NACS North American Catalysis Society

SWCS Southwest Catalysis Society

SOUTHWEST CATALYSIS SOCIETY

2023 SPRING SYMPOSIUM

Friday, April 28, 2023

L2D2 Engineering Lecture Hall

University of Houston

7:45 AM – 4:30 PM

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The SWCS officers and I welcome you to the 2023 Southwest Catalysis Society Spring Symposium, Friday, April 28, 2023, to be held in the L2D2 Engineering Lecture Hall at The University of Houston.

We are delighted to present 8 invited speakers and 39 poster presentations at this year's symposium. The 2023 SWCS Excellence in Applied Catalysis Award will be presented to Ive Hermans from the University of Wisconsin-Madison. Furthermore, meritorious posters by students and postdocs will be identified with Best Poster Awards. See Page 3 for a detailed outline of the Program.

The 2023 Spring Symposium registration fee is $20 for students and post-doctoral researchers, and $60 for all other attendees. The fee includes North American Catalysis Society and SWCS annual membership dues, coffee/snacks, and lunch. We highly recommend online pre-registration at:

https://www.swcatsoc.org/

For on-site registration we will only accept credit cards (Visa, MasterCard, Discover, and American Express) for the registration fee. Event tickets and receipts will be sent via e-mail, so please be prepared to enter your e-mail address when you register.

Please see Page 4 for meeting venue and parking locations.

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

We hope you will join us at the Symposium!

Praveen Bollini

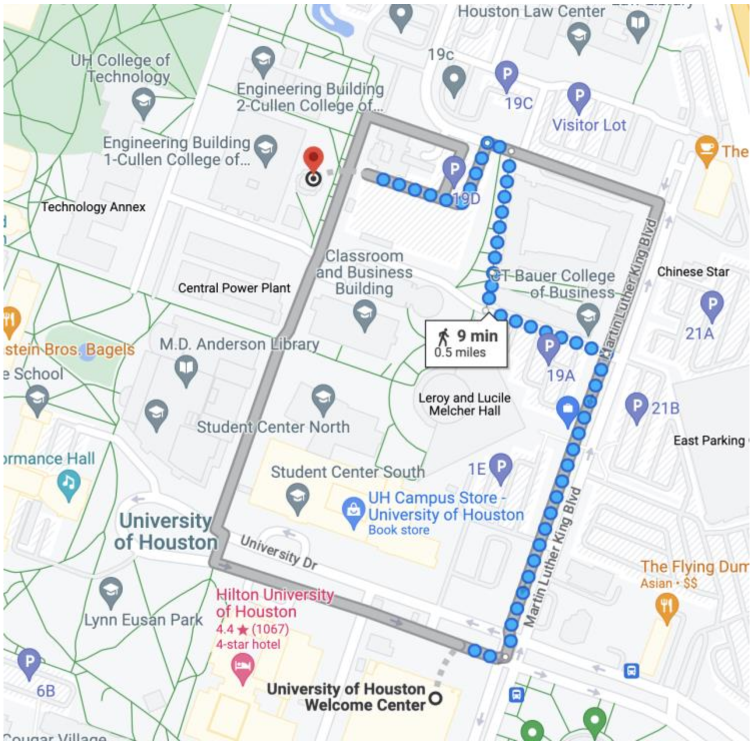
University of Houston

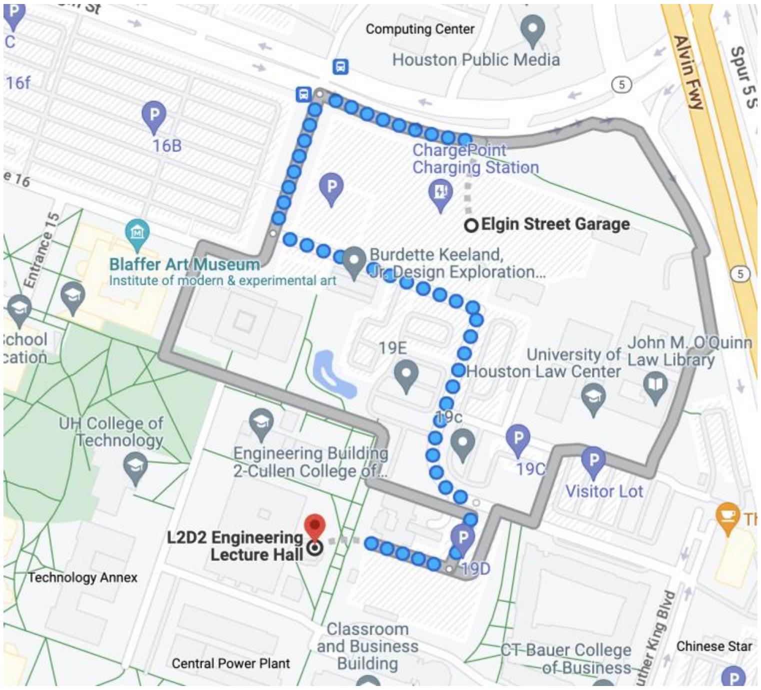
Chair, SWCS

2023 PROGRAM

Talks will be held in the L2D2 auditorium; poster sessions and coffee breaks/lunch will be held in the Engineering Commons adjacent to the auditorium.

7:45 AM	**Registration, check-in, coffee**
8:20 AM	**Opening remarks – Praveen Bollini** (Chair, SWCS)
8:30 AM	**Manos Mavrikakis**, University of Wisconsin-Madison *Catalytic performance descriptors: An atomic-scale perspective*
9:15 AM	**Susannah L. Scott**, UC Santa Barbara *Valorization of polyolefins via catalytic upcycling: From monomers to higher value molecules*
10:00 AM	**Coffee Break & Poster Session**
10:45 AM	**Linda J. Broadbelt**, Northwestern University *Unraveling Complex Catalytic Chemistries through Automated Network Generation and Reaction Pathway Analysis*
11:30 AM	**Deng-Yang Jan**, Honeywell UOP *UOP Zeolitic Materials (UZM) in Aromatics, Derivatives and LAB Production*
12:15 PM	**Lunch Break (Catered) and Poster Session**
1:30 PM	**Ive Hermans**, University of Wisconsin-Madison **Winner, 2023 SWCS Excellence in Applied Catalysis Award** *Accelerating Serendipity in Heterogeneous Catalysis*
2:15 PM	**2023 SWCS Excellence in Applied Catalysis Award Presentation,** Alejandra R. Rivas Cardona, Chair – Award Selection Committee
2:20 PM	**Dongxia Liu**, University of Delaware *Membrane Reactor: Coupling Catalytic Reaction and Separation for Dehydrogenation of Light Alkanes*
3:00 PM	**Beata Kilos**, Dow *Sulfide catalysts for the selective vapor-phase methoxycarbonylation of ethylene*
3:40 PM	**Abdoulaye Djire**, Texas A&M University *Novel Materials and Chemistries for Carbon-Neutral Energy*
4:20 PM	**Poster Awards, Tracy Lohr** (Chair-Elect, SWCS)
4:30 PM	**End – Happy Hour (Rooftop Patio – The Nook Café and Bar** **Address: 4701 Calhoun Rd, Houston, TX 77004)**





Symposium location:

L2D2 Engineering Lecture Hall: 4726 Calhoun Rd, Houston, TX 77204

Recommended parking locations ($18 per day):

1) UH Welcome Center Garage (top map): 4400 University Dr, Houston, TX 77004

2) Elgin Street Garage (bottom map): 4224 Elgin St, Houston, TX 77004

Catalytic performance descriptors: An atomic-scale perspective

Manos Mavrikakis
Department of Chemical & Biological Engineering, University of Wisconsin-Madison

Activity, selectivity, and stability are the key performance descriptors for catalysts. In this presentation, we will describe insights for explaining an outstanding performance of bimetallic electrocatalysts by proposing novel models based on fundamental surface science concepts. We will also attempt to provide a more realistic picture of the catalyst's surface and its active sites as a function of reaction conditions and the identity of reactants and that of key intermediates. We conclude that challenging well-established assumptions regarding model catalytic surfaces can offer significant benefits to our fundamental understanding of reaction mechanisms.

Biography

Manos Mavrikakis is the *Ernest Micek Distinguished Chair*, the *James A. Dumesic* Professor, and the *Vilas Distinguished Achievement* Professor of Chemical Engineering at the University of Wisconsin-Madison. He received a Diploma in Chemical Engineering from NTUA in Greece, and a PhD in Chemical Engineering & Scientific Computing from the University of Michigan, Ann Arbor. Following postdocs at the University of Delaware and the Technical University of Denmark, he joined the faculty of Chemical Engineering at UW-Madison. His main research interests include the elucidation of detailed reaction mechanisms for thermal heterogeneously catalyzed and electrocatalyzed reactions and the identification of improved catalytic materials from first-principles-based microkinetic modeling. He has coauthored ~300 publications. Mavrikakis is an elected *Fellow* of *APS* (2013), *AAAS* (2014), and *AVS* (2016). He served as his Department Chair (2015-2018) and was a *Visiting Miller Research Professor* at UC Berkeley – Chemistry in 2019. He received the 2009 *Paul H. Emmett* award and the 2021 *Burwell Lectureship* from the North American Catalysis Society, the 2014 *R. H. Wilhelm* award from AIChE, and the 2019 *Gabor A. Somorjai* award from ACS. He served as editor-in-chief of *Surface Science* between 2012 and 2020.

Valorization of polyolefins via catalytic upcycling: From monomers to higher value molecules

Susannah L. Scott

Department of Chemical Engineering, University of California, Santa Barbara

Polyolefins are the largest use of carbon feedstock and their manufacturing is one of the largest sources of CO_2 emissions in the modern global chemical industry. Recycling waste polyolefins (POs) to value-added compounds and materials could contribute to a circular carbon economy, while reducing the impact of plastic waste on the environment. The challenge is that POs are remarkably recalcitrant to chemical recycling, due to their lack of chemical functionality and low solubility. Until recently, chemical transformations focused on producing low-value gasoline- and/or diesel-range hydrocarbons for combustion as transportation fuels. We discovered catalysts to convert PE to alkylaromatics with average carbon number $C_{\sim 30}$ at ca. 280°C, in the absence of external H_2. The tandem reaction couples endothermic dehydroaromatization with exothermic C-C bond hydrogenolysis. The product long-chain alkylaromatics are potentially high-value chemicals with broad commercial applications as solvents, refrigeration fluids, and precursors to anionic surfactants. An even lower temperature approach couples (transfer) dehydrogenation of PE with catalytic olefin isomerization and ethenolysis to generate light olefins which can be repolymerized to new POs.[3]

Biography

Susannah Scott is a Distinguished Professor in both Chemical Engineering and in Chemistry & Biochemistry at the University of California, Santa Barbara. She received her Ph.D. in Inorganic Chemistry from Iowa State University, under the direction of Jim Espenson and Andreja Bakac, for her work on the activation of O_2 and transition metal-catalyzed oxidation mechanisms. She was awarded a NATO Postdoctoral Fellowship for work with Jean-Marie Basset at the Institut de recherches sur la catalyse (CNRS) in Lyon, France. In 1994, she joined the faculty of the University of Ottawa (Canada), where she was named a Canada Research Chair. In 2003, she moved to the University of California, Santa Barbara, where she currently holds the Duncan and Suzanne Mellichamp Chair in Sustainable Catalysis and is Chair of the Santa Barbara Division of the University of California's Academic Senate. She is an Executive Editor for ACS Catalysis, and a member of the Board of Reviewing Editors for Science. Her research interests include the design of heterogeneous catalysts with well-defined active sites for the conversion of conventional and unconventional carbon-based feedstocks, as well as environmental catalysts to promote air and water quality.

Unraveling Complex Catalytic Chemistries through Automated Network Generation and Reaction Pathway Analysis

Linda J. Broadbelt, Department of Chemical and Biological Engineering, Northwestern University

Catalytic reactions are often characterized by their complexity and involve hundreds of interacting species in more than thousands of reactions. However, a detailed elucidation of reaction pathways and mechanisms is key in understanding complex catalytic chemistries and developing new catalysts for improved yields and selectivity of the desired products. In this presentation, methods for the assembly of large reaction networks comprised of known and novel reactions and molecules based on generalized reaction operators gleaned from known biochemical and chemocatalytic reactions will be described. In the realm of biocatalysis, enzyme substrate promiscuