderived hydrocarbons represent two potential fuels of the future. Hydrogen, the simplest of all molecules, is being investigated globally as an energy carrier for use in specialized engines and PEM fuel cells due to its clean combustion and lower heating value of 119 MJ/kg. Similarly, plant and animal wastes are now blended with conventional crude oil, and then refined into sustainable aviation fuels (SAF) and diesel. These resources have vastly different drivers and challenges that need to be addressed by the energy industry across many different platforms.

An impetus for this presentation is to educate the community on the potential value of these alternative fuels and how industry is approaching their implementation. This seminar will also highlight the opportunities and challenges associated with commercialization of the catalyst technologies required to upscale these sources from lab to commercial success.

Biography

Michael A. Reynolds is the *Senior Principal Scientist* for Shell Catalysts and Technologies in Houston, Texas where he leads programs for catalyst discovery and development in conventional refining, renewables, and the energy transition. His research focus includes commercial catalyst development for sustainable aviation fuel (SAF) and bio-to-diesel; developing catalyst fundamentals for ortho-to-parahydrogen conversion relevant to hydrogen storage; and applying crystal engineering fundamentals for new materials in water treatment applications.

Since 2012, Dr. Reynolds has served as an Adjunct Professor at Rice University's Department of Chemical and Biomolecular Engineering where he participates in student doctoral committees and teaches lectures on special topics. He is a strong practitioner and believer in collaboration with academic partners and national laboratories to solve societal challenges. He has led multidisciplinary R&D projects with partner universities including Rice, the University of Houston, UC Santa Barbara, MIT, and the University of Illinois in Champaign/Urbana with one project resulting in an *ACS Partnership for Progress and Prosperity* award with Rice (2022). Dr. Reynolds is an author of over 32 patents, 30 peer reviewed publications, and has been an invited speaker at 40+ universities and conferences since joining Shell. He is an *ACS Fellow* and has served in elected positions in the Southwest Catalysis Society, and the American Chemical Society ENFL Division throughout his career. Dr. Reynolds is a graduate of Michigan State University (B.S. Chemistry), Iowa State University (Ph.D.), and was a post-doctoral associate at the University of Illinois-Urbana/Champaign. He enjoys tennis, traveling internationally, and spending time on his farm in Illinois or the Great Lakes with family for vacations.

Binuclear Cobalt Complexes Activate C-H Bonds during Ethane Ammoxidation in Aluminosilicates

David Flaherty

Professor (Thomas C. DeLoach Jr. Endowed Professorship), School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia

The ammoxidation of light alkanes to nitriles (e.g., $2\ C_2H_6 + 3\ O_2 + 2\ NH_3 \rightarrow 2\ CH_3CN + 6\ H_2O$) provides opportunities to valorize alkanes under modest temperatures, avoiding the disadvantages of steam cracking or non-oxidative dehydrogenation reactions. Cobalt-exchanged aluminosilicate zeolites (e.g., ZSM-5) catalyze the ammoxidation of ethane, but the active form of cobalt, the role of Brønsted acid sites, and the reaction pathways for this complex multi-step chemistry remain unclear. Cobalt-incorporated aluminosilicates materials can possess distinct speciation of Co species (Co^{2+} at Al pair sites (CoZ_2), Co_3O_4, cobalt phyllosilicate, and cobalt aluminate) based upon synthesis protocols and used. Temperature programmed reduction and ion-exchange processes reveal the forms of Co present, and with comparisons to rate measurements, indicate that catalysts comprised primarily of CoZ_2 give the greatest carbon selectivities for conversion of C_2H_6 into CH_3CN and C_2H_4 in the presence of NH_3 and deliver C_2H_4 when contacting mixtures of C_2H_6 and O_2.

Turnover rates and selectivities measured as functions of contact time show CH_3CN forms as the dominant organic product at infinitesimal conversion over Co-exchanged aluminosilicates (5 kPa C_2H_6, 7.5 kPa O_2, 5 kPa NH_3, 573 – 643 K). *In situ* UV-Vis and *ab initio* calculations give evidence that the coordination and ligand-field of the Co centers evolves significantly upon heating and introducing NH_3. The Co^{2+} centers present in dehydrated forms bind NH_3 to form mobile cobalt amines ($Co(NH_3)_4^{2+}$) that detach from the zeolite framework. Rates for C_2H_6 consumption increase quadratically with cobalt loading in the presence of NH_3 but increase only linearly in the absence of NH_3, which shows that CH_3CN and C_2H_4 form at catalytically competent binuclear Co complexes. Ethane-derived products form at these complexes by kinetically relevant C-H bond activation, as demonstrated by normal kinetic isotope effects in comparisons between rates measured with C_2H_6 or C_2D_6. These observations give strong evidence that cobalt exchanged zeolites form molecular complexes *in situ* at high temperatures (>573 K) and these mobile species activate O_2 to produce binuclear metal peroxide and oxo complexes and activate C-H bonds in alkanes. Notably, the topology of aluminosilicates do not influence the ability of dehydrated Co^{2+} centers to bind NH_3 and form ($Co(NH_3)_4^{2+}$) complexes, however, larger mean pore diameters of aluminosilicates lead to lower normalized rates and a reduced ability to form the binuclear Co complexes.

Biography

David Flaherty is the Thomas C. DeLoach Jr. Endowed Professor in the School of Chemical and Biomolecular Engineering at the Georgia Institute of Technology. He leads a group that develops understanding and design principles for the use of solid catalysts to resolve challenges for the sustainable production of chemicals and energy carriers. Research focuses on generating new insight into chemical phenomena that emerge when reactions occur on complex and dynamic catalyst, often solid-liquid interfaces. Knowledge of these systems comes from kinetic, spectroscopic, synthetic, and computational perspectives intended to develop principles needed to harness diverse chemical interactions. Prof. Flaherty received the Department of Energy Early Career Award; National Science Foundation CAREER Award; the American Vacuum Society, Early Career Research Award; the Eastman Foundation Distinguished Lecturer in Catalysis; and the Emmett Award in Fundamental Catalysis from the North American Catalysis Society.

Flaherty serves as Editor-in-Chief for *Journal of Catalysis* and on the editorial advisory board of multiple other journals. He assisted in organizing the 26th and 29th North American Catalysis Society Meetings in multiple roles of the CATL Division of ACS. He started his independent career at the University of Illinois at Urbana-Champaign, where he was promoted to full professor and received numerous campus awards for teaching and scholarship. His group relocated to Georgia Tech in 2023.

Ethylene Oxide (EO) Catalysis and Its Industrial Application

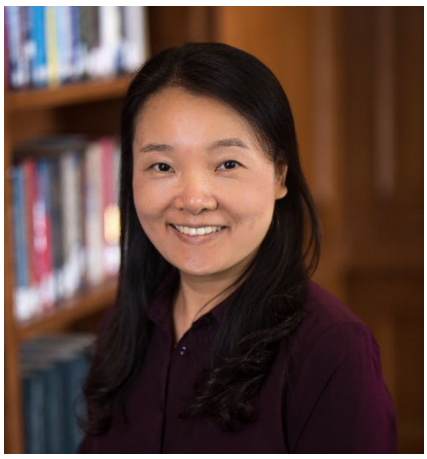
Li (Julie) Zhu
Vice President, R&D
Scientific Design LLC, A SABIC Company

The production of Ethylene Oxide (EO) through ethylene epoxidation is a key catalytic process in the chemical industry, as EO serves as a critical intermediate for various valuable chemicals. EO is primarily used in the production of Ethylene Glycol (EG) via thermal or catalytic hydration. EO and EG are essential precursors for products like polyester resins, antifreeze, sterilizing agents, surfactants, lubricants, paints, and pharmaceuticals. SABIC, the parent company of SD, is one of the leading EO/EG producers globally.

For decades, the industrial production of EO has relied on the epoxidation of ethylene in fixed-bed reactors, using silver-based catalyst supported on alpha alumina. Advancement in catalyst and process technology have significantly enhanced catalyst performance, resulting in reduced capital and operational cost, as well as lower CO2 emissions.

This presentation will provide an overview of the evolution and progress in EO catalysis from industrial perspective. It will highlight key advances driven by both fundamental and applied EO catalysis research and explore potential future research that could further improve the reaction efficiency, sustainability, and economic viability of this critical industrial process.

Biography



Julie joined Scientific Design LLC (SD, a SABIC company) in 2022 as the Vice President of R&D. In this role, she oversees all R&D activities, including product innovation, deployment, and support, while collaborating across multidisciplinary teams to drive and execute business strategies.

Prior to joining SD, Julie spent seven years at SABIC and over nine years at GE Global Research, both global industry leaders with extensive R&D organizations. Starting as a scientist, she progressed into technical leadership roles with increasing responsibilities, delivered and contributed to many technology and innovation advancements within these leading organizations. Julie holds ~20 patents and patent applications, along with 10+ journal publications and invited book chapters.

Julie holds a PhD in Chemistry from Louisiana State University, an Executive MBA from Rice University, and a BS in Chemistry from Nankai University.

Navigating the Boundaries between Fundamental and Applied Research in Zeolite Catalysis

Jeffrey D. Rimer
Abraham E. Dukler Professor of Chemical Engineering, University of Houston, Department of Chemical and Biomolecular Engineering, 4226 Martin Luther King Blvd., Houston, TX 77204

The diverse network of confined pores in zeolites have been widely used for shape-selective catalysis in the (petro)chemical industry and in applications related to energy transition and the evolving environmental landscape. This talk will focus on recent progress made in our group on the design and characterization of zeolite catalysts where our work lies at the boundary between fundamental and applied research. The complex pathways of zeolite crystallization make it difficult to control their physicochemical properties;[1] however, we have made significant progress in understanding zeolite nucleation and growth mechanisms using a combination of experimental and computational approaches that include the first high-temperature in situ scanning probe microscopy measurements of zeolite surface growth.[2, 3] Our long-term objective is to apply this knowledge to the development of state-of-the-art catalysts where we seek to improve the physicochemical properties of materials, including one of the most common obstacles in zeolite crystal engineering: overcoming the inherent mass transport limitations of nanopores. In this talk, I will highlight several methods to tailor zeolite crystal size, morphology, and composition in ways that reduce diffusion limitations and/or control acid siting, thereby enabling the design of catalysts with superior performance compared to materials obtained by conventional synthesis routes.[4, 5] Our research has explored methods of structure direction employing organics, inorganics, and combinations thereof to reduce synthesis times and tailor physicochemical properties. Additional studies of zeolite synthesis have shown how heteroatoms can be integrated in both conventional and hierarchical zeolites to enhance catalyst performance.[6] Among the hierarchical zeolites we have recently synthesized are self-pillared pentasils that exhibit four-fold increases in both catalyst lifetime and total turnovers; and a new class of catalysts, referred to as *finned zeolites*, which are prepared by seeded growth to introduce fin-like protrusions with identical crystallographic registry as the interior crystal.[7] Examples of 1-, 2-, and 3-dimensional zeolites will be discussed using methanol to hydrocarbons (MTH) and olefin cracking as benchmark reactions, as well as advanced characterization techniques such as high-resolution electron tomography, operando spectroscopy, novel acid titration methods, and molecular modeling to correlate structural features of hierarchical zeolites and their diffusion properties with enhanced catalyst performance.

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2. Choudhary, M.K., R. Jain, and J.D. Rimer, In situ imaging of two-dimensional surface growth reveals the prevalence and role of defects in zeolite crystallization. Proceedings of the National Academy of Sciences of the United States of America, 2020. 117(46): p. 28632-28639.
3. Lupulescu, A.I. and J.D. Rimer, In Situ Imaging of Silicalite-1 Surface Growth Reveals the Mechanism of Crystallization. Science, 2014. 344(6185): p. 729-732.
4. Le, T.T., W. Qin, A. Agarwal, N. Nikolopoulos, D.L. Fu, M.D. Patton, C. Weiland, S.R. Bare, J.C. Palmer, B.M. Weckhuysen, and J.D. Rimer, Elemental zoning enhances mass transport in zeolite catalysts for methanol to hydrocarbons. Nature Catalysis, 2023. 6(3): p. 254-+.
5. Le, T.T., K. Shilpa, C.S. Lee, S.M. Han, C. Weiland, S.R. Bare, P.J. Dauenhauer, and J.D. Rimer, Core-shell and egg-shell zeolite catalysts for enhanced hydrocarbon processing. Journal of Catalysis, 2022. 405: p. 664-675.
6. Abutalib, A., D. Parmar, J. Kim, and J.D. Rimer, Pairing Ga/Al-Zeolites with tailored acidity as tandem catalysts for the conversion of alcohols to olefins. Journal of Catalysis, 2024. 433.
7. Dai, H., Y.F. Shen, T.M. Yang, C.S. Lee, D.L. Fu, A. Agarwal, T.T. Le, M. Tsapatsis, J.C. Palmer, B.M. Weckhuysen, P.J. Dauenhauer, X.D. Zou, and J.D. Rimer, Finned zeolite catalysts. Nature Materials, 2020. 19(10): p. 1074-+.

Biography

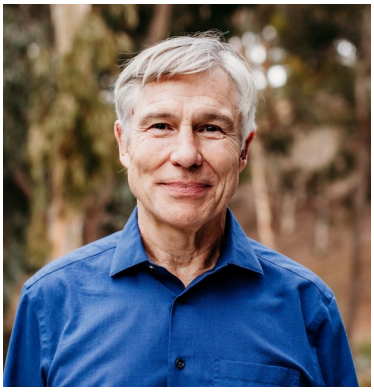
Jeff Rimer is the Abraham E. Dukler Endowed Chair and Professor of Chemical Engineering at the University of Houston. Jeff received B.S. degrees in Chemical Engineering and Chemistry from Washington University in St. Louis and Allegheny College, respectively. He received his Ph.D. in Chemical Engineering from the University of Delaware and spent two years as a postdoctoral fellow at New York University prior to joining Houston in 2009. Jeff is a Senior Member of the National Academy of Inventors, a Fellow of the American Institute of Chemical Engineers (AIChE), and has received numerous awards that include the NSF CAREER Award, the 2016 Owens Corning Early Career Award and 2017 FRI/John G. Kunesh Award from AIChE, the 2018 Norman Hackerman Award in Chemical Research from The Welch Foundation, the 2020 Edith and Peter O'Donnell Award in Engineering from TAMEST, and the 2024 Catalysis Club of Philadelphia Award. He is a former chair of the Southwest Catalysis Society, an executive committee member for the International Zeolite Association, and has chaired two Gordon Research Conferences on Crystal Growth & Assembly and Nanoporous Materials & Their Applications. He currently serves as the Director of Graduate Studies and Program Director for the Welch Center for Advanced Bioactive Materials Crystallization. Jeff is also an Associate Editor of Crystal Growth & Design and serves on the advisory boards of five other journals.

Recent Adventures in the Applications of Operando X-ray Absorption Spectroscopy to Catalyst Characterization at SSRL

Simon Bare
SSRL, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

The Consortium for Operando and Advanced Catalyst Characterization via Electronic Spectroscopy and Structure (Co-ACCESS) is a research program funded by the US Department of Energy, Basic Energy Sciences and is located at SSRL. Its aim is to provide resources and know-how to catalysis researchers who wish to conduct their research at SSRL and has a strong focus in in-situ/operando catalyst characterization. In this talk I will provide a brief overview of our goals and capabilities before highlighting some of our recent collaborative research. These highlights include: (i) Development of methods and tools to aid the catalysis researcher prepare for their experiments and process the data after the experiment, and (ii) Development of approaches to provide more quantitative understanding of the structure of, in particular, single atom catalysts. I will conclude with a look to the future of new time resolved XAS capabilities under development at SSRL.

Biography



Simon R Bare is a distinguished scientist at SLAC National Accelerator Laboratory. He earned his B.Sc. in Chemistry and Ph.D. in Surface Chemistry from the University of Liverpool, UK. He was a postdoctoral fellow at both Cornell University and Lawrence Berkeley National Laboratory. He then transitioned in industry and held various positions in catalyst research at The Dow Chemical Company over 10 years, and then at UOP, a Honeywell Company for 19 years. He then had a career change and joined Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory in 2016.

His research is focused on in-situ/operando catalyst characterization using techniques available at synchrotrons, with a focus on X-ray absorption spectroscopy to develop structure-property relationships. He enjoys developing and applying new catalyst characterization techniques. His group, the Consortium for Operando and Advanced Catalyst Characterization via Electronic Spectroscopy and Structure (Co-ACCESS), develops methodology to allow any catalysis researcher to perform their experiments effectively, efficiently, and safely at Stanford Synchrotron Radiation Lightsource (SSRL). His group currently collaborates with over 30 catalysis-focused research groups in the US and globally. He has authored over 200 publications and holds 10 US patents.

He is a fellow of the AAAS is the 2025 recipient of the ACS CATL Division Exceptional Achievements Award and had held many leadership positions, including being a member of BESAC from 2008-2017. Mentorship, encouragement, and inclusivity are high on his value system. He fully embraces the concept that collaboration is the key to drive science forward of we are to meet the climate goals of 2030 and 2050.

ExxonMobil Global Outlook: Our view to 2050

Javier Guzman
Global Energy and Technology Senior Advisor, Corporate Strategic Planning at ExxonMobil

The world will need to increase access to reliable, affordable energy from a broad set of solutions for economic development and modern living standards. Large energy disparity still exists between developed and developing countries. Growing energy consumption supports economic expansion, enabling longer, more productive lives for the growing global population. The Global Outlook is ExxonMobil's view of energy demand and supply through 2050, based on a long-term assessment of economic trends, advances in technology, consumer behavior and climate-related public policy.

By 2030, carbon emissions are projected to fall for the first time as economic activity expands. Hard-to-decarbonize commercial transportation and industrial activity will account for nearly half of the world's emissions in 2050. Reducing emissions to achieve a below 2°C pathway will require supportive policy, technology innovation, and market incentives to drive faster deployment of all available solutions. Oil and natural gas remain the largest energy sources. Electricity use grows in all sectors, with generation from solar and wind growing the fastest. Coal is displaced by lower-emission sources, including both renewables and natural gas. Commercial transportation and industrial feedstocks drive continued demand for oil.

We will discuss the role of catalysis in this context and as the world evolves towards 2050.

Biography

Javier Guzman is the Global Energy and Technology Senior Advisor in Corporate Strategic Planning at ExxonMobil. He is responsible for developing insights in strategic topics related to energy, technology, and markets that inform ExxonMobil Global Outlook. Javier has served in several technical and managerial leadership positions, including in technology, chemicals, and fuels. Prior to his industrial career, he worked in academia. He currently serves in the U.S. Department of Energy Basic Energy Science Advisory Committee. He serves as a member of multiple advisory boards of engineering schools and research centers. Javier holds a Ph.D. degree in Chemical Engineering from the University of California and did postdoctoral training in chemistry in Europe.

POSTER ABSTRACTS

1. A Global Kinetic Model for High Temperature Homogeneous Oxidative Dehydrogenation of Ethane

Syed Ahsan Imam, Praveen Bollini, Vemuri Balakotaiah
William A. Brookshire Department of Chemical & Biomolecular Engineering,
University of Houston, TX 77004

Ethylene is an indispensable chemical commodity to produce a variety of important products including polyethylene, ethylene oxide, vinyl chloride and various others. Steam cracking is being employed in the industry to produce ethylene with naphtha or ethane as the feedstock and being of endothermic nature, it requires elevated temperature input typically 750-900 deg C (tube temperature can rise to 1100 deg C) requiring 16-23 GJ/ton (naphtha feed) energy requirement and accounting for 260 Mt/yr of CO2 emissions. It has also been reported that nearly 70% of ethylene cost is attributed to the energy requirement. This high temperature requirement can adversely affect the life of reactor tubes and require periodic shutdown for coke removal.

Ethane partial oxidation has surfaced as a potential alternative considering lower reaction temperature requirement and decrease in coke formation compared to ethane cracking. Several catalysts have been reported in the literature; however, little work has been presented in the past incorporating homogenous chemistry which can be an emergent competing alternative to the aforementioned. The influence of homogeneous chemistry plays a pivotal role even with a catalytic system when high temperature operation is anticipated and may stand out under certain process conditions; therefore, it is utmost necessary to corroborate such behavior independently.

For the kinetic model perspective, previous studies were mainly focused on micro-kinetics comprising of several species and reaction steps. The present work focuses on explaining seven-reactions/eight-species based global kinetic model for high temperature homogeneous oxidative dehydrogenation of ethane. Model predictions are compared with available literature data as well as obtained experimental data to validate the approach as well as the kinetic constants to determine conversion, product distribution profile in terms of selectivity and yield under various feed ratios, space time and temperature conditions. Thermodynamics and effect of different characteristic time scales in ascertaining isothermal and adiabatic conditions in a laboratory scale tubular reactor and to briefly elucidate reaction pathway assessment, product co-feed experiments, influence of cracking chemistry and overall modeling approach are also elucidated in the study.

2. Photocatalytic Degradation of Perfluorooctanoic Acid using Pyrene-based Covalent Organic Frameworks with Diacetylene Linkers

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Poly- and per-fluoroalkyl substances (PFAS) are artificial fluorinated compounds employed in various applications that are linked to negative health effects. Traditional methods, such as adsorption, do not destroy PFAS, creating the need for frequent regeneration and disposal of the toxic materials. For that reason, the development of materials that can both adsorb and catalytically degrade PFAS is attractive for creating sustainable and effective remediation strategies. Covalent organic frameworks (COFs) are promising materials for PFAS photodegradation, given their low cost, easy tunability, and photocatalytic activity. In our experimental and computational study, we report a pyrene-based covalent organic framework (COF) with a diacetylene linker (Py-DEBD) capable of acting as both an adsorbent and heterogeneous photocatalyst for the degradation of PFAS contaminants. The adsorption and photocatalytic activity of Py-DEBD were tested in batch photodegradation experiments (Figure 1a – 1c), showing that over 99% of PFOA was removed from the solution, and 32% defluorination was achieved within 24 h of treatment. The concentration of short-chain byproducts initially increased during the photodegradation experiment, with some of them showing a decrease in their concentration after continued irradiation, suggesting that these intermediates are also photochemically degraded. Density functional theory simulations indicate that Py-DEBD has a favorable adsorption behavior towards PFAS with calculated solution state adsorption energies (ΔEads) in the range of −0.7 to −1.0 eV. Excited state TD-DFT calculations also showed that the adsorption of PFOA onto the surface of Py-DEBD initiates an oxidative photoinduced charge transfer mechanism under UV irradiation, leading to PFOA oxidation. Electron density difference maps of the S0 → S1 transition (Figure 1d) show that the excitation of the bare COF results in charge transfer from the pyrene node to the diacetylene linker, whereas the electron transfer occurs from the PFOA anion to the diacetylene linker region of Py-DEBD when adsorbed PFOA is present. Based on these results, we propose that PFOA first adsorbs on the Py-DEBD framework and that electron transfer from the PFOA to the COF is promoted when the PFOA–Py-DEBD complex enters an excited state under illumination. Control experiments and DFT simulations show that the pyrene and diacetylene units are important to the oxidative degradation of PFOA. Especially the diacetylene linker was found to be able to bind photogenerated PFAS radicals to accelerate the reaction, which is supported by DFT calculations showing that [PFOA]● radical binding to the –C≡C– group of the acetylene linker lowers the PFOA oxidation potential by approximately 0.30 eV, thus facilitating the oxidation process. Overall these results support a decarboxylation-hydroxylation-elimination-hydrolysis (DHEH) mechanism for PFOA photo-oxidative degradation.

3. **Low temperature methane partial oxidation and coupling over Rh/ZSM-5 in a high-pressure continuous flow reactor**

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Rh-based catalysts have been used in industrial methanol carbonylation to produce acetic acid since the late 1960s. Recently, zeolite-supported Rh catalysts have been shown to be highly effective in the oxidative carbonylation of methane to acetic acid. However, most research employed high-pressure batch reactors with long residence times. Continuous flow reactors have been rarely used, with the majority of those being operated under ambient pressure. There exists a knowledge gap regarding reaction kinetics measured on these two distinct reactor systems. Here, we constructed a high-pressure continuous flow reactor with steam cofeeding to demonstrate methane oxidative carbonylation and to elucidate reaction kinetics. CH3OH, CH3COOH, and other oxygenates are produced using a reactant mixture of CH4, CO, O2, and steam. The influence of space velocity, Rh loading, Si/Al ratio of the zeolite support, and CO partial pressure were investigated.

4. **Morphology of Fe/S clusters during CNT growth**

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This study reveals the morphology of Fe catalysts when CNT growth is occurring. To understand their composition, energetics, and dynamics, grand canonical Monte Carlo (GCMC) modeling and molecular dynamics (MD) calculations were employed. GCMC simulations explored sulfur incorporation in iron clusters under varying chemical potentials, revealing that sulfur preferentially adsorbs on the cluster surface at lower potentials and diffuses into the core at higher potentials, significantly altering the clusters' structure and composition. MD simulations examined the dynamics of Fe cluster aggregation at 1000 K. Smaller clusters aggregate into larger ones, but also occasionally dissolve back into smaller fragments. The ratio of the aggregation and dissociation events was used to extract cluster sticking coefficients across different cluster sizes and sulfur concentrations. The results show that sulfur enhances the aggregation of larger clusters, flattening the size-dependent slope of sticking coefficient versus cluster size, thus showing that S helps cluster growth. This comprehensive analysis sheds light on the structural and dynamic behavior of Fe-S systems, providing critical insights into their catalytic properties and mechanisms.

5. **Transition Metal-Doped Clays for PAH Remediation: Electron Transfer-Driven Catalysis Revealed by DFT and Experiment**

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Polynuclear aromatic hydrocarbons (PAHs) pose significant health risks to both humans and animals due to their persistence and toxicity in contaminated soils. Clays infused with transition metal cations present a promising solution for PAH remediation. In this study, we investigate the efficacy of Fe^{3+}- and Cu^{2+}-doped bentonite clays in removing pyrene, a representative PAH, through combined molecular simulations and experimental analysis. Our results demonstrate that these clays exhibit high pyrene removal capacities even at low temperatures, driven by electron transfer from the Highest Occupied Molecular Orbital (HOMO) of pyrene to the transition metal cations. Fe^{3+} and Cu^{2+} act as electron acceptors and reduction centers, facilitating radical formation during the pyrolytic process and thereby enhancing PAH degradation. To

quantify the reducibility of these catalytic centers, we computed hydrogen adsorption energies using Density Functional Theory (DFT). The calculations revealed stronger hydrogen binding on clays doped with higher-valent transition metals, correlating with increased removal efficiencies. Experimental comparisons further confirmed this trend, with Fe^{3+}-doped clays outperforming their Fe^{2+} counterparts. We also observed that PAHs with lower ionization potentials exhibited faster removal rates, highlighting the importance of electron transfer as a key mechanistic step. Extending beyond Fe^{3+} and Cu^{2+}, additional transition metal dopants were screened, demonstrating similar catalytic behavior via electron accommodation and promotion of hydrogen atom abstraction from PAHs. Reaction barrier calculations revealed a clear Brønsted–Evans–Polanyi (BEP) relationship, further elucidating the reactivity trend.

Overall, this work showcases the catalytic potential of transition metal-doped clays and emphasizes the role of electronic structure and reducibility in guiding PAH remediation strategies. Our findings offer new insights into catalyst design and underscore the importance of integrating machine learning and simulation for developing sustainable solutions to environmental contamination.

6. Improving Ethyl Acetate Selectivity in Ethanol Dehydrogenation through Proximity Effects in Supported Cu Catalysts

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Ethanol has been proposed as a liquid organic hydrogen carrier (LOHC) that could potentially displace compressed H_2 as an energy source. Ethyl acetate is a much more viable dehydrogenation product compared to acetaldehyde owing to the high volatility and carcinogenicity of the former, rendering ethyl acetate selectivity a key metric for ethanol's viability as an LOHC molecule. In this study, we exploit interfacial effects in Cu catalysts to maximize ethyl acetate selectivity during the non-oxidative dehydrogenation of ethanol.
The synthesis involved the preparation of copper dispersed over tetragonal Zirconia support (Cu/t-ZrO_2) using the incipient wetness impregnation method, along with control samples: Copper dispersed over Silica (Cu/SiO_2) and bare t-ZrO_2 support. A mixed metal oxide sample, $CuZrO_x$, was prepared using the co-precipitation method. Structural and surface characterizations were conducted using BET surface area measurements, X-ray diffraction (XRD), H_2 temperature-programmed reduction (H_2-TPR), N_2O selective chemisorption, and Fourier transform infrared (FTIR) spectroscopy. Results revealed CuO–ZrO_2 interfaces proposed to be essential for esterification chemistry[1] as being key to ethyl acetate selectivity. Catalytic ethanol dehydrogenation performed over these different samples under atmospheric pressure showed that Cu/SiO_2 exhibited more than 95% acetaldehyde selectivity at around 35% ethanol conversion at 200°C, while t-ZrO_2 alone showed negligible activity, indicating ethanol dehydrogenation occurred on copper sites (Figure 1). Additionally, a double bed consisting of Cu/SiO_2 followed by t-ZrO_2 improved acetaldehyde reactivity without affecting ethyl acetate selectivity (4%) much. To capture proximity effects in the chemistry, physically mixed and thoroughly grounded beds were tested under similar reaction conditions, their product distribution compared with Cu/t-ZrO_2 revealed significantly higher ethyl acetate selectivity (20%) than those of the mixed beds. To maximize interfacial sites, the $CuZrO_x$ sample where Cu is doped into the amorphous ZrO_2 when subjected to ethanol feed, achieved even better results of ethyl acetate selectivity (38%). Here, a clear increasing trend in ethyl acetate selectivity was observed in between consecutive runs where essentially Cu and the ZrO_2 moieties were brought near one another through their synthesis. We also evidence the effectuation of ethyl acetate formation through hemiacetal-mediated steps[2] and elucidate the participation of Cu, ZrO_2, and Cu-Zr interfacial domains in different steps within the overall reaction network. This work highlights the critical role of metal-support interfaces in effecting ethanol dehydrogenation to ethyl acetate, and the use of synthetic and reaction engineering variables to amplify proximity effects in improving desired product selectivity for LOHC applications specifically, and dehydrogenation reactions more generally.

Keywords: Ethanol dehydrogenation, Ethyl Acetate Synthesis, Interfacial sites, Mixed Metal Oxide
References:
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2. *Journal of Molecular Catalysis A: Chemical*, **2004,** *216,* 147–156.

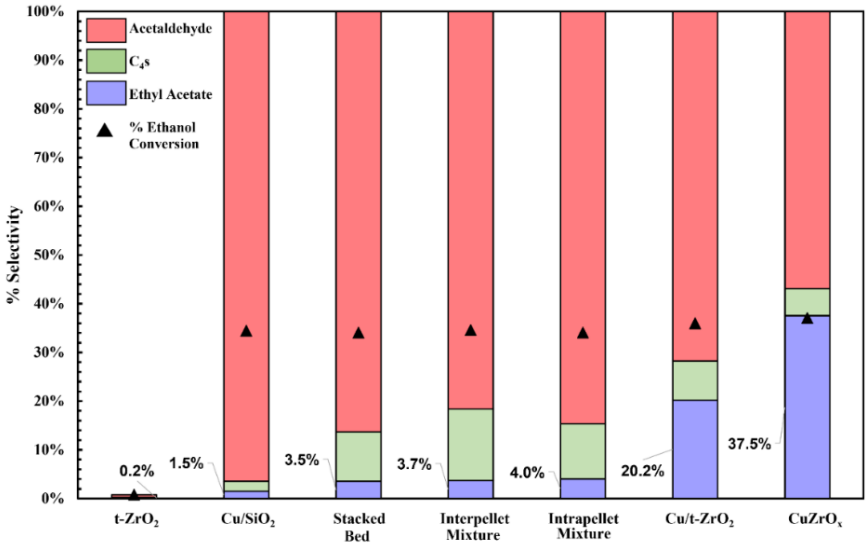

Figure 1: Product distribution for various bed configurations subjected to 5 kPa of Ethanol, 2.4 kPa of CH_4 (internal standard), balance He at 200 °C under 1 atm.

7. Generalizing the behavior of dynamic Ir complex metal oxide catalysts for the oxygen evolution reaction in acid

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Hydrogen is an important reactant and energy carrier to store renewable energy and decarbonize difficult-to-abate industries like steel and ammonia manufacturing. Over 50 countries have outlined national strategies to expand hydrogen infrastructure, targeting cost reductions such as the U.S. D.O.E.'s goal for $1/kg by 2030. To complement the variability of renewable energy generation, proton-exchange membrane water electrolyzers (PEM-WE's) can efficiently produce hydrogen under high yet rapidly variable current densities. However, the only acid-stable oxygen evolution reaction (OER) catalyst, iridium, drives high CAPEX which increases the levelized cost of hydrogen. Iridium-based complex metal oxides may decrease CAPEX by improving the OER activity and decreasing the loading of iridium, but changes to the active surface, the intrinsic activity, and their connection to the pristine catalyst remain unclear.

Here, we evaluate the pristine and steady-state active surfaces of a suite of double perovskites (A_2BIrO_6) to understand how the dynamic surfaces evolve and how their active surfaces relate to the pristine catalysts. Compared to standard rutile IrO_2, these perovskites initially exhibit increased geometric activity. Increasing activity is associated with surface roughening as the non-Ir metals preferentially leach leaving behind a disordered, iridium-rich surface. We determine that thermodynamically unstable perovskites converge to similar surface structures and activities at steady-state, despite varied initial compositions. This convergent behavior suggests that pristine catalyst design may have limited impact on steady-state performance. These findings highlight the need to prioritize thermodynamic stability and dynamic surface evolution in catalyst development for PEM-WE's.

8. **Optimization of a Catalytic Monolith Reactor Design for Carbon Efficient Ethylene Production from Natural Gas**

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Ethylene is one of the largest volume chemicals and holds its significance in the petrochemical industry to produce variety of chemical intermediates and polymers. Yet, production of ethylene is almost exclusively limited to highly energy intensive ethane steam cracking. Researchers have extensively studied oxidative dehydrogenation of ethane (ODHE) and oxidative coupling of methane (OCM) to produce ethylene with lower energy consumption. However, both are limited to commercialization due to heat management concerns. In this work, we demonstrate the feasibility of carrying out these partial oxidation reactions in an autothermal monolith reactor through 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). It is also shown that operation of the reactor in the external mass or heat transfer controlled regime with strong interphase gradients can lower ethylene selectivity. 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. Moreover, ethylene yield can be further improved via cofeeding ethane with methane for which direct shale (natural) gas can be utilized. 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.

9. **Development of Photocatalytic Covalent Organic Frameworks for PFAS Degradation**

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Poly- and perfluoroalkyl substances (PFAS) are synthetic organofluorine compounds extensively utilized in various industrial and consumer products which has led to pervasive environmental contamination and harmful health effects. Strong carbon-fluorine (C–F) bonds render PFAS recalcitrant to conventional wastewater treatment processes. Covalent Organic Frameworks (COFs), a class of emerging porous crystalline organic materials, have garnered attention for their high surface area, exceptional chemical stability, low cost and tunability, making them attractive candidates for photocatalytic PFAS degradation. Herein, we present the development of COFs designed to efficiently adsorb and photochemically degrade PFAS. Pyrene and Porphyrin based Covalent Organic Frameworks (COFs) with diacetylene linkers were explored for their ability to adsorb and photodegrade perfluorooctanoic acid (PFOA). Batch photodegradation experiments showed that under photocatalytic conditions at pH 2, over 99% of PFOA was removed from the solution, with 32% defluorination achieved within 24 hours using Pyrene COF. DFT calculations confirmed that PFOA favorably adsorbs onto the COF framework indicating strong physisorption consistent with experimental observations. It was also demonstrated that photoinduced charge transfer under UV irradiation facilitates PFOA oxidation. These findings support the decarboxylation-hydroxylation-elimination-hydrolysis (DHEH) mechanism for PFOA photo-oxidative degradation. Computed oxidation potentials revealed that binding of the generated [PFOA]● radical to the –C≡C– moiety on the diacetylene linker reduces the thermodynamic barrier for oxidation by approximately 0.30 eV, highlighting the role of diacetylene units in facilitating the oxidative degradation of PFOA. The

effect of COF charge on PFAS adsorption was investigated by comparing the PFOA adsorption efficiency in a batch reactor on a charged COF (EB-COF: Cl) and an uncharged COF (Tp-DPPP). EB-COF:Cl showed 4 times higher PFOA adsorption efficiency compared to Tp-DPP. Molecular dynamics simulations revealed that electrostatic interaction between PFOA and charged COF results in faster dynamic movement of PFAS and enhanced adsorption. This study presents profound insights into the development of innovative materials for combating PFAS contamination in water bodies worldwide.

10. Decoupling Path Dependent and Independent Elements from Transient Degrees of Rate Control for Oscillatory Steady States and Beyond

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Nonlinearities embedded within catalytic kinetics may give rise to self-sustained temporal oscillations even under isothermal conditions. Such is the case in Fig. 1A which demonstrates CO*, O* and unreactive PdO concentrations modulating with time during CO oxidation over Pt/ Pd catalysts. The transient nature of these reactions convolutes the ability to identify a rate determining step (RDS) as applying the conventional degree of rate control (DRC) formalism often provides uninterpretable results due to coupling between magnitudinal and directional elements. For instance, DRCs plotted in Fig. 1B exhibit oscillations with inconsistent amplitudes despite having regularly patterned rates in Fig. 1A. Herein, we propose that unlike at steady state (SS), non-SS solutions have a path dependent component that must be removed from the DRC to isolate the desired path independent DRC. Unlike the conventional DRC, path independent DRCs plotted in Fig. 1C exhibit consistent amplitudes and sum to unity, a hallmark of accurately computed SS DRCs. Path independent DRCsindicate the rate determining step (RDS and highest DRC) is the adsorption of species most absent from the catalyst surface. For instance, at 100 min the surface is void of O* (Fig. 1A) while O2 adsorption has the highest path independent DRC (Fig. 1C) and is thus the RDS. This study suggests that current DRC definitions must have path dependent elements removed to accurately identify transient RDSs. In fact, this method can even be extended to simple catalytic mechanism subjected to concentration step changes thereby hinting at a universal relationship between path dependent, independent and overall transient DRCs.

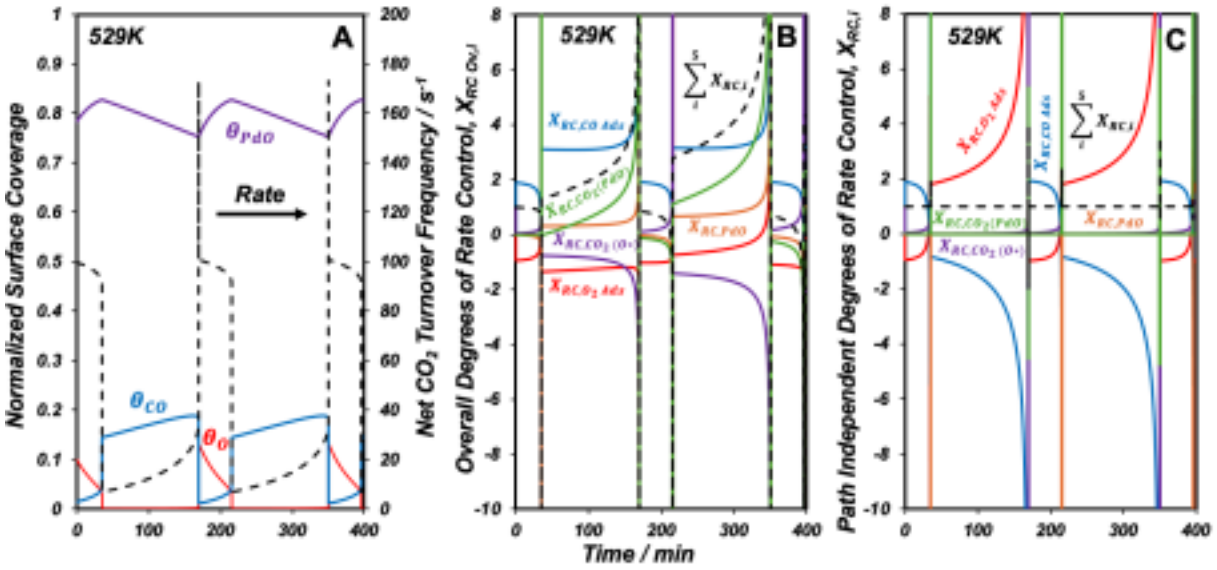

Figure 1: (A) Normalized surface coverages, CO_2 turnover frequency, (B) overall and (C) path independent DRCs versus time at 529K during CO oxidation over Pt/Pd catalysts.

11. AuPd Single Atom Alloy Catalysts for Electrochemical CO2 Reduction

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The electrochemical reduction of carbon dioxide (CO2R) is a promising technology for advancing carbon-neutral energy systems by converting atmospheric CO2 into valuable chemical products. 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. Recent techno-economic analyses instead suggest that selective production of carbon monoxide (CO) followed by downstream upgrading is the most economically favorable option.

Here, we developed a gold-palladium (AuPd) single atom alloy catalyst to achieve selective and efficient formation of CO from CO2. The activity of Au in CO2 reduction is limited by the CO2 activation step. To address this, we introduced more active Pd dopants to enhance CO formation rate by facilitating CO2 adsorption. However, Pd clusters are known to facilitate the hydrogen evolution reaction (HER), which reduces selectivity toward CO production. To mitigate this issue, we designed isolated Pd sites within the Au host lattice, effectively minimizing Pd-Pd neighboring sites that drive hydrogen formation. This atomic-level tuning of the catalyst surface enables enhanced CO production while suppressing undesired hydrogen evolution, offering a promising pathway toward efficient and selective CO2-to-CO conversion.

12. Humidity-Driven Direct Air Capture with Mixed Metal Hydroxides

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Moisture Swing Adsorption (MSA) presents an opportunity for effecting Direct Air Capture (DAC) at a single temperature, and is characterized by a low energy consumption and operational simplicity. In this approach, sorbents adsorb CO2 under dry conditions and subsequently release it at elevated relative humidity levels. Over the past decade, the most extensively researched moisture swing sorbent has been ion exchange resin that incorporates carbonate anions. These resins alternate between the adsorption of CO2 as bicarbonate species in dry conditions and the retention of carbonate anions under wet conditions. In this study, we explore robust, earth- abundant porous nickel hydroxides for their application in MSA within DAC systems. Our mixed metal hydroxide material demonstrates a swing capacity between 0.25 – 0.28 mmol/g over six consecutive cycles with the assistance of pressure swing (humid argon for desorption), which is comparable to capacities reported in the literature for moisture swing applications. Additionally, we present the first recorded, to the best of our knowledge, FTIR evidence on adsorbed bicarbonate–carbonate species alternation pertinent to this technology. 4 times higher PFOA adsorption efficiency compared to Tp-DPP. Molecular dynamics simulations revealed that electrostatic interaction between PFOA and charged COF results in faster dynamic movement of PFAS and enhanced adsorption. This study presents profound insights into the development of innovative materials for combating PFAS contamination in water bodies worldwide.

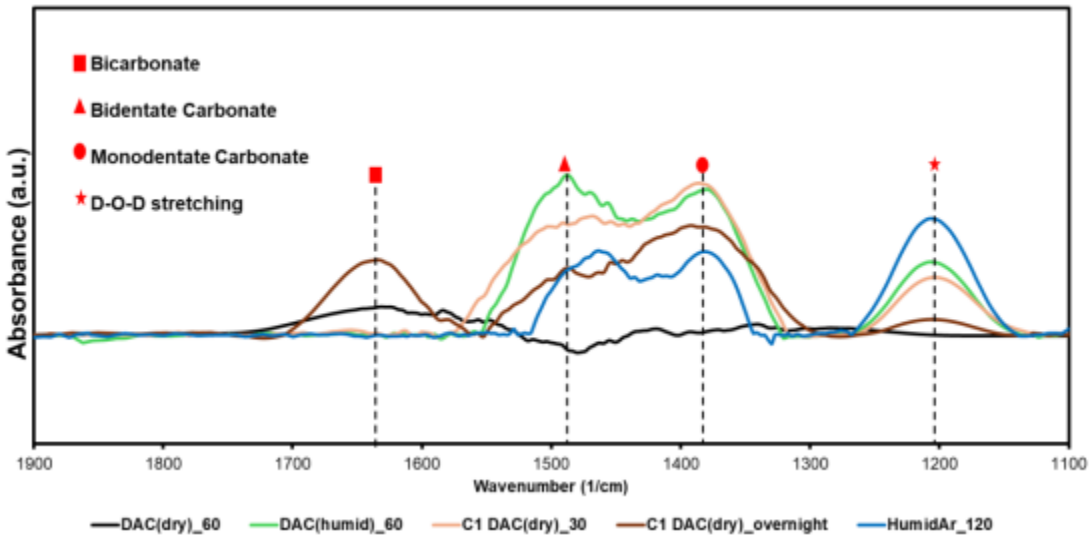

Figure 1: FTIR analysis of α-NiCe0.1(OH)x under dry and humid CO2 conditions, illustrating speciation shifts during moisture swing adsorption. DAC(dry/humid) _number refers to the CO2 environment and time when the spectra were collected in minutes. "C1" indicates a re-exposure cyclic experiment. Under dry CO2 (DAC_dry_60), strong bands at ~1645 cm-1 indicate predominant bicarbonate formation via reaction with surface hydroxyls. In humid CO2 (DAC_humid_60), bicarbonate signals diminish while bands corresponding to monodentate and bidentate carbonates emerge and stabilize (~1410 and ~1490 cm-1), suggesting that the presence of adsorbed water competes for surface hydroxyls for bicarbonate formation. Upon overnight exposure to dry CO2, bicarbonate bands reappear, indicating regeneration of OH− sites through water desorption. A switch to humid argon results in a broad decrease in all bicarbonate and monodentate carbonate bands, confirming that pressure-assisted humidity enables effective desorption. These results demonstrate that while humidity alone cannot fully regenerate the surface, combining it with inert gas flow enables effective MPSA cycling on NiCe0.1(OH)x.

13. Tandem Methanolysis and Catalytic Transfer Hydrogenolysis of Polyethylene Terephthalate to p-Xylene Over Cu/ZnZrOx Catalysts

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The improper disposal of post-consumer plastics presents a waste management challenge and adversely affects our ecosystems [1]. End-of-life plastics are untapped carbon sources and could serve as drop-in replacements for compounds such as fuels, oils, and platform chemicals. As such, chemically repurposing plastic waste has become a strategy for a circular plastic economy. Polyethylene terephthalate (PET) is the most produced polyester globally and can be upcycled to jet-fuel components at end-of-life. PET can be solvolyzed to its monomer, terephthalic acid (TPA), or TPA derivatives like dimethyl terephthalate (DMT), but the key challenge of removing the O atoms remains. PET or DMT has been hydrogenated to C7-C8 compounds under high-pressure H2, but storage and transportation limitations hinder its large-scale use. Alternately, H2 can be produced *in-situ* by dehydrogenating liquid organic hydrogen carriers (LOHCs) [2]. In this work, we employ methanol for (1) the methanolysis of PET to DMT and (2) as a LOHC to generate H2 in situ for DMT hydrogenolysis to p-xylene (PX) on Cu supported on reducible ZnZrOx (Cu/ZnZrOx)[3]. In a one-pot catalytic transfer hydrogenolysis (CTH) system using methanol as a LOHC for the hydrogenolysis of DMT, we found that Cu supported on reducible metal oxides (In2O3, CeO2, and

ZnZrOx) completely converted DMT to methyl p-toluate (MPT) and PX, while the supports alone and Cu on redox-neutral SiO2 (Cu/SiO2) had <10% conversion. Cu/ZnZrOx yielded 97% PX and was employed further. We confirmed the role of methanol as the LOHC by externally supplying ~10 bar H2 (comparable to the H2 generated *in-situ*) and found similar PX yields. Then, by varying the initial methanol loading and supported by thermodynamic calculations, we found that methanol in the vapor phase was critical for the CTH reaction due to destabilizing interactions of the surface H with the liquid phase. Over 24 h, PET was first rapidly solvolyzed to DMT, whose ester groups were then sequentially hydrogenolysed to yield MPT and PX. PXRD patterns indicated Zn-Zr solid solution in the tetragonal (t) phase with the exposed CuO (111) facet. H2-TPR revealed that the deposition of Cu enabled easier reduction of the ZnZrOx support through oxygen vacancy formation and XPS analyses of pre- and post-reaction catalysts that showed a reduction in the Zr(IV) to Zr(δ) ratio, indicating the formation of Zr sub-oxide species upon reduction and during reaction. DFT calculations on a Cu nanorod on t-ZrO2(101) revealed that the Cu-ZnZrOx interfacial sites provided a favorable free energy pathway for both hydrogenolyses of the DMT ester groups and the dehydrogenation of methanol compared to Cu(111). The PX yield dropped over 3 runs when the catalyst was directly reused, likely due to carbon deposition, but the activity was largely recovered by regenerative calcination between runs.

14. When will electrolyte composition influence electrocatalytic water splitting activity?

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Electrocatalytic water splitting is a promising avenue to store intermittent renewable electricity as chemical bonds in hydrogen and oxygen molecules. Understanding the activity of electrocatalysts has traditionally been based on an analysis of the interactions between an electrode surface and adsorbed reaction intermediates. However, recent work has identified that the supporting electrolyte surrounding catalyst active sites can have a significant influence on surface chemistry. The pH of the electrolyte and presence of different electrolyte ions can strongly impact experimental reaction rates and mechanisms, but a comprehensive understanding of this phenomena is lacking. Here, I will discuss my results of combined experimental and computational studies on how pH and alkali metal cations influence the experimental reaction rates and mechanisms for the hydrogen evolution reaction and oxygen reduction reaction. Ultimately, our findings further two key criteria for electrochemical reactions to be sensitive to electrolyte composition: the reaction needs to occur at a potential negative of the metal's potential of zero total charge and the rate-determining elementary steps needs to involve intermediates or transition states that are sensitive to electric field strength. These insights may help broaden our understanding of catalysis in complex media and provide intuition for optimizing catalysis beyond the active site.

15. Kinetic Modeling of the Role of Water and Pd in Ethane Oxidation to Acetic Acid over Pd-MoV Oxides

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This study examines the co-production of ethylene and acetic acid from ethane through oxidative dehydrogenation (ODH) using $MoV_{0.4}Ox$ catalysts, with and without trace Pd loadings. Unlike traditional steam cracking, ODH provides milder reaction conditions, significantly decreasing energy consumption and CO_2 emissions linked to ethylene production and potentially generating valuable oxygenate coproducts, like acetic acid. Varying-contact-time and product co-feed experiments for converting ethane demonstrate that ethane initially converts to ethylene, which can then undergo further oxidation to produce acetic acid and COx. The introduction of extremely low amounts of Pd dispersed throughout the catalyst

(MoV0.4Pd4e-4Ox) significantly improved acetic acid selectivity at the cost of ethylene. A kinetic model was proposed for the non-Pd-containing case where V sites convert ethane into ethylene, acetic acid, and COx. This model showed that water plays a crucial role by populating the catalyst surface with hydroxyl species that aid in forming acetic acid by offering active sites for the readsorption and conversion of ethylene generated by ODH of ethane. For the Pd-containing catalysts, a novel ethane activation pathway is proposed that directly involves surface hydroxyl species in the rate-determining initial C-H bond cleavage on Pd sites. This proposed model was compared with a model that only allowed Pd sites to convert ethylene and not ethane. Including an ethane activation route over Pd sites allows the kinetic model to better predict the effects of O2 and H2O pressure on the performance of the MoV0.4Pd4e-4Ox catalysts. This work illustrates that both water concentration in the reactor feed and Pd content in the catalyst can be strategically tuned to influence the product distribution towards either ethylene or acetic acid, providing valuable insights for developing more environmentally sustainable processes for manufacturing these chemicals.

16. Reaction pathways and intermediates for CO2 methanation over Ni-Ce mixed metal oxides

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The methanation of CO2 is receiving increasing recent attention in light of the need for viable strategies for capturing and converting CO2 from dilute sources. In this context, Ni-Ce mixed metal oxides have emerged as a singlecomponent dual-function material for the direct air capture and conversion of CO2 to methane. Although these materials clearly outperform other sorbent-catalyst systems for the capture and conversion of CO2, the nature of the active sites involved in the conversion of CO2, as well as the identity 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 CO2 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 evidence the participation of H-assisted CO2 activation routes in which the rate determining formation of formate/carboxyl species precedes C-O bond scission (Figure 1a). CO2 methanation reversibilities (Z3) remain larger than CO methanation reversibilities (Z1) over a wide range of CO co-feed pressures (Figure 1b), pointing to the prevalence of H-assisted methanation routes over Ni-Ce oxides that circumvent the need for the formation of CO* as an intermediate [3]. In-situ FTIR spectra reveal the presence of bidentate carbonates, bidentate formates, and formyl species on the surface under CO2 methanation conditions. To understand the role of these formate species, the formate adlayers formed under methanation conditions were subjected to either an Ar or a H2 flow. Formate decomposition rates are insensitive to the presence of H2, indicating that they are likely spectator species under the conditions used. Zero-order kinetics in CO2 and fractional order (0.2 to 0.5) kinetics in H2 can be rationalized to be resulting from kinetically relevant H-assisted CO2 activation occurring on surfaces covered with carbonates. The lack of CO2 inhibition points to the absence of competitive adsorption between CO2 and H2, and indicates participation of two distinct sites, aligning with prior literature [4]. As shown in Fig. 1c, comparable values of rate constants obtained from steady state catalytic experiments and transient stoichiometric carbonate decomposition measurements across various H2 pressures help corroborate H-assisted carbonate activation as the rate-determining step in the catalytic sequence. Overall, the work provides a mechanistic basis for the understanding and development of catalysts for the conversion of CO2 from dilute sources to value-added chemical products such as methane and methanol.

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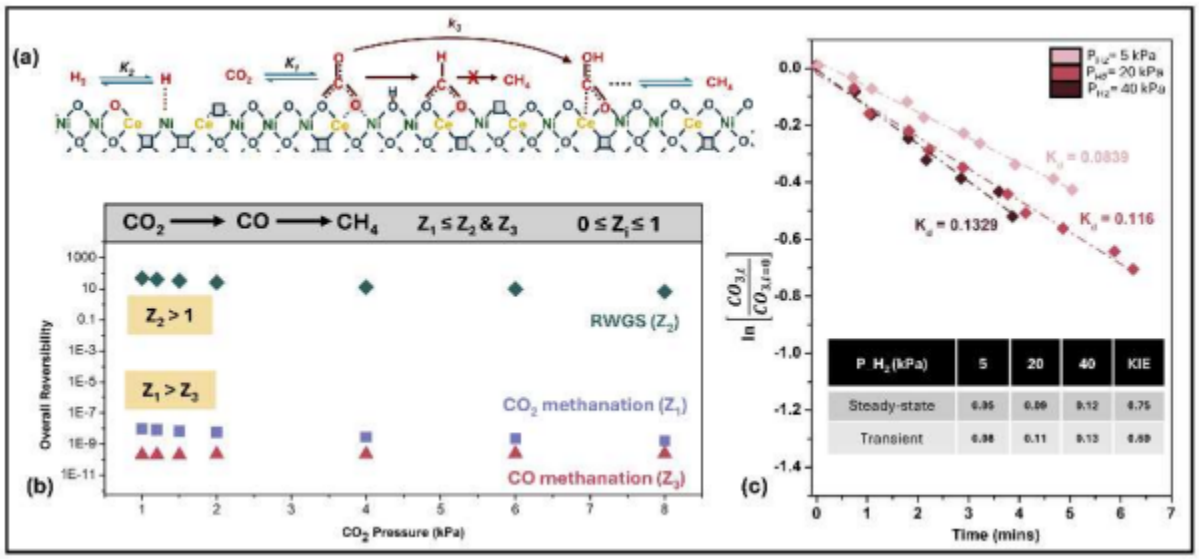

Figure 1. (a) Proposed reaction pathway for CO2 methanation. (b) Overall reversibility of RWGS, CO2 and CO methanation reactions. (c) Rate constants and KIE from steady state and transient carbonate decomposition experiments.

17. Accessing Phenoxyimine Calcium Complexes via Manipulation of the Schlenk Equilibrium

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Compared to transition metals, s-block metals are widely underexplored despite their potential as a more accessible and inexpensive alternative. Access to well-defined alkaline earth metal complexes exhibits many chemical challenges, with the most significant roadblock concerning the highly favored ligand redistribution by the Schlenk equilibrium to form bischelate homoleptic complexes. Herein, two synthetic routes to access calcium-amide precatalysts are investigated, namely a one-pot salt metathesis and a concerted metalation of protonated tridentate phenoxyimine precursors. Initial attempts through both preparative methods resulted in the formation of mostly homoleptic ligand products. Investigation by a stepwise approach allowed for the isolation of new tridentate sodium and calcium-iodide complexes, and the consequent transmetallation steps were studied to access heteroleptic calcium-amide complexes. It was found that ligand redistribution is heavily dependent on both solvent and ligand effects but can be modulated with rigid ligand scaffolds and precipitation of coordination polymers using polar solvents containing two Lewis basic sites. Further application of these calcium-amide complexes as precursors towards highly reactive calcium-hydride complexes is also investigated.

18. Understanding Strong Metal Support Interactions for Electrocatalysis

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Cost effective fuel cells and electrolyzers are key to a clean energy future. A major barrier is the high cost of precious metal catalysts that form the basis of these technologies. Material innovations have been made to improve activity and stability through alloying, doping, core-shell nanoparticles and modifying shapes. Here, we leverage strong metal-support interactions (SMSI) as another strategy to influence electrocatalytic properties of metals. SMSI has been well explored in thermal catalysis for its geometric, electronic and stabilizing effects. However, a significant gap exists in our understanding about its behavior in electrochemical environments. Using our system of 3% (by wt.) platinum supported on titanium dioxide (Pt/TiO_2), we have explored activity and stability effects of SMSI for energy conversion reactions. We have also explored the stability of SMSI overlayers in oxidizing acidic environment.

We confirmed encapsulation in pure H_2 at 600°C. The reversibility of SMSI upon exposure to oxidizing conditions is well-known. To understand whether SMSI overlayer is stable in electrochemical conditions (0-1.1V vs RHE, pH 1), we employed carbon monoxide (CO) stripping measurements and high-resolution transmission electron microscopy. A significant loss in the CO stripping peak was observed for the 600C-Pt/TiO_2 (Fig. 1a) indicating presence of the encapsulating layer. The 600C-Pt/TiO_2 was put through voltage cycling and imaged ex situ. Post cycling, the overlayer could be observed intact (Fig. 1b). SMSI improved stability of Pt, observed through a long-term cycling test (Fig. 2). Finally, it was seen that while ORR activity was significantly reduced upon encapsulation, HER/HOR activity didn't change.

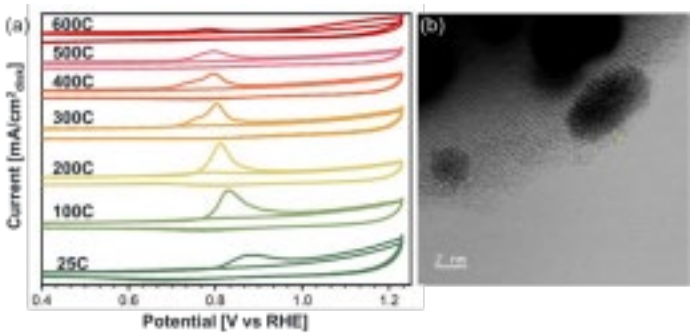

Figure 1. (a) CO stripping peaks for anatase TiO_2 supported Pt reduced under pure hydrogen at the mentioned temperatures. (b) HR-TEM image of encapsulated Pt particle post electrochemical cycling

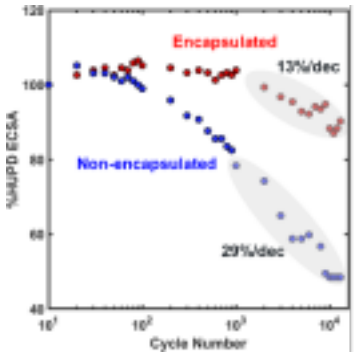

Figure 2. Normalized change in the electrochemically active surface area of supported platinum nanoparticles calculated using hydrogen underpotential deposition method.

19. 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.

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20. Indirect electrochemical conversion of (bi)carbonate to formate in a porous solid electrolyte reactor

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Electrochemical carbon capture and conversion are typically done by two separate steps and involve an energy-intensive CO_2 regeneration process in between. Here, we propose to indirectly convert (bi)carbonates, which are carbon-rich sorbent in alkaline-based carbon capture processes, into formates in a porous solid electrolyte (PSE) reactor by skipping the CO_2 regeneration step. By directly feeding (bi)carbonates into the PSE layer while performing CO_2 reduction reaction (CO_2RR) electrolysis, high purity of CO_2 gas was simultaneously regenerated while forming the formate product within the PSE chamber. Impressive electrochemical performances were demonstrated, with CO_2RR at the cathode

occurring with Faradaic efficiency of up to 96.4 ± 2.3 %, no CO_2 loss to electrolyte, and high CO_2 recovery efficiency at ~ 90% from bicarbonate feeds. Lastly, we showed that the electrolyzer can operate for at least 100 hours at 100 mA/cm^2 while maintaining *ca.* 85 % average CO_2 recovery efficiency. Overall, this approach is highly beneficial as it brings economic value to alkaline carbon capture and CO_2 conversion to formate, paving the way for its practical implementation.

21. PLASMA-ENHANCED CATALYST AEROSOL ENGINEERING FOR HIGH-YIELD CNT PRODUCTION IN A FCCVD PROCESS

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The scalable synthesis of carbon nanotubes (CNTs) via deep injection floating catalyst chemical vapor deposition (DI-FCCVD) is often constrained by inefficient catalyst utilization. In typical systems, less than 5% of the introduced iron precursor (e.g., ferrocene) actively contributes to CNT growth. This inefficiency limits production throughput and control over CNT morphology and selectivity. Improving catalyst efficiency while maintaining material quality is essential for advancing CNT manufacturing at scale.

In this work, we present a plasma-enhanced catalyst delivery strategy integrated within a deep injection FCCVD reactor. By confining ferrocene decomposition to an upstream RF plasma zone, we decouple catalyst nanoparticle formation from carbon source decomposition. This allows for independent control of nucleation timing and location, enabling a more targeted delivery of active particles into the CNT growth zone.

We investigate the impact of plasma power (10–90 W), injection depth (11–13.5 cm), and precursor chemistry—iron alone and with sulfur and hydrogen additives—on catalyst aerosol dynamics and CNT production. Lower plasma powers consistently yield higher production rates, likely due to earlier and more localized nucleation of catalyst nanoparticles. In contrast, higher powers decompose more precursor but delay nucleation past the optimal growth region, reducing efficiency.
Offline scanning mobility particle sizer (SMPS) measurements confirm that sulfur increases particle number concentration and narrows the size distribution, while hydrogen enhances aerosol stability. These effects improve catalyst utilization and boost CNT yield. Across all tested chemistries, coaxial gas injection further enhances flow dynamics and particle delivery, achieving production rates up to ~930 mg/hr.
Importantly, these gains in yield do not come at the expense of quality. Raman spectroscopy and thermogravimetric analysis (TGA) confirm the synthesis of high-crystallinity, few-walled CNTs with aspect ratios exceeding 4500. Run-to-run consistency also improves under plasma-stabilized, chemically tuned conditions.

Together, these results demonstrate that tuning aerosol dynamics—through plasma power, precursor formulation, and flow engineering—is key to maximizing catalyst utilization in deep injection FCCVD reactors. By combining plasma-assisted nanoparticle formation with coaxial flow and additive chemistry, we establish a robust, scalable method for high-yield, high-quality CNT production. This framework sets the stage for future efforts to optimize aerosol-mediated nanomanufacturing through real-time particle control and reactor design.

22. Modeling of Formic Acid Electro-Oxidation under Dynamic Reaction Conditions

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Formic acid (FA) is a promising liquid energy carrier due to its high energy density and ability to generate hydrogen or serve directly as a fuel in low-temperature fuel cells. Steady-state electro-oxidation of FA follows the Sabatier principle, but recent experimental insights reveal that dynamic operation—specifically potential cycling—can enhance turnover frequencies (TOFs) on platinum, bypassing steady-state constraints [1].

This study develops a kinetic model to uncover the mechanistic basis for such dynamic enhancements at low pH, where intrinsic kinetics dominate, and mass transport limitations are minimized. A detailed microkinetic network was constructed, incorporating both direct and indirect oxidation pathways and their potential-dependent behavior. Sensitivity and degree-of-rate-control (DRC) analyses were employed to identify kinetically relevant steps under varying pH and potential conditions.
Model predictions successfully reproduce literature trends in TOF with respect to potential sweeps, and simulations reveal that surface coverage dynamics—modulated by applied potential— can play a crucial role in dictating pathway selectivity and catalytic performance. Notably, the indirect CO-mediated pathway dominates at low potentials, while direct oxidation steps prevail at higher potentials. These findings support the hypothesis that potential programs can exploit transiently switching mechanisms to amplify FA oxidation rates beyond the Sabatier limit.

Ongoing work focuses on optimizing potential cycling protocols to identify resonance conditions that maximize the cycle-average TOF. This framework offers a generalizable strategy for exploiting programmable catalysis across energy-relevant electrochemical systems.

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23. Isolation and Reactivity of Multidentate *s*-block Carbene Complexes

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S-block metals have gained attention in recent years due to their earth abundance and biocompatibility. Well defined complexes of this type have been isolated using neutral ligands, such as carbenes, to study the reactivity of low valent coordination complexes. Most known examples are focused on utilizing sterically bulky and monodentate N-heterocyclic carbene (NHC) ligands with few examples of chelating or pincer-type carbene systems. Therefore, we aim to utilize bidentate pyridine(carbene) and tridentate pyridine(dicarbene) ligand systems to study the effect of a chelating carbene-based ligand on an alkaline earth (Ae) metal center, with particular focus on magnesium and calcium metal centers. Synthesis of the alkaline earth metal complexes was accomplished by using magnesium dialkyl as well as magnesium and calcium diamide precursors to access the corresponding pyridine(carbene) and tridentate pyridine(dicarbene)AeR_2 (R = Et, CH_2SiMe_3) and $Ae(N(SiMe_3)_2)_2$ complexes. The new complexes were characterized by multinuclear NMR spectroscopy, single crystal XRD, and XPS. The reactivity of the well-defined magnesium and calcium complexes with small molecules is also explored in depth.

24. Metal Oxide Mobility in Zeolite: Impact on Hydrocarbon Pools and its Inhibition via Silicalite-1 Coating during CO_2 Hydrogenation

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The tandem hydrogenation of CO2 to hydrocarbons (HC) with green H2 offers a sustainable route to synthesize carbon-neutral fuels and chemicals, which combines two reactions in a single reactor: (i) methanol (CH3OH) synthesis from CO2 and H2 over redox sites of metal oxides and (ii) methanol-to-hydrocarbons (MTH) conversion over Brønsted acid sites (BAS) of zeolites.[1] As such, the proximity of the active sites plays a crucial role for efficient CO2 hydrogenation. In our recent study, we probed that the efficacy of oxide/zeolite systems depends on the effective transfer of intermediate CH3OH, which could be improved by increasing the proximity between redox sites and BAS. However, metal oxide mobility can dramatically influence the reactivity of such bifunctional systems.[2] Therefore, we aim to probe how metal oxide mobility can affect HC pool (HCP) mechanism within zeolite pores and how their mobility can be inhibited.

Metal oxides were synthesized by co-precipitation method. Silicalite-1 (S-1) coating was performed in a hydrothermal method by mixing 1.54 g of tetrapropylammonium hydroxide (TPAOH), 12.64 g of distilled water, 2.4 g of ethanol, and 2.5 g of TEOS and stirred at room temperature for 5 hours. In2O3 particles (0.5 g) was added and sonicated for 10 min, followed by stirring at 90 °C for 24 h. The solid was isolated, dried and calcined (550 °C). The catalytic conversion of CO2 hydrogenation was evaluated in a tubular stainless steel fixed-bed reactor. The products were analyzed by an online gas chromatograph.

Our study on the proximity-dependent reactivity of In2O3 and HZSM-5 system revealed that HC space-time-yield (STY) can be enhanced ~8× by increasing proximity of redox sites and BAS from milliscale to microscale (Figure 1A).[3] However, increasing the proximity further to nanoscale caused the migration of In2O3 (Figure 1B) into HZSM-5 micropores (Figure 1C) and subsequent ion exchange of BAS with Inδ+ (Figure 1D), inhibiting the acidity of HZSM5 and its C-C coupling ability. [4] We observed a similar phenomenon for ZnZrOx when integrated with a silicoaluminophosphate, SAPO-34, where BAS exchanged with Znδ+ . This led to our hypothesis that metal oxide mobility dictates i) the likelihood of BAS exchange with cations, and ii) affects HCP. Hence, we probed C3/C2 HC ratio (indicative of relative propagation of olefin to aromatic cycles) and paraffin-to-olefins (P/O) ratio during reaction. We revealed that while Inδ+ inhibited HCP yielding C3/C2~0 and P/O~0, Znδ+ enhanced hydrogen-transfer yielding ~5× higher P/O ratio and decreased olefin selectivity, compared to its microscale proximity admixture where ion exchange did not occur (Figure 1E).[2] This leads to the next question of how metal oxide mobility inside zeolite could be inhibited. Hence, we aimed at coating metal oxides with S-1 shell (Figure 1F). Figure 1G shows the performance of S-1 coated In2O3 (In2O3@S-1) at nanoscale proximity with HZSM-5 (denoted as In2O3@S-1/HZSM-5_n), which exhibited ~5× higher yield of C2+ HC as compared to In2O3/HZSM-5_n, indicating ion exchange of BAS with Inδ+ was likely inhibited. Additionally, In2O3@S-1/HZSM-5_n exhibited ~2× higher C5+ HC than microscale proximity (In2O3/HZSM-5_m), indicating efficient transfer of CH3OH favored methylation, enhancing C5+ selectivity at nanoscale proximity.

Overall, the S-1 coating improved stability of bifunctional oxide/zeolite systems by suppressing the mobility of metal oxides and their cation exchange with BAS. The enhanced stability translated to improved catalytic performance during tandem CO2 hydrogenation.

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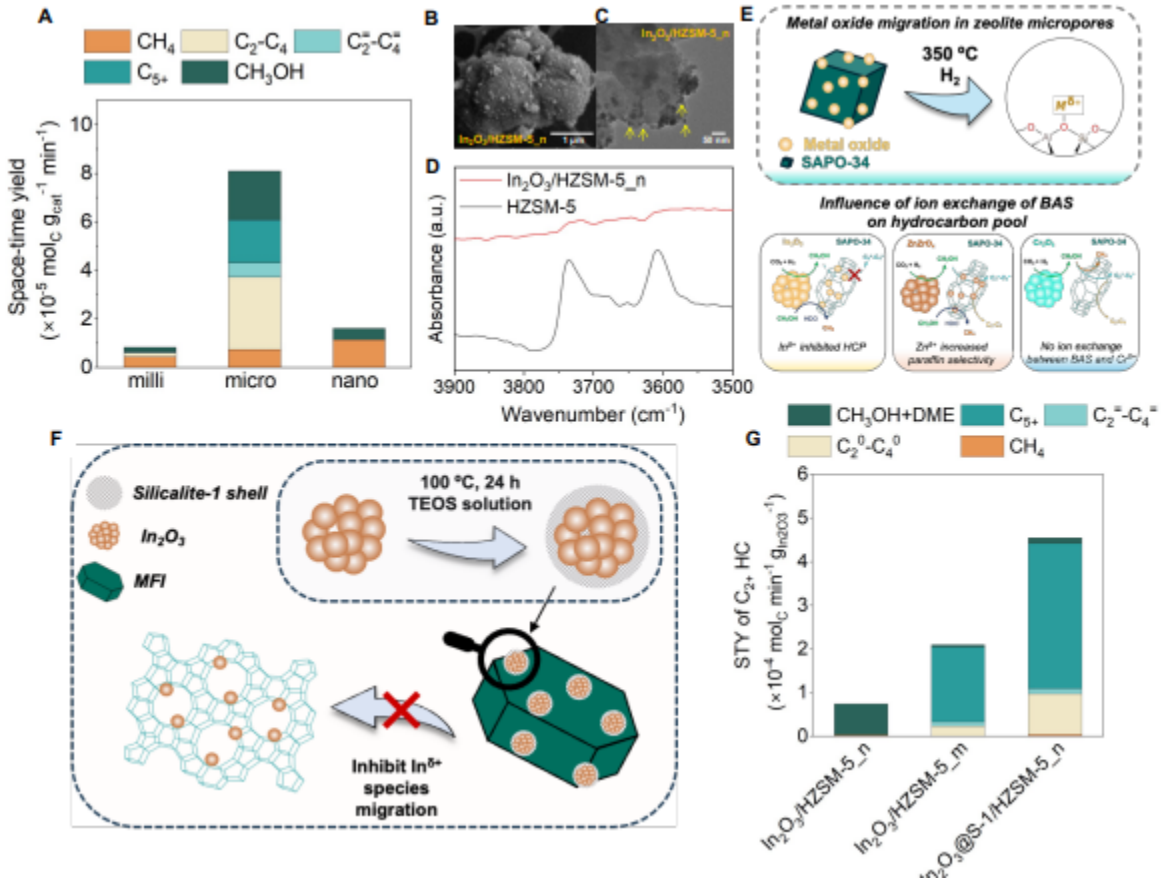

Figure 1. A) Proximity-dependent reactivity of In2O3/HZSM-5 (350 °C, 9000 ml h–1 gcat –1 , 3 MPa). B,C) SEM and TEM of In2O3 and HZSM-5 at nanoscale proximity. D) FTIR spectra indicating ion exchange of BAS with Inδ+ . E) Influence of oxide mobility on HCP. F) Coating In2O3 with S-1 shell. F) Comparison of catalytic performance of In2O3@S-1/HZSM-5 with In2O3/HZSM-5 at micro and nanoscale proximity (330 °C, 15000 ml h–1 gcat –1 , 3 MPa).

25. Surface Charge to Control Adsorbate Binding Beyond Periodic Trends

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Despite the rapidly growing interest in dynamically enhancing catalytic performance to overcome constraints imposed by steady-state operation, fundamental insight into the nature of stimuli-active site interactions remains scarce. It has been demonstrated that catalytic condensers direct charge to active sites on supported catalytic nanoparticles. However, whether it is feasible to condense sufficient magnitudes of charge such that a significant change in the binding energies (BE) of adsorbed intermediates and transition states is attained remains elusive to experimental techniques. In this work, we show that binding energy changes up to ~ 2.0 eV could be attained by applying net charges of +0.17 h+ per surface atom to transition metal surfaces (e.g., Ru, Pt). On the other hand, no discernible change in BE is observed for applied net negative charges (electron addition) across the variety of d-block elements tested (i.e., Pt, Ru, Cu, Ni, and Au). Conversely, atomic adsorbates such as hydrogen, oxygen, or carbon atoms show minimal change in BE in response to applied negative or positive charge. The previous finding points toward a possible role of adsorption configuration over the surface in dictating sensitivity to charge. Additionally, we investigated the validity of Linear Scaling Relationships (LSRs) for charged surfaces. Our analysis reveals that LSRs are valid for metal surfaces under charge, pending a prudent choice of descriptor. For instance, we found that using the BE of atomic adsorbates, namely atomic oxygen and carbon as descriptors to predict the BE of oxygenates and CHx (X=1-3) species, respectively, fails to yield the expected linear correlation. The poor correlation in the previous case was ameliorated if the BE of OH and CH is used to correlate the BE of oxygenated and CHx (X=1-3) species, respectively, over the same subset of metal surfaces.

26. Electrocatalytic Defluorination of PFAS on Palladium Nanoparticle Based Cathodes

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Per- and polyfluoroalkyl substances (PFAS) are a class of extremely persistent and recalcitrant chemicals of emerging concern that threaten public health due to their toxicity at low concentrations. Thus, technological innovation for PFAS degradation is urgently needed to remediate contaminated water sources. Electrocatalytic degradation of PFAS is a modular and tunable approach to destroy PFAS that offers the potential to be highly energy-efficient, scalable, cost-effective, and usable under ambient temperatures and pressures with no requirement for added chemicals. This study investigates indirect catalytic reduction of PFAS using palladium nanoparticles (PdNPs) and electrochemically generated hydrogen. Reductive processes can result in extensive PFAS defluorination, and these byproducts should be more amenable to subsequent biological treatment. PdNPs have been used to catalyze reductive dehalogenation processes by generating H*, a powerful reducing agent derived from H2. Mechanistically similar reductive dechlorination has been demonstrated for various chlorinated organics via electrochemical generation of hydrogen on a cathode coated with PdNPs. This reductive process has been shown to defluorinate PFAS by flowing hydrogen gas through a non-porous hollow fiber membrane coated in PdNPs. However, this approach has never been tested electrocatalytically. Furthermore, electrochemically generated hydrogen for reductive defluorination offers an economical and energy efficient way to generate H* and eliminates the need for H2 gas, which is expensive and poses an explosion risk. We hypothesize that electrocatalytic, indirect reduction of PFAS via H* on PdNPs will be an energy efficient and chemical free method of overcoming the challenging step of degrading

perfluorinated PFAS for eventual mineralization and toxicity elimination. We have successfully electrodeposited PdNPs onto carbon electrodes, that can be used as cathodes for electrochemical hydrogen generation and ideally subsequent H* generation. The use of these fabricated electrodes suggests that PdNPs play an important role in electrocatalytic reductive defluorination of PFAS. For example, at -10V applied potential, similar rates of Fgeneration are achieved, indicative of defluorination. However, at -1V applied potential cathode with PdNPs achieves a F- generation rate similar to that at -10V, while the carbon cathode is completely inactive. Specific experimental results of catalyst preparation, PFAS defluorination, and mechanistic analysis will be presented.

27. Commercializing Transformative Electrified Photoreactor Technology Platform for Sustainable Chemical Production

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Syzygy Plasmonics is at forefront of commercialization of a revolutionary, first-of-its-kind combustion-free, electrified photoreactor platform designed to replace traditional fossil fuel-based thermal reactors. This technology combines several cutting-edge innovations, including (i) breakthrough plasmonic photocatalyst invented at Rice University and further developed and scaled by Syzygy, and (ii) modular all-electric photoreactor systems with a compact footprint, capable of efficiently harnessing photons to drive chemical reactions using plasmonic catalysts at virtually any scale. This new and unique approach to chemistry using light from highly efficient solids-state lightening sources has enabled driving chemical reactions with unusually high efficiencies under notably milder conditions and less catalyst volume compared to traditional thermal routes, offering enhanced energy efficiency and greater control over the reaction. With thousands of hours of successful on-site testing, demonstrations, and third-party validation, Syzygy's commercially ready, modular, and scalable photoreactor system, Rigel™, has proven its capabilities in clean hydrogen and syngas production. Building on this momentum, Syzygy is now positioned to accelerate sustainable aviation fuel (SAF) production from biogas, , offering a truly combustion-free, low-emissions alternative to traditional fuel synthesis methods. By enabling the electrification of chemical production with renewable energy, Syzygy's technology represents a critical step toward decarbonizing the industrial sector. This breakthrough platform not only supports global climate goals but also empowers industries to achieve energy independence, reduce operational costs, and future-proof their operations in a carbon-constrained world.

28. 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.

29. Propane Dehydrogenation on Pt/Carbon Felts using Conventional and Joule Heating

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Electrification of chemical industry represents one of the critical strategies to address the ongoing rise in CO_2 emissions. In fact, around 80% of the energy consumed in the U.S. chemical industry is used for heat generation via fossil fuel combustion. By transitioning energy-intensive processes that require high temperatures (700–1000°C) to electrified reactors, the industry can consume less energy while enabling greater process efficiency and intensification. However, this transition is still in its early stages and requires extensive research, particularly in material selection, catalyst design, and reaction kinetics under Joule heating conditions. In this study, we investigate one of the most endothermic reactions- propane dehydrogenation, usually operated in the 550-700°C temperature range, and used as a method for addressing shortages in propylene supply from the cracking of naptha feedstock. We provide a comparison between conventional and joule heating methods for propane dehydrogenation reaction under similar reaction conditions. Carbon felts, which have a high resistivity and surface areas, are chosen as the heating element and as the catalyst support for Platinum. Reactions are carried out in the 500-650°C temperature range above which homogenous contributions are dominant. During the reaction, the temperature map on the surface of carbon felt for different configurations under joule heating was analyzed using an infrared camera, and higher power inputs were found to lead to a more uniform temperature distribution. Catalyst deactivation is observed under both heating methods and the conversion obtained from the joule heating method were found to be similar to conventional heating. The ‘Pt/carbon felt’ is successfully regenerated either by treating it with 6 vol% hydrogen at 500°C or 6 vol% oxygen at 350°C by removing the deposited coke under both methods, suggesting a lack of Pt sintering during reaction. The identical reactivities and selectivities under conventional and joule heating conditions indicate that improvements in electrified reactor performance will need to originate from shorter timescales for heat and mass transfer rather than changes in active sites, mechanisms, or kinetics induced under 'electron flow'.

30. Pilot-scale Near-Complete Boron Nitride Photocatalytic Mineralization of PFAS via Synergistic UVC/VUV Radiation

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Heterogeneous photocatalysis offers a sustainable strategy for degrading per- and polyfluoroalkyl substances (PFAS), eliminating the need for continuous chemical addition (1). However, many existing systems lack the efficiency to achieve complete PFAS mineralization, and scale-up challenges further hinder practical deployment (2,3). In this study, we demonstrate the effective photocatalytic degradation of perfluorooctanoic acid (PFOA) and a complex 13-compound PFAS mixture using hexagonal boron nitride (h-BN) under UVC and VUV irradiation in a multi-liter flow-through reactor. h-BN achieved >99% PFOA degradation within 1 hour and ~90% defluorination within 7 hours, substantially outperforming benchmark catalysts (P25-TiO2) and VUV light alone. Degradation of a broad spectrum of PFAS compounds was also demonstrated in deionized water and simulated semiconductor industrial wastewater, maintaining performance despite high ionic strength. Notably, PFBS remained persistent, underscoring the need for improved strategies for short-chain PFAS. These results advance the current technology readiness level of PFAS photocatalysis by demonstrating the treatment of chemically diverse PFAS mixtures in industry-relevant water matrices.

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31. Rational design of nanoscale stabilized oxide catalysts for OER with OC22

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The efficiency of H_2 production via water electrolysis is typically limited by the sluggish oxygen evolution reaction (OER). As such, significant emphasis has been placed upon improving the rate of OER through anode catalyst design. More recently, Open Catalyst 2022 (OC22) has provided a large dataset of density functional theory (DFT) calculations for OER intermediates on the surfaces of oxides. When coupled with state-of-the-art graph neural network models, total energy predictions can be achieved with a mean absolute error as low as 0.22 eV. In this work, we interpolated a database of the total energy predictions for all slabs and OER surface intermediates for 4,119 oxide materials in the original OC22 dataset using pre-trained models from the OC22 framework. This database includes all terminations of all facets up to a maximum Miller index of 1 with adsorption configurations for O* and OH*. To demonstrate the utility of this database, we address one of the major pitfalls in electrocatalyst design: Pourbaix or aqueous stability under harsh reaction conditions. Optimal OER activity generally necessitates reaction conditions such as moderately high temperatures, applied potentials and acidity, all of which disqualifies a large pool of candidate anode catalysts due to aqueous instability. Herein, we propose nanoscale stabilization as a possible solution to expand the pool of existing candidates by improving Pourbaix stability under the prerequisite reaction conditions. To do so, we design a screening framework that can filter materials based on overpotential, surface stability, and stability at the nanoscale using the predicted total energies in our database. From our assessment, we were able to identify 48 and 69 viable candidates for OER under the bulk and nanoscale regime respectively.

32. Steric Hindrance in Zeolites: Implications for Catalytic Reactions of Amines

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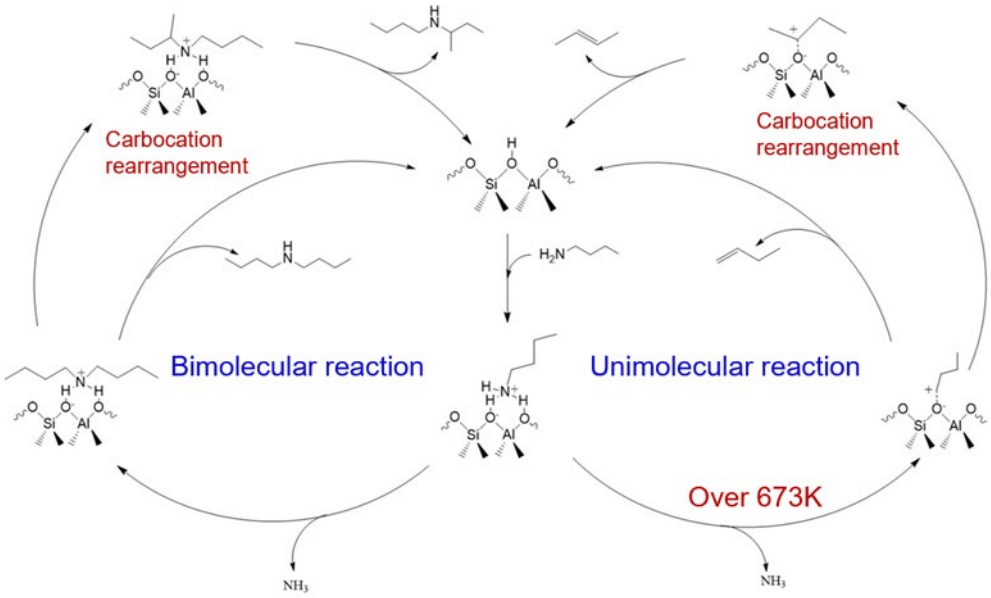
The small, standardized pores of zeolites play a crucial role in determining their catalytic behavior. The well-defined pore channels within the framework influence molecular diffusion and the stability of different reaction pathways. Industrially, ZSM-5 is often selected for applications where shape selectivity is desired. Tert-butylamine (TBA) and sec-butylamine (SBA), whose kinetic diameter (~6.0 Å) are similar to the pore diameter of ZSM-5 (5.5 Å), undergo a unimolecular Hofmann Elimination over H-ZSM-5 via a carbocation-mediated E1-like mechanism. However, n-butylamine (NBA), which has a significantly smaller kinetic diameter (4.3 Å) than the pore size, experiences weaker steric hindrance and thus does not follow one distinct pathway. The bimolecular reaction can produce di-n-butylammonium through the interaction of two n-butylammonium molecules or an n-butylammonium and an NBA molecule, while the unimolecular reaction is similar to the Hofmann elimination of TBA via an E1-like mechanism. Secondary products such as n-sec-butyl-butylamine and sec-butene may also arise via carbocation rearrangement. Based on the study on TBA and SBA, unimolecular kinetics was

insensitive to Al content, depending only on alkylamine carbocation stability (rtertiary > rsecondary > rprimary). Under conditions of complete surface coverage, the apparent rate reflects the intrinsic kinetics of the rate-determining elimination step. In contrast, the bimolecular reaction exhibited a first order dependence on the partial pressure of NBA. The kinetics for the bimolecular reaction is influenced by the combined effects of adsorption, surface reaction, and desorption processes.



33. Computational Prediction of Hydrodehalogenation Trends on Rhodium

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Halogenated aromatic compounds are persistent environmental pollutants formed as byproducts of industrial processes. Catalytic hydrodehalogenation (HDH) provides an efficient and sustainable method for neutralizing these compounds under mild conditions. Supported rhodium catalysts, particularly Rh/Al_2O_3, have shown effective C–X bond cleavage (X = F, Cl, Br) in aqueous-phase HDH, with reaction rates scaling with C–X bond dissociation energies. X-ray photoelectron spectroscopy confirms that metallic rhodium is the active species, while catalyst deactivation is linked to halide accumulation on the surface. To understand the underlying mechanism and kinetic behavior, we employed density functional theory (DFT) and microkinetic modeling to study PhX (X = F, Cl, Br, I) on Rh(111). Adsorption studies indicate that halobenzenes preferentially adopt flat geometries at low surface coverage. The differential binding energy for halogens remains constant at low coverage but decreases linearly with increasing coverage until reaching saturation coverage, which depends on the halogen species. Calculated activation barriers for dehalogenation follow a linear Brønsted–Evans–Polanyi relationship. Microkinetic simulations at low coverage suggest that surface coverage, particularly with strongly binding halogens like fluorine, can significantly affect surface speciation at steady states, indicating that coverage effects are critical to catalytic performance. Ultimately, this work furthers the development of efficient catalytic technologies for sustainable halogenated pollutant remediation.

34. Chemical-free light-driven destruction of per- and polyfluoroalkyl substances (PFAS) using non-toxic boron nitride (BN)

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Per- and polyfluoroalkyl substances (PFAS) are persistent environmental pollutants resulting from their use in chemical and materials processing, as well as in aqueous firefighting foams.[1] Photocatalytic oxidation emerges as an effective treatment method that requires only a light source, eliminating the need for additional reagents. Various materials, including TiO_2 and several composites, have been explored for the photocatalytic degradation of PFAS. While TiO_2 is readily available on the market, it is not effective. Conversely, the advanced composites demonstrate greater efficiency but are not commercially accessible.[2] In this study, we successfully demonstrated that our commercially derived boron nitride (BN)-based materials can effectively degrade 24 types of PFAS listed in US EPA Methods 533 and 531.7.[3] Furthermore, we established that BN-based materials can treat real groundwater samples containing parts per billion (ppb) levels of PFAS, establishing a much wider range of PFAS concentrations at environmentally relevant conditions. We also identified a commercially available UV/catalyst slurry reactor as an appropriate treatment unit for PFAS-contaminated water. Our data revealed that the BN-based photocatalyst outperformed both TiO_2 and UV-only photolysis in treating 16 liters of ppb-level perfluorooctanoic acid (PFOA) under recirculating (batch) mode. This study highlights that the use of BN-based materials for PFAS degradation under UV irradiation offers a safer, more environmentally friendly, and energy-efficient alternative to conventional methods, such as incineration and plasma treatment.

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35. Chromatographic Dynamic Chemisorption: An Alternative to Conventional Estimation of Metallic Dispersion

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A supported metal catalyst consists of metal nanoparticles dispersed on a support [1]. The fraction of the exposed active metal atoms is defined as dispersion [2], which is crucial for reporting standardized rates for kinetic investigations. Chemisorption is commonly employed as a relatively inexpensive, accessible, and simple method for estimating supported metal catalyst dispersion [3]. This work goal is to develop a reliable experimental technique for measuring the dispersion of supported metal catalysts, using tools and equipment readily available in a catalysis focused research laboratory. Compared to existing adsorption-based methods, the chromatographic nature of the technique provides the added advantage of the ability to separate and independently quantify species desorbing from the catalyst surface (e.g. CO vs CO2), avoiding significant sources of error in dispersion estimates. Using commercially available chromatography software and accessories, dispersion measurements were completely automated. The applicability of this technique was demonstrated for multiple supported platinum group metal catalysts varying in metal loading (0.1-5 wt%) and support identity (Alumina, Carbon, and Silica). Accuracy was confirmed using a 0.5 wt% Pt on Alumina catalyst of known dispersion (31 ± 5), which was experimentally matched using the developed technique (26 ± 5). All dispersion results were carried out assuming adsorption stoichiometry of CO moles per mole of Pt to be 1:1. Furthermore, the effect of various catalyst powder particle size ranges was also tested and showed that the size of particles in the analyzed bed is not a crucial contributing factor in this analysis method. To corroborate the fact that CO pulse chemisorption was representative only of the metal active sites where CO is strongly adsorbed and not the support, the dispersion variation was studied versus the catalyst bed temperature, and it showed no dispersion dependence on the inlet temperature.

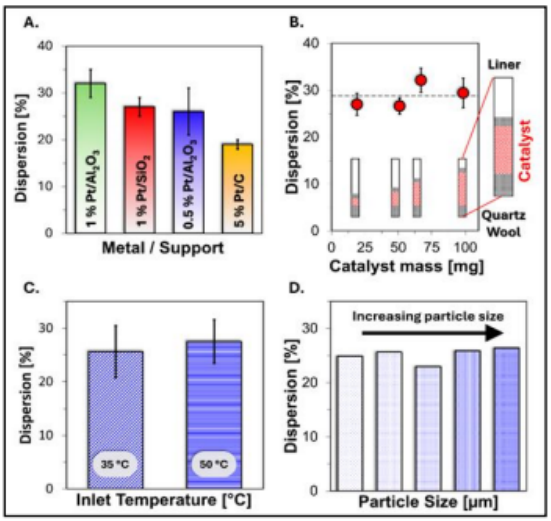

Figure 1. **A.** Dispersion of Pt catalysts with various support identities like alumina, silica, and carbon **B.** Dispersion of 1% Pt/SiO_2 at different bed sizes and a schematic of an inlet liner packed with catalyst **C.** Dispersion of 0.5% Pt/Al_2O_3 at two different catalyst bed temperatures **D.** Dispersion of 0.5% Pt/Al_2O_3 at different particle size (0 –53, 53 –106, 106 –250, 250 – 500, and 500 – 1000 µm)

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36. Crystal Engineering of Siliceous AFI Zeolites: Mechanistic Insights from (Non-)xeeded Syntheses

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The ability to synthesize high-quality zeolite materials with controlled morphology, porosity, and framework composition is critical for advancing their performance in applications such as adsorption, separations, and catalysis. Zeolite SSZ-24 (AFI-type) is particularly attractive due to its large, onedimensional 10-membered ring channels, which offer high diffusivity and shape selectivity; however, their synthesis remains a challenge due to slow crystallization kinetics, narrow synthesis compositions, and their affinity to crystallize as siliceous materials with difficulties for heteroatom incorporation. In this presentation, we will discuss a comprehensive investigation of AFI crystallization using both seeded and non-seeded hydrothermal synthesis routes. Systematic parametric studies revealed the pivotal roles of silica source selection, organic structure-directing agent (OSDA) concentration, and NaOH content in achieving phase-pure AFI products with reasonable yield. Remarkably, fully crystalline AFI zeolite was obtained within 48 hours in the absence of seeds—contrasting literature that reports the need for multi-week synthesis timelines to produce similar product. This rapid, seedless route was enabled by the use of colloidal silica as the Si source wherein we observed an optimal particle size and composition were needed in addition to tailored OSDA/Si and NaOH/Si molar ratios. Time-resolved analyses of solids extracted from syntheses using X-ray diffraction (XRD), electron microscopy (SEM and TEM), and atomic force microscopy (AFM) showed a two-stage growth mechanism: the first step involving nonclassical transformation of an amorphous precursor, followed by a classical layer-by-layer process of crystal surface growth. Seed-assisted syntheses using different zeolite crystal structures as seeds (e.g., CHA, FAU, and AFI) demonstrated distinct nucleation kinetics and selective templating behaviors, which were further supported by computational studies probing interfacial compatibility and energy landscapes. In parallel, the incorporation of heteroatoms (e.g., Al, B, and Ga) into the AFI framework was evaluated. Our findings revealed that Al and Ga promoted the crystallization of competitive phases (e.g., CHA), whereas boron was able to be introduced into the AFI lattice without compromising crystallinity or porosity. Textural analysis using N_2 and Ar as probe gases confirmed that B-AFI retained high micropore volume and BET surface. Overall, this study provides mechanistic and synthetic insights into AFI crystallization and establishes a rational design approach for tailoring the properties of these materials for diverse applications.

37. Effect of Support on PdZn Intermetallic Catalysts for the Semi-Hydrogenation of Acetylene

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Acetylene hydrogenation is required to purify ethylene feed streams prior to its polymerization to polyethylene because trace acetylene is detrimental to the lifetime of the downstream polymerization catalyst. Palladium (Pd) based catalysts are typically used for this process due to Pd's high hydrogenation activity coming from its ability to dissociate molecular hydrogen thereby facilitating the reaction. While Pd based catalysts are very active for the hydrogenation reaction, they leave much to be desired in terms of selectivity as the over-hydrogenation to ethane is facile. To negate this, diluting Pd with another less active metal (e.g. Ag, In, Zn) has been a successful strategy through the reduction of Pd ensemble size. In this work, we study the impact of support on the formation of PdZn intermetallic particles and consequential performance in the semi-hydrogenation of acetylene. We find the ZnO supported catalyst to be more active and selective than an SiO_2 supported catalyst. Importantly, we highlight how this difference manifests in kinetic parameters including activation energy and reaction order with respect to hydrogen.

38. Controlling Zeolite Crystallization and Hierarchical Structure via Seeding Strategies

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Zeolites are nanoporous aluminosilicates that are widely used commercial catalysts owing to their shape selectivity and tunable physicochemical properties, which can be tailored for different catalytic processes. Recent efforts to optimize zeolite catalyst performance have focused on reducing mass transport limitations. Two of the most effective strategies to overcome these challenges are the synthesis of nanosized zeolites and the introduction of meso-/macropores (i.e., hierarchical zeolites). However, existing methods to synthesize hierarchical zeolites often require costly organic reagents, multi-step procedures, or harsh conditions, which limit their industrial scalability.

In this work, I demonstrate how seed-assisted methods can generate hierarchical zeolites with tunable properties. These insights are used to develop a scalable synthesis pathway for a new class of hierarchical zeolites, underscoring their potential for industrial commercialization. The underlying methodology employed in these syntheses is a seed-assisted strategy using organic-free growth conditions to prepare self-pillared pentasil (SPP) materials composed of five-membered ring zeolites (predominantly ZSM-5), where nanosheets possess smaller dimensions than most state-of-the-art MFI-type zeolites.

In the first part of the research, I investigate how synthesis parameters, such as seed structure and reagent selection, affect the kinetics and final properties of aluminosilicate SPPs. A range of organic structure-directing agents (OSDAs) were assessed as a way of enhancing the synthesis method to produce larger product yield with minimal organic content. We find that specific composite building units (CBUs) shared between the seed and product phases influence the extent of pillaring during interzeolite transformation. We find correlations between the structural similarity of zeolite seeds and products, offering predictive power in designing new materials.

The second part of the research explores post-synthesis treatments that enhance the hydrothermal stability and catalytic performance of SPP materials beyond those of conventional analogues. This method is broadly applicable to a range of zeolite crystal structures. One unique advantage of these treatments is the removal of intrinsic defects within as-synthesized materials, which we have found to be common in most ZSM-5 catalysts, including commercial materials. The various methods used for post-treatment can lead to different effects that enhance catalyst performance, such as passivation of external surfaces with siliceous outer rims that improve mass transport and eliminate undesired reactions occurring on external acid sites.

These studies collectively provide new strategies for the rational design of hierarchical zeolites through seed-assisted synthesis – an area currently limited by gaps in our understanding of complex mechanisms of zeolite crystallization. Moreover, these findings support the scale-up of SPP materials for catalytic applications

relevant to the (petro)chemical industry. Collectively, this work contributes to the development of more sustainable, industrially relevant materials that aligned with the broader goals of commercial research and development.

39. Enhancing Mass Transport in One-Dimensional Zeolites by Facile Post-synthesis Treatments

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One-dimensional zeolites have distinct pore topologies for shape-selective catalysis, yet their performance in conventional reactions is frequently compromised by severe diffusion limitations. In this presentation, we will discuss how post-synthesis modification of zeolite ZSM-23 (MTT) using a protocol analogous to the generation of finned zeolites dramatically improves its mass transport properties. This is accomplished by a facile secondary growth process that introduces surface roughness on the exterior surfaces of ZSM-23 crystals. High resolution electron microscopy images show that roughened interfaces are step bunches of unfinished layers with ultra-small dimensions that present a series of short one-dimensional (1D) channels with significantly reduced diffusion path lengths (10 – 50 nm) compared to the 1D pores of the parent seed crystal (1 μm). This procedure also removes intrinsic defects of as-synthesized MTT crystals, resulting in reduced mass transport limitations. This is reflected in an approximate 45% increase in micropore volume, reaching a value of 0.10 cm^3/g that is markedly higher than most ZSM-23 catalysts reported in literature.

Comparison of structure-performance relationships for these materials against conventional and nano-sized ZSM-23 catalysts were established using the methanol to hydrocarbon (MTH) reaction as a benchmark for assessing differences in catalyst activity and selectivity. Modified ZSM-23 catalysts exhibit a dramatic enhancement in turnover number and product selectivity. Moreover, these materials produce a much higher propene/ethene ratio compared to commercial ZSM-5 (MFI) catalysts. The improved mass transport of ZSM-23 catalysts after secondary growth also extends their lifetime at much shorter reactant contact times without any observed changes in the mechanism of coking.

In this presentation we will also discuss preliminary data where we have extended analyses of secondary growth to large-pore 1D zeolites, such as ZSM-12 (MTW) and mordenite (MOR). Our findings reveal comparable increases in pore volume following a facile secondary growth process across a broad range of Si/Al ratios. Diffusion measurements using various hydrocarbons indicate the presence of intrinsic defects in these structures. We show that these defects are either partially or completely eliminated after secondary growth, thereby enhancing micropore accessibility. Collectively, these findings highlight potential opportunities for exploring modified 1D zeolites as catalysts for commercial applications.

40. Theoretical Investigation on Nucleation, Growth and Energetics of Co and Ni Nanoparticles on CeO2(111)

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Co and Ni nanoparticles (NPs) supported on ceria have been widely used to catalyze technologically important reactions including three-way catalysis, water-gas shift, and hydrocarbon reforming. Understanding the nucleation, structure and chemical state of these metal NPs on CeO2(111) is therefore of interest in heterogeneous catalysis. We used periodic density functional theory (DFT) calculations and minima hopping algorithm to explore Co and Ni NPs consisting of up to 23 metal atoms on CeO2(111). An adatom of Co adsorbs much more strongly than an adatom of Ni, and correspondingly a Co adatom is calculated to have a higher diffusion barrier than a Ni adatom, although both are too high to enable appreciable adatom diffusion at ambient temperature. The formation of polyatomic Ni NPs is more exothermic than that of Co NPs of the same size, indicating intrinsically weaker interaction of Ni with ceria

than Co while the cohesive energy of Ni metal is nearly identical to that of Co. Co and Ni atoms in the NPs are either in a sub-oxidation state if they are located at the interface, or in a neutral state if they do not contact the oxide surface. DFT calculations further suggest the possibility of oxygen reverse spillover from ceria to Co and Ni NPs even on the terrace sites of ceria. Overall, our theoretical results clarify the fundamental understanding of interaction of Co and Ni NPs with ceria, providing a more robust basis on which to understand catalytic reactions taking place on them and guidance to improving catalyst design.

41. GaN Formation in CHA Zeolite through Framework Gallium Scavenging

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Beyond its significance in optoelectronics and semiconductors, gallium nitride (GaN) has gained attention in the field of catalysis owing to its discovery as a thermal catalyst for non-oxidative aromatization of alkanes. In this presentation, we discuss recent investigations of a new in situ method for generating extra-framework GaN encapsulated within the small pores of a Ga-chabazite (or Ga-CHA) zeolite. This is accomplished by the concerted demetallation of framework Ga in the presence of a nitrogen source (e.g., NH_3 gas) at high temperature. This method involves nitridation through the decomposition of ammonia with concomitant extraction of framework gallium, forming a GaN within the cha cages. This approach avoids post-synthesis impregnation with GaN particles, which is challenging to accomplish with steric effects imposed by small-pore zeolites. GaN formation was validated by multiple techniques that include: (1) a visible shift in the color of extracted powders from white (H-Ga-CHA) to yellow ([GaN]-Ga-CHA), intensifying with increases in Ga content; (2) powder X-ray diffraction (PXRD), which confirmed peak shifts of framework Ga to those of GaN after treatment with ammonia; and (3) X-ray photoelectron spectroscopy (XPS), which shows an increase in extra-framework GaN with higher Ga content. A series of [GaN]-Ga-CHA catalysts were prepared with different Ga content and their performance as catalysts in the ethane dehydrogenation (EDH) reaction was tested. Our findings reveal that the parent sample, H-Ga-CHA, containing predominantly framework Ga, exhibits low activity. Conversely, the in situ generation of [Ga]-Ga-CHA containing extra-framework GaN exhibits higher initial rates of ethylene formation. Collectively, this study is a proof of principle for the method of scavenging metals in zeolites frameworks to generate multifunctional catalysts in situ, thereby circumventing the difficulties associated with encapsulating large active sites in small pores of zeolite catalysts.

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42. Formic Acid Electro-oxidation: Elucidating Enhancements under Dynamic Oscillations

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Selective acceleration of catalytic turnover within heterogeneous catalysis has conventionally been approached through material advances. The Sabatier principle illustrates the limits on material properties to enhance rates, where stronger adsorbate binding leads to desorptionlimiting regimes, and weaker binding leads to reaction-limiting regimes. Oscillating between distinct regimes of rate control using external energy stimuli has been shown to enhance the observed rates for formic acid electro-oxidation by up to ~50x (Fig. 1A). Under static conditions, apparent kinetic parameters (i.e., reaction order, activation energy) have been routinely utilized to kinetically interrogate catalytic surfaces, providing quantitatively predictive and fundamentally derived rate expressions. Despite their prior utility, such kinetic interrogation approaches have yet to be employed under dynamic conditions. Here, we investigate how common kinetic parameters like apparent reaction orders and activation barriers manifest under dynamic conditions. While dynamic catalytic turnover rates are reflected within the time domain (i.e., time average), analytical derivations of dynamic kinetic parameters are proposed to be an extent of reaction weighted average of their respective values at each energetic state within an oscillation. To probe the hypothesis, we measured the apparent activation barriers and reaction orders for formic acid oxidation over Pt under dynamic conditions (Fig. 1B, 1C), which were found to be independent of frequency and quantitatively scaled with the extent of reaction weighted averages. Recognizing the scaling of apparent kinetics under oscillatory conditions by the extent of reaction at each distinct energetic state provides greater predictive capability that helps reduce the experimental parameter space when designing a programmable catalytic surface.

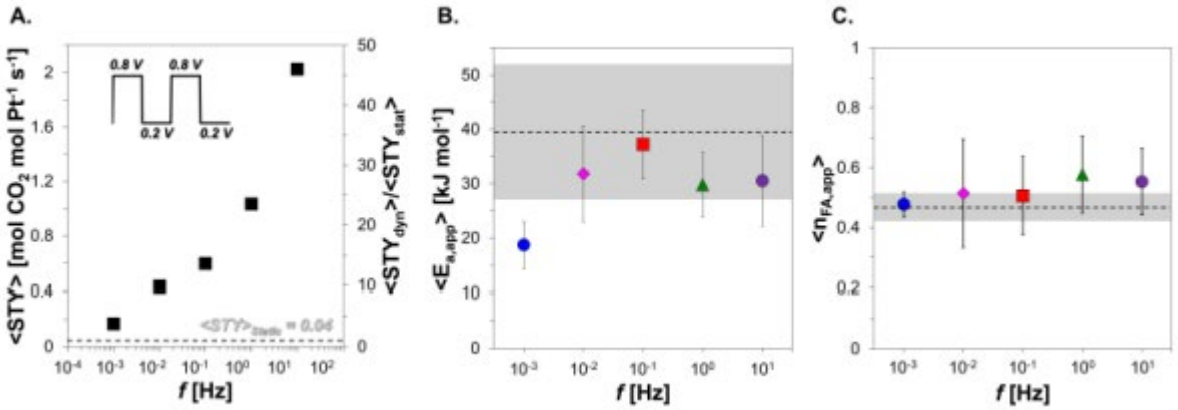

Figure 1. A. Frequency response rate: the observed site time yield and enhancements under dynamic conditions at 295 K, 50% duty cycle, 0.25 M HCOOH, and pH 0.6. B. Apparent activation energies at different frequencies. The dashed line indicates the static average apparent barriers, and the gray region indicates the error in estimating the static average apparent barrier. The temperature of the reaction was varied between 285 and 305 K at 0.25 M HCOOH, 50% duty cycle, and pH 0.6. C. Apparent reaction order at different frequencies. The dashed line indicates the static average apparent reaction order, and the gray region indicates the error in estimating the static average reaction order. The concentration of formic acid was varied between 50 and 2500 mM HCOOH at 295 K, 50% duty cycle, and pH 0.6.

43. Unveiling Electronic and Geometric Structure Sensitivity of Pd-on-Ni Catalyst for Enhanced Nitrite Reduction

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Pd-based catalysts have potential for the effective catalytic remediation of nitrate via its conversion to non-toxic dinitrogen. However, the rarity and cost of noble metal Pd catalysts presents significant sustainability and economic barriers. These issues can ideally be addressed by using earth-abundant secondary metals that replace the majority of Pd and, simultaneously, enhance the performance of the catalyst. In this presentation, we report gamma-alumina (γ-Al_2O_3) supported structure-controlled Pd decorated on Ni nanoparticles ("Pd-on-Ni-NPs/Al_2O_3") synthesized via a simple aqueous colloidal method for NO_2^- hydrogenation to non-toxic dinitrogen. The optimized Pd-on-Ni-NPs/Al_2O_3 (0.47 wt% Pd, 0.74 wt% Ni) lowered catalyst cost by ~2× and simultaneously achieved a ~3× increase in catalytic activity for NO_2^- reduction compared to a standard 1wt% Pd/Al_2O_3 catalyst. XPS and CO-DRIFTS studies revealed that the enhanced activity and selectivity of Pd-on-Ni-NPs/Al_2O_3 stem from electronic interactions between Pd and Ni, resulting in electronically rich Pd which enhances catalytic activity of NO_2^- reduction, and geometric effects of clustered Pd which direct reaction selectivity to N_2 over ammonia. This study demonstrates that the incorporation of Ni expands the prospects of improved denitrification for Pd-based catalysts.

44. Engineered gas input for stable electrochemical CO2 reduction

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Salt formation has been widely recognized as a primary factor in poor operational stability of the electrochemical carbon dioxide reduction reaction (CO2RR). Here we demonstrate that flowing CO2 gas into an acid bubbler, which carries trace amounts of acid vapor into a gas diffusion electrode for silver-catalyzed CO2RR to carbon monoxide (CO), can prevent salt accumulation. In a 100-cm2 scaled-up CO2RR membrane electrode assembly electrolyzer with single serpentine flow channels, the acid-humidification method achieved 4,500 hours of stability milestone at 100 mA cm–2 without compromising the CO faradaic efficiency, whereas a conventional water-humidified CO2 feed only operated stably for ~80 hours. The acid-humidification approach was extended to bismuth, copper, and zinc CO2RR catalysts.

45. Probing the Role of Interfacial Caton Concentration in Modulating CO2 Reduction Kinetics

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Electrochemical CO_2 reduction (CO_2R) offers a promising route for storing intermittent renewable energy in chemical bonds. [1] While modifying catalyst composition and structure and structure of active sites impact catalytic activity and selectivity, the microenvironment around active sites also plays a significant role.[2] Notably, electrolyte cations can dramatically influence catalytic performance, yet the underlying mechanisms remain debated. [3] Existing models often incompatible with one another, and fail to explain experimental observations beyond the reaction chemistry or catalytic material under investigation. Moreover, it is unclear

how to extend insights of cation effects using alkali metal cations (Li+ , Na+ , K+ and Cs+) to design cationic ionomers/binders, which would be more practical for use in electrolyzer devices.[4] There is therefore a critical need to establish a comprehensive model describing cation effects across electrocatalysis. Recent work from our group demonstrates that in dry aprotic solvents, CO_2R rates vary significantly with the size of organic alkylammonium cations.[5] We showed that tuning the metal cation distance [Ag–C^+(Å)], dictated by quaternary cation's alkyl chain length, modulates interfacial electric field strength, which stabilizes the kinetically relevant CO_2 activation step and tune reaction rate. However, these promoting effects may not solely arise from cation-electrode separation. Changes in quaternary cation size could alter other electrical double-layer (EDL) properties, complicating our mechanistic interpretation. To address this, we now employed a class of functionalized organic cations to systematically control and vary interfacial cation concentration at the electrified interface of silver catalyst. From a series of electrokinetic, impedance spectroscopy and computational calculation, we propose a physical model to clarify how cation identity influences electrocatalysis. Beyond deepening our understanding of catalysis in electrochemical environments, this work offers new strategies for designing selective and efficient electrolyzers critical for decarbonizing the fuels and chemical industries.

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46. Enhancing Diffusion and Catalyst Lifetime of Zeolites By Novel Secondary Growth and Post-Treatment Methods

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Reducing limitations for internal molecular diffusion in zeolites is critical to improving catalyst activity and stability for commercial applications such as hydrocarbon cracking and methanol-to-hydrocarbons (MTH) reactions. The intrinsic confined pore networks in zeolite structures give rise to well-defined shape-selectivity, which can result in highly selective products, but oftentimes at the expense of reduced activity and lifetime owing to the large crystal sizes of conventional zeolites that impose mass transport restrictions. For example, zeolites with one-dimensional pores are highly selective to propylene in naptha cracking, but they deactivate faster than 2D or 3D analogues due to limited diffusion leading to extensive coking and pore mouth blockage. Such limitations can be overcome via a facile post-synthesis treatment to produce fins, which are small protrusions on external surfaces of seed crystals. This secondary growth technique has been demonstrated for zeolites with 3D (MFI) and 2D (FER) pore networks wherein finned catalysts markedly outperform their parent seeds in MTH and butene isomerization reactions, respectively. Here, we will discuss how this approach can be used to design finned 1D zeolites, using MTT as a prototypical example. Our findings show that molecular diffusion in finned MTT zeolites is faster, resulting in reduced rates of coking and longer catalyst lifetime relative to the conventional counterparts. Zeolites are also known to be prone to intrinsic defects during synthesis. We also demonstrate post-synthesis treatment methods aimed to reduce defects in zeolites thereby improving their diffusion properties and catalytic performance (e.g. total turnovers and lifetime) beyond what can be achieved with conventional as-synthesized materials.

47. Synthesis of Multidentate *S*-block Carbene Complexes Towards Polymerization

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Polymers are a cornerstone of modern society as exemplified by the resultant plastics and materials incorporated into everyday consumer products. While regio- and stereocontrol with transition metal initiators have been thoroughly explored, group 2 metal catalysts are less studied. On the other hand, magnesium complexes, a main group metal in contrast to a transition metal, has been shown to polymerize lactones and β-Butyrolactone, but not α-olefins. Given this ability to polymerize other substrates, in addition to its relative abundance and lower toxicity than transition metals, magnesium complexes represent an attractive precursor for olefin oligomerization. This work demonstrates the synthesis and characterization of well-defined magnesium complexes bearing two different ligand scaffolds: the redox active α-diimine ligand (DI), and the redox-innocent pyridine(carbene) (CN). By investigating the redox active and non redox active ligands, insight to how the ligand impacts the electronics of the complex, and effect on bonding motifs, can be explored.

Synthesis of these complexes involved using commercially available Grignard reagents, which were turned into the homoleptic species, $MgR_2(dioxane)_2$ (R = CH_2CH_3, C_6H_5, C_6H_4F, $CH_2Si(CH_3)_3$), by the Schlenk Equilibrium, a solution-state process that favors formation of homoleptic over heteroleptic complexes. These reagents were characterized by ^1H, ^{13}C, and other heteronuclei. Additionally, solvent effects were investigated with MgR_2. Upon obtaining these reagents, direct metalations were performed on the ligands to give $(CN)MgR_2(solv)$ and $[(DI)MgR(solv)]_2$. These precursors and subsequent complexes were characterized by NMR spectroscopy, in addition to SC-XRD and GC-MS studies. Complexes synthesized include a magnesium ethyl α-diimine complex, with the bidentate α-diimine ligands coordinated onto one magnesium center in a dimeric form. Even though the complex has its maximum coordination fulfilled, further *in situ* studies show that the magnesium center can continue to be reactive, due in part to the redox active nature of the ligand. In addition, the analogous complex was formed with the carbene-based CN ligand, using the same diethyl magnesium reagent, and is hypothesized to have formed a magnesium center with one bidentate ligand coordinated onto one magnesium center with two ethyl groups as a monomeric complex.

48. Isopotential Electron Titration for Quantifying Metal-Adsorbate Charge Transfer

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A significant challenge in catalysis is overcoming the limitations of steady-state catalytic turnover, where the material limit for modern catalysts can be described by The Sabatier volcano plot [1]. A proposed solution is through oscillating the binding energy of kinetically relevant adsorbates. By controlling parameters such as frequency and magnitude, a more favorable potential energy surface can create significant enhancements in catalytic turnover through the oscillation of different kinetic regimes. However, the ability to predict reaction conditions in thermal catalysis where enhancements in catalytic turnover exist remains elusive. Charge transfer between an adsorbate and catalyst surface, which dictates changes in binding energy

and catalytic activity, can be used to identify desired reaction conditions. However, measuring charge transfer under reaction conditions is limited. Isopotential Electron Titration (IET) offers a rapid, non-destructive technique to quantify charge transfer in-situ, making it an asset for understanding the interactions that occur on catalyst surfaces. The extent of charge transfer was measured by modifying bulk-phase hydrogen activity while forcing a metal-insulator semiconductor (MIS) stack to electrochemical equilibrium. Results showed hydrogen adsorption induced a net charge transfer to the platinum surface, scaling linearly with temperature. Normalized per hydrogen atom, each donated 1.89 ± 0.005 mm e^- mol Pt^{-1} consistent with a Bader charge analysis, which predicted 4 mm e^- mol Pt^{-1}. Upon desorption, an equal and opposite charge transfer occurred. Understanding these interactions allows for quantification of changes in surface charge, which ultimately leads to programmable control of the interactions between catalyst surfaces, and the moieties that reside on them. This provides catalysts an opportunity to surpass the Sabatier optimum and achieve enhanced reaction rates.

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49. Understanding the dynamics of Pd-Au bimetallic catalyst for vinyl acetate synthesis using *in-situ*/operando analysis

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Vinyl acetate (VA) is a vital industrial intermediate used in the synthesis of polymers such as polyvinyl alcohol, polyvinyl acetate, and polyethylene-vinyl acetate, which find widespread applications in textiles, adhesives, coatings, and pharmaceuticals. Industrial production of VA is typically carried out via the gas-phase acetoxylation of ethylene over supported palladium-based heterogeneous catalysts. Although bimetallic Pd–Au alloy catalysts are known to improve activity and durability, the process still produces a considerable amount of carbon dioxide (CO_2) as a major byproduct. Given that CO_2 is a major greenhouse gas contributing significantly to global warming, even a modest improvement in product selectivity has substantial environmental benefits. For instance, increasing VA selectivity by just 1% (from 90% to 91%) can yield 8% more VA and 6% less CO_2, potentially reducing global CO_2 emissions by millions of metric tons. In this work, we report the design and performance of facet-engineered core–shell Pd-on-Au nanocubes supported on silica, which demonstrate nearly an order of magnitude higher catalytic activity compared to conventional PdAu alloy catalyst. The enhanced performance is attributed to the well-defined morphology of the Au nanocube cores, with predominantly {100} facets. The presence of Pd-dimers on these facets provide an ideal spatial arrangement that facilitates the coupling of acetate and ethylene in the presence of Pd dimers. Specifically, the 4.08 Å distance between these Pd-dimers species on Au(100) closely approximates the ideal 3.3 Å predicted by Goodman's model, thus promoting selective VA formation while suppressing undesired side reactions.[1,2] Remarkably, these core–shell Au@Pd nanoparticles achieve this performance using nearly ten times less palladium than traditional catalysts, offering significant advantages in terms of both cost and resource efficiency. These results highlight the promise of morphology-controlled bimetallic nanostructures as a platform for the development of next-generation catalysts with improved atom economy, higher selectivity, and reduced environmental impact.

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50. Designing Ti-Zeolites with Gradients in Heteroatom Composition for Improved Olefins Epoxidation

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Tuning traditional aluminosilicate zeolite properties is one of the promising topics in zeolite study. One such technique is incorporation of heteroatoms into zeolite: framework Si and Al elements are replaced by other elements, resulting in improved zeolite properties such as acidity, adsorption, pore structure, particle size and so on. Several elements like B, Ge, V, Sn, Ti, Ga, among others, have been introduced into different zeolite frameworks. Among these, Ti-based zeolites have garnered much interest in recent years due to its acidic properties in catalyzing oxidation based reactions, such as olefin epoxidation. Among them, Titanium Silicalite-1 (TS-1) is the most important candidate being studied.

Titanium silicalite-1 (TS-1) is one of the main catalysts for hydrogen peroxide olefins epoxidation reaction. However, the low epoxides selectivity on traditional bulk TS-1 is the major challenge for TS-1. In order to reduce the side reaction, which is the olefin oxides ring open reaction, reducing the products diffusion path length is a feasible way. In this work, we designed new TS-1 morphology to enhance epoxides surface mass transfer. Firstly, TS-1@silicalite-1 (egg-shell) is prepared by secondary growth, using olefins epoxidation reaction showed that egg-shell samples has higher selectivity over bulk TS-1. Moreover, a series of fin-like TS-1 grow on silicalite-1 samples are also prepared, which the fin size are around 50 nm. In previous work, it is proved that those small protrusions grown on Al-MFI could enhance the surface mass transfer and extend catalyst lifetime over MTH reaction. In comparison, finned TS-1 showed similar enhancement in catalyst performance. Herein, with two new designed TS-1, we tend to believe that the outer active shell is considered as a pseudo nanosheet which could enhance the mass transfer, and these small protrusions on inert surface act like pseudo-nanoparticles.

51. Single metal atoms embedded in nitrogen-doped graphene (M−N−C)

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Single metal atoms embedded in nitrogen-doped graphene (M−N−C) have emerged as a promising catalyst for a wide variety of reactions. In addition to the pyridinic site, there is another site responsible for the catalytic activity, but its structure is under debate. Here, we resolve its structure using first-principles calculations. Using Fe−N−C as a representative example, we systematically explore numerous possible structures and discover a new moiety with comparable energy to the pyridinic. This moiety features a hybrid coordination environment between pyridinic and porphyrinic and is located at the edge of graphene sheets or pores. We further calculate its X-ray absorption spectrum, catalytic thermodynamics for oxygen reduction reaction (ORR), and stability under ORR conditions, all of which support its existence. Lastly, we show that this site also exists in other M−N−C with different M elements. This study uncovers a new and important structure in M−N−C and paves a critical step toward site engineering for improved catalytic performance.

52. Constant-Potential Machine Learning Force Field for Electrochemical Interface

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Better understanding and prediction of electrochemical interface requires large-scale atomistic simulations. Machine learning force field (MLFF) has proven to be an effective approach. However, current ML models do not work for electrochemical interface, because they are not able to treat electrons with grand canonical ensemble. Here we solve this problem by developing a constant potential MLFF (CP-MLFF) model and implementing it into MACE. Specifically, we design an architecture based on equivariant graph neural network, which can take the number of electrons as input, and accurately predict the Fermi level. The CP-MLFF model allows us to address an important question: how long the simulation should be in order to sufficiently sample the electrochemical interface for accurately calculating the activation energy? Our work provides a useful method and tool enabling accurate and efficient large-scale simulation of electrochemical interface.

53. Tandem Adsorption and Photodegradation of Perfluorooctanoic Acid using Pyrene-based Covalent Organic Frameworks with Diacetylene Linkers

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Per/polyfluoroalkyl substances (PFAS) are anthropogenic water contaminants linked to adverse epidemiological health effects. Current methods for PFAS removal include the use of ion exchange resins or activated carbon to adsorb PFAS contaminants, but these adsorbents produce a waste stream that still contains PFAS. Adsorbents that can both remove and degrade PFAS contaminants are attractive for the development of simple, energy-efficient, and sustainable water treatment technologies. Herein, we present a combined experimental and computational study of pyrene-based covalent organic frameworks (COF) with diacetylene linkers, named Py-DEBD, as both an adsorbent and heterogeneous photocatalyst for the degradation of PFAS contaminants. We tested Py-DEBD for the adsorption and photocatalytic degradation of PFOA in batch photodegradation experiments and monitored the solution concentrations of PFOA, F^-, and short-chain PFCA byproducts before and after irradiation. As the pH decreased from 4 to 2, PFOA adsorption capacity and degradation rate increased. For photocatalytic degradation experiments at a pH of 2, over 99% of PFOA was removed from the solution, and 32% defluorination was achieved within 24 h. Density functional theory simulations demonstrate favorable adsorption of PFOA onto the Py-DEBD and show that photoinduced charge transfer under UV irradiation leads to PFOA oxidation, supporting the decarboxy-lation-hydroxylation-elimination-hydrolysis (DHEH) mechanism for PFOA photo-oxidative degradation. Both experiments and simulations show that the pyrene and diacetylene units are important to the oxidative degradation of PFOA. This work demonstrates that COFs provide a platform for the development of photo-active adsorbent materials for light-induced PFAS decomposition.

54. Computational Insights into Non-Thermal Effects in Photothermal CO_2 Methanation on Ru catalysts

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Gas-phase photothermal catalysis has recently emerged as a promising strategy for converting CO_2 into value-added chemicals and sustainable fuels, offering a dual-energy approach that combines both photonic and thermal energy to drive catalytic reactions under mild conditions. This dual-energy approach shows remarkable potential in facilitating catalytic transformations by decreasing activation barriers and improving product selectivity. However, the interactions involved are complex, particularly in validating non-thermal contributions with precise temperature measurements, optimizing strategies to enhance non-thermal effects, and developing a comprehensive microscopic understanding. CO_2 methanation on Ru catalysts which is also known as the Sabatier Reaction, exhibits significant enhancements in CH_4 production rates under 1 sun illumination, with over a 100-fold increase in reaction rate when white light serves as both the thermal and photonic source under identical operating conditions, underscoring substantial non-thermal contributions. These contributions are further validated by the observed wavelength-dependent reaction rate enhancements.

In this study, we employ density functional theory (DFT) to investigate the electronic characteristics driving the CO_2 methanation reaction on Ru catalysts. Density of states (DOS) analysis reveals strong CO_2 chemisorption on Ru surfaces, evidenced by the hybridization of metal *d*-states and adsorbate molecular orbitals. It was previously hypothesized that the marked reduction in the HOMO-LUMO gap in free, gas-phase CO_2 upon strong chemisorption may explain the rate enhancement by photons. Our electronic structure investigation, however, reveals the LUMO of chemisorbed CO_2 lies fully below the Fermi level. As alternative explanations for the observed photo enhancement we propose that light can assist either the desorption or dissociation of surface CO* intermediates. Our preliminary results suggest that specific wavelengths of incident light provide sufficient energy to promote either of these processes. Overall, our study elucidates the role of non-thermal effects in photon-assisted catalysis and provides mechanistic insights into how metal–adsorbate electronic interactions can be tuned to enhance photothermal processes.

55. 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 (IrO_2), despite its catalytic prowess, is limited by scarcity, and promising alternative catalysts like Ruthenium Oxide (RuO_2) 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 to investigate iridium's role in enhancing the stability of RuO_2. 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 over 1,500 at a current density of 2 A/cm² 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.

56. Realistic Atomistic Simulation of Heterogeneous Electrocatalysis

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Gaining an atomistic understanding of the electrochemical interface is crucial for numerous applications. However, traditional atomistic simulation methods often oversimplify key aspects of heterogeneous electrocatalysis, such as solvation dynamics and surface charge, which limit their accuracy. Furthermore, the lack of information on activation energies impedes the understanding and design of catalysts. In this presentation, I will showcase my efforts in developing more realistic simulation methods and their application to advance the understanding and design of heterogeneous electrocatalysis systems, with a focus on single–atom catalysts for oxygen reduction as a case study.

57. Selective Catalytic Dehydrogenation of Liquid Organic Hydrogen Carriers through Visible Light Photolysis

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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 insulating metal oxides (e.g. silica, alumina), 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. Regardless of temperature, an apparent quantum yield of ~ 30 % was observed to the desired dehydrogenation of formic acid. 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.

58. Recontextualizing the energy efficiency for dynamic modulation of formic acid electro-oxidation

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Catalysis is a rapidly developing field which demands a constant search for new and sustainable catalysts, developing new materials, which can be costly and tedious. Dynamic catalysis is a novel field that addresses these limits by using potential modulations to achieve greater rates and exceed the Sabatier maximum. Previous research on platinum catalyzed formic acid electro oxidation has shown that applied potential oscillations can yield rates up to 20 times higher than Sabatier maximum. However, the conditions under which energy is effectively harnessed versus inefficiently dissipated remain unknown. There is a need to understand the mechanism and time scales through which the energy is delivered in this dynamic system. Herein, we investigate the energetic electrochemical efficiency of electro oxidation of formic acid on platinum, an extensively studied chemistry with well-defined mechanisms, using transient potential decay techniques and a theoretical understanding of net and gross electron balance. It was seen that the net faradaic efficiency remained unaffected across the frequency spectrum, though the gross efficiency decreased which must be considered in the context of electrochemical oscillation. The gross efficiency was found to decay beyond a certain critical frequency (fcritical), which was dictated by the rate of relaxation (krelax), during the potential decay to open circuit. This study helps us to comprehend the efficiencies in the dynamic environment, as well as the timescale over which one needs to consider the energetic inefficiencies.

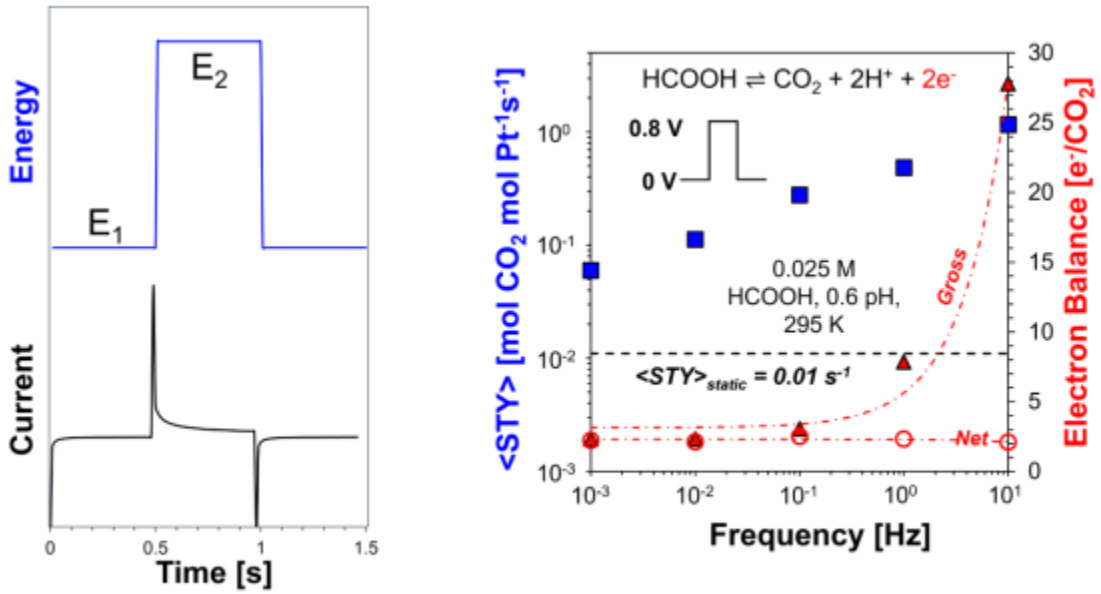

Figure 1. Net (○), and gross electron balance (▲) for formic acid electro-oxidation over polycrystalline Pt.

59. Theoretical analysis of the formate dehydrogenation on Pd(111), Pt(111) and Ni(111) catalysts

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The dehydrogenation of formate salts in the aqueous phase presents a promising solution for on-demand hydrogen production. Although formate salts are limited in their hydrogen content, they offer several advantages over metal hydrides and LOHCs, including low cost, ease of storage, safety, non-toxicity, and operation under mild conditions. According to the literature, among monometallic catalysts, Pd uniquely shows notable activity for hydrogen production at ambient temperature, while other common metals, including Pt and Ni, are essentially inactive[1]. The underlying reason for this unique behavior of Pd remains unresolved, possibly due to the ongoing debate surrounding the reaction mechanism of formate dehydrogenation in literature. We perform DFT-based calculations to analyze the state of Pd(111), Pt(111), and Ni(111) surfaces when exposed to an aqueous formate solution, and compare different metal surfaces to identify the factors governing the activity of Pd and elucidate why it alone exhibits this exceptional catalytic performance.

Reference:
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60. CCC Carbene Pincer Mg Complexes and Reactivity: NHC Ring Expansion and Decarbonization

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The growing interest in chemistry of main group elements stems from their key attributes' biocompatibility, low toxicity, low cost and high abundance. Their reactivity is often controlled by carefully tailoring the ligand scaffold. In this regard, structurally constrained pincer ligands have emerged as promising tools to modulate reactivity by manipulating electronic and steric properties.

Herein, we present two different bis carbene pincer CCC ligand frameworks: ^{Br}C^C^C and ^{H}CCC. The more flexible ^{Br}C^C^C ligand, with CH_2 bridges, affords the dimeric cyclic magnesium compounds. In contrast, the structurally constrained ^{H}CCC ligand facilitates the formation of a well-defined bimetallic magnesium compound, $CCCMg_2Et_3$, in nonpolar solvents. However, in polar solvents such as THF, it undergoes a unique tandem C-H activation and carbene decarbonization transformation. This reaction is thoroughly investigated using deuterium labelled studies. Additionally, the bimetallic $CCCMg_2Et_3$ provides a suitable framework for the synthesis of heterobimetallic compounds. For the preliminary reactivity, we have successfully prepared the CCC-Mg(Et)-Ni(COD) bimetallic compound. The identity of the prepared molecules is ascertained using multinuclear NMR spectroscopy and X-ray crystallography. The future work in this direction will focus on advancing these molecules for small molecules activation for catalysis.

61. Cation tuning of solid state electrolyte devices for hydrogen peroxide electrosynthesis

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The solid state electrolyte (SSE), or porous solid electrolyte (PSE), reactor has recently emerged as a green alternative for production of pure liquid chemicals/fuels, removing the need for post-synthesis separations. Since the inception of SSE reactors in the electrolysis field, progress has been made in terms of active and selective catalysts for fuels, but long-term stability still remains the greatest challenge to its

commercialization. In this work, we explore methods of extending reactor operability through the application of hydrogen peroxide (H_2O_2) electrosynthesis via the 2-electron oxygen reduction reaction ($2e^-$-ORR). We demonstrate that we can decrease the overpotentials in the reactor by addition of alkali metal cations to the solid electrolyte (SE) chamber, and by fully saturating the SE particles, we can decrease the cell voltage by > 2 V. Further, we investigated the effect various alkali metal bicarbonates have on cell stability by measuring the mass balance of cations and water in the cell. We discover that water travels with cations across the anion exchange membrane (AEM) to the cathode via electroosmotic drag, and the water flux decreases in the presence of $K^+ > Cs^+ > Na^+$. The trend of time of AEM flooding, which results in cell failure, is $K^+ > Cs^+ \approx Na^+$, and the trend of cation molar flux across the AEM is $K^+ > Cs^+ > Na^+$. Therefore, while the time of AEM flooding cannot be attributed to a higher water flux across the membrane, the cell stability may instead hinge on the ability to maintain high cation flux, which lowers cell voltage and hence reduces hot spots on the membrane.

62. Interzeolite Transformation Intermediates as Hybrid Catalysts for the Conversion of Bulky Molecules

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A new family of X-ray amorphous zeolites with unique structural properties has been developed through controlled partial interzeolite transformation. [1,2] These materials, referred to as Interzeolite Transformation Intermediates (ITIs), are composed of zeolitic building units and exhibit both enhanced accessibility and strong acidity. A key advantage of this approach is the ability to finely tune the properties of the solids by simply interrupting the transformation process at different times.

Specifically, the transformation of FAU into MFI was carried out using a long-chain quaternary amine, serving both as a structure-directing agent and porogen, the different materials were obtained by the interruption of the transformation at various stages. This strategy enabled the synthesis of superior hybrid catalysts whose structures incorporate building units from both FAU and MFI frameworks (Figure 1). Catalytic performance could be optimized by precisely controlling the interruption time during transformation.

To evaluate the capability of the hybrid zeolites in converting bulky molecules, catalytic cracking of 1,3,5-triisopropylbenzene (TiPBz) was performed (Figure 3). The hybrid catalysts comprising FAU and MFI units demonstrated a 5-fold increase in selectivity towards the desired product, 1,3-diisopropylbenzene, compared to commercial FAU, and a 7-fold increase in conversion at constant selectivity relative to MFI zeolite. Moreover, these intermediates consistently yielded lower amounts of the two unwanted over-cracking products (cumene and benzene) than conventional FAU and MFI zeolites at comparable conversions.

In conclusion, the partial interzeolite transformation strategy enables the fine-tuning of both the physicochemical properties and, consequently, the catalytic performance of the hierarchical catalysts by simply stopping the transformation at different times. This approach opens countless opportunities for the development of new hierarchical catalysts (ITIs) with optimized properties and superior catalytic activity, particularly for reactions where conventional zeolites show significant diffusion limitations.

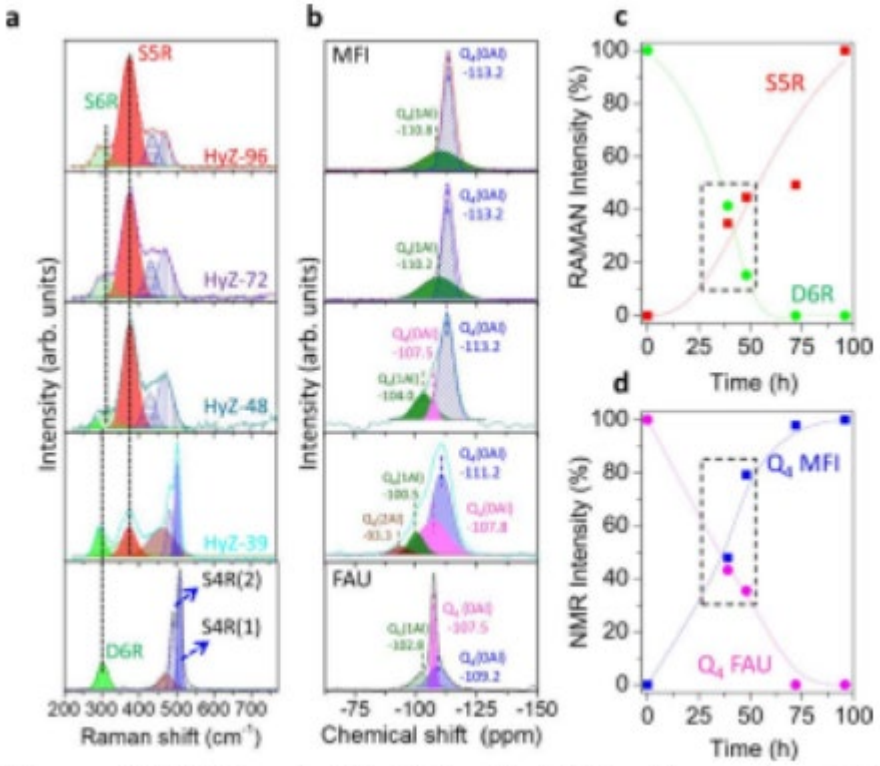

Figure 1. a) UV-Raman and b)^{29}Si NMR spectra of the hybrid zeolites. Evolution of the percentage of c) UV-Raman intensity and d) the Q4 intensity in the ^{29}Si NMR.

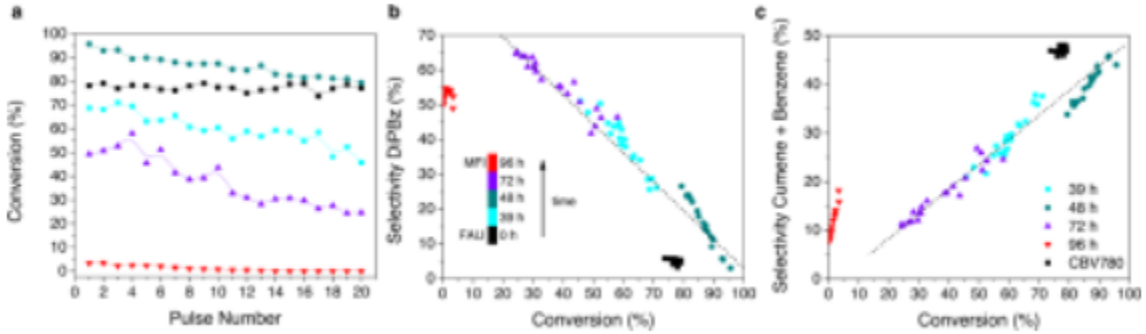

Figure 2. a) Conversion in the catalytic cracking of TiPBz. Evolution of the selectivity for b) 1,3-diisopropylbenzene and c) cumene and benzene.

63. Engineering the Morphology of Aluminum Oxide for Advanced Catalyst Supports

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Al_2O_3 is widely employed as a catalyst support due to its thermochemical inertness [1]. Over the past decades, extensive research has been conducted to improve catalytic performance of metal-supported catalysts on Al_2O_3; however, acid sites on the support can lead to side reactions, which catalyst performance via reduced selectivity.

Due to the lack of understanding about the preferential locations of acid sites on Al_2O_3, designing the advanced Al_2O_3 support with the developed textural properties while minimizing acid sites is challenging.
This poster presentation will describe our studies focused on new synthetic methods to tailor the morphology of Al_2O_3 crystals with the goal of optimizing their physicochemical properties as support for commercially relevant reactions. For this study, we synthesized a library of Al_2O_3 materials with varied morphological properties using several methods: (i) hydrothermal, (ii) hard-templating, and (iii) molten-salt synthesis. All samples exhibit identical bulk structure but distinct crystal habits (i.e., exposed crystallographic planes), textural properties (i.e., surface area, porosity), and surface geometries (i.e., roughness). We also tested the acidic properties of each material using the 1-butene double-bond shift reaction as a benchmark. Our findings reveal that the inherent surface acidity (i.e., strength and density) is strongly influenced by the nature of exposed facets, as the coordination structure and density of surface hydroxyl groups are governed by the underlying crystal structure.

References
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64. Rational Design of Iron-Encapsulated Small-pore Chabazite Zeolites

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In heterogeneous catalysis, metal-substituted zeolites are used as active materials for a variety of reactions that include (but are not limited to) syn gas to olefins, selective catalytic reduction of NOx using ammonia (NH_3-SCR), methanol to olefins, dehydrogenation, and oxidation reactions, among others. The catalytic performance depends on the localization of metal species at (extra)- framework positions. Furthermore, metal size, location and their distribution throughout the zeolite structure are crucial for establishing structure–activity relationships, thereby advancing the design and optimization of efficient zeolite catalysts. In this presentation we focus on the introduction of iron into CHA-type zeolites (SSZ-13 and SAPO-34), which are small-pore zeolites with 3-dimensional network of channels and cages. We use a combination of bottom-up and top-down synthesis approaches to place metals (e.g., Fe, Co, etc.) in (extra)-framework sites. In this project we used a combination of characterization techniques to determine the physicochemical properties of these materials with the long-term goal to establish structure-performance relationships in benchmark reactions. Our findings reveal key differences in metal occlusion based on the selection of metal precursors (e.g., organometallic vs. nitrate salts) and the synthesis route that includes one-pot hydrothermal, inter-zeolite transformation, and mechanochemical methods. This presentation will focus on the design of both Fe@SSZ-13 and Fe@SAPO-34 catalysts using commercially viable approaches that bypass traditional ion-exchange processes and overcome common challenges of metal incorporation in small-pore zeolites. Overall, the methodologies introduced in this study could potentially serve as a framework for synthesizing other metal@zeolite materials as optimized catalysts for applications in the emerging energy and environmental landscapes.

65. CO_2 cycloaddition of epichlorohydrin over CALF-20 as acid catalyst

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Calgary Framework 20 (CALF-20), a zinc-based metal organic framework (MOF) with 1,2,4-triazolate and oxalate linkers, has attracted great attention in the gas adsorption and separation field due to its superior carbon dioxide (CO_2) uptake performance under humidity. Here, we present our work on CALF-20, covering its phase transformation, its rapid microwave-assisted synthesis method, as well as catalytic studies of CO_2 cycloaddition over CALF-20.

A few literatures reported that the original CALF20 structure (α-phase) can be transform into β phase and τ-phase under pure humid conditions and thermal-humid conditions, respectively. The previous computational report has shown that the β-phase has higher CO_2 adsorption capacity compared to α-phase. The coordination number of α-CALF-20 changes from 5 to 4 when it is transformed into β-CALF-20 resulting in a contraction of the pore. However, due to reversible nature of α to β phase transformation, the humidity induced β-phase could not be maintained during characterization. Herein, we showed that based on our experimental and computational studies, α to β phase transformation can be achieved solely through thermal treatment without involvement of water molecules (figure 1a) and the obtained β-phase CALF20 (β^T-CALF-20) remains stable under degassing condition (at 150°C), during the CO_2 physisorption testing and afterward (figure 1b). Additionally, we demonstrate a microwave assisted one-pot synthesis of CALF-20. Integrating microwave assisted method can shorten synthesis time to just in 90 seconds – over 1,900 times faster than conventional solvothermal synthesis, simplifying the synthesis process and scaling up of CALF-20 production. The resulting CALF-20 preserved β^T-CALF-20 structure after drying at 150°C. This confirms that β^T-CALF-20 can be obtained regardless of the synthesis method.

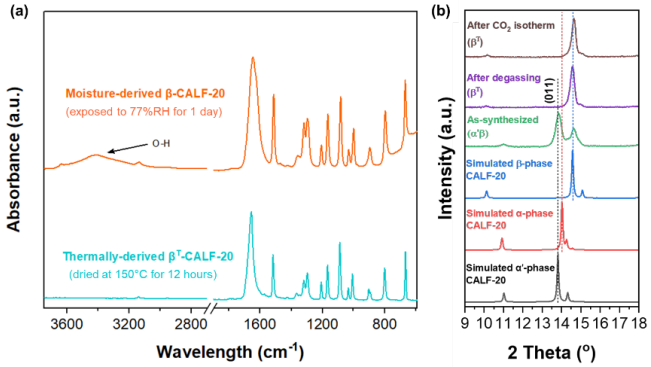

Figure1. a) Fourier transform infrared (FTIR) spectra of CALF-20 comparing between thermally-derived β^T-CALF-20 vs. moisture-derived β-CALF-20 and (b) PXRD patterns of CALF-20 after degassing and after CO_2 isotherm measurement in comparison with that of as-synthesized powders along with simulated patterns.

Even though there are several reports on adsorption and separation properties of CALF20 as well as its structure, there has been no intense report on the catalytic properties of CALF-20. Here, we utilized our β^T-CALF-20, synthesized via the rapid microwave-assisted method and thermally treated at 150°C in convection oven, as a catalyst for CO_2 cycloaddition of epichlorohydrin (ECH) to cyclic carbonate in semi-batch reactor using tetrabutylammonium bromide (TBAB) as co-catalyst. The ECH conversion achieves > 80% with 120°C reaction temperature within 2 hours. Additionally, preliminary kinetic information was obtained (figure 2b-2d), showing the reaction order and an activation energy of approximately 50 kJ/mol, regardless of any observed deactivation. The thermal stability of β^T-CALF-20, its functional group and crystal structure (figure 2e-2g) before and after reaction were confirmed by thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD), respectively. By utilizing temperature programmed desorption of ammonia (NH_3-TPD), we observed that β^T-CALF-20 has an NH_3 uptake ca. 2,400 μmol/g which is comparable to some solid acid catalysts (e.g., SAPO-34). We hypothesize a reaction mechanism that Lewis acid sites, potentially from the unsaturated metal node of β^T phase owing to its reduction in coordination

number, on β^T-CALF-20 attacks negative charge of oxygen atom of the epoxide ring. The co-catalyst facilitates ring-opening before the opened epoxide ring undergoes CO_2 insertion and later forms a five-membered ring of cyclic carbonate (figure 2a).

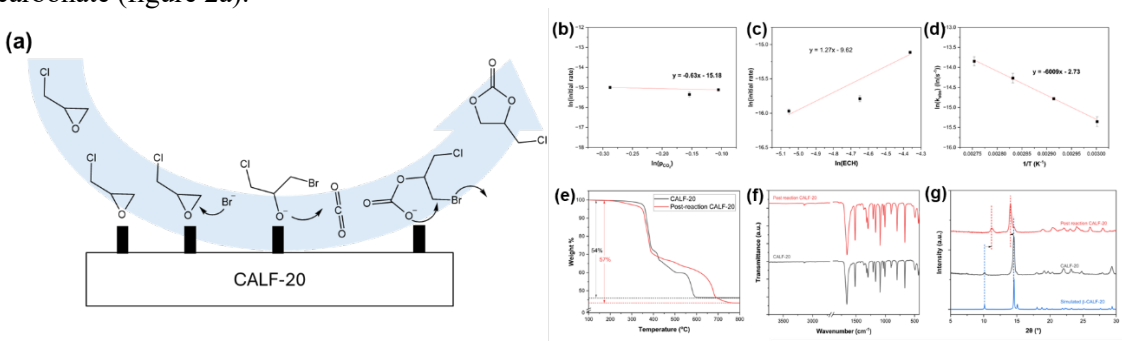

Figure 2. (a) Hypothesized CO2 cycloaddition of epichlorohydrin reaction mechanism over CALF-20. CO_2 cycloaddition over CALF-20 at (b) different CO_2 partial pressure, (c) different ECH concentration and (d) Arrhenius plot of the reaction. (e) TGA profiles (f) FTIR spectra and (g) XRD patterns before and after reaction of CALF-20. Reaction condition: temperature = 120°C, p_{CO2} = 0.86, time = 2 hours, catalyst 0.5%mol_{ECH}, co-catalyst = 0.4 %mol_{ECH}

To conclude, our work reveals that α to β phase transformation of CALF-20 can be conducted via purely thermal induction and the structure is still stable even after degassing and characterization. Moreover, CALF-20 can be successfully synthesized through the rapid microwave assisted synthesis and obtained the same β^T-CALF-20 structure as the solvothermal method after thermal treatment. Lastly, we prove the presence of acid site on β^T-CALF-20 and its utilization as a catalyst for the CO_2 cycloaddition of epichlorohydrin.

66. CO_2 Design to Guide Aqueous and Non-Aqueous CO 2 Electrolysis to Scale-up

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Electrochemical CO_2 reduction (CO_2R) can convert captured CO_2 into chemical feedstocks and fuels using renewable electricity and water, but scaleup has been limited. To guide academic research towards the most important problems facing industrial-scale CO_2R, we use a physics-informed technoeconomic assessment that addresses the sensitivity of overall process cost towards improvements at the electrolyzer scale, identifying the most impactful research directions for the field to pursue. The assessment confirms the importance of better materials (membranes, catalysts), which has been the focus of the field, and of cheaper electricity.[1] We also find a critical and overlooked need for improved reactor design due to the tradeoff between single-pass conversion and selectivity for CO_2 electrolyzers.[2]

While aqueous electrolyzers have been prioritized for their low cell voltages, they suffer from low selectivity and high costs for producing valuable C_{2+} products. We present an additional techno-economic assessment focused on CO_2R to oxalic acid, a 2-electron C_2 product formed only in aprotic non-aqueous electrolytes. Extending our prior work on aqueous CO_2R, we discuss the impacts of electrolyzer and electrolyte design on the process design and cost of non-aqueous CO_2R. We show that oxalic acid can be produced at $2.87/kg in a small-scale process with minimal technology developments beyond the current state-of-the-art, approaching the market price of $0.7 – 2.5/kg. Its cost competitiveness is driven by its market value and 2-electron reaction pathway. We also present a recommended pathway towards economical CO_2R to oxalic acid. Key priorities for achieving cost targets include increased current density, extended cell lifetimes, and optimized flow cell configurations. Additionally, lowering cell resistance by enhancing electrolyte conductivity or reducing catholyte chamber width is crucial. This assessment highlights the immense potential of non-aqueous CO_2R, which has been largely overlooked compared to aqueous CO_2R.

(1) Da Cunha, S. C.; Resasco, J. Insights from Techno-Economic Analysis Can Guide the Design of Low-Temperature CO_2 Electrolyzers toward Industrial Scaleup. *ACS Energy Lett.* 2024, *9* (11), 5550–5561. https://doi.org/10.1021/acsenergylett.4c02647.
(2) Da Cunha, S. C.; Resasco, J. Maximizing Single-Pass Conversion Does Not Result in Practical Readiness for CO2 Reduction Electrolyzers. *Nat. Commun.* 2023, *14* (1), 5513. https://doi.org/10.1038/s41467-023-41348-w.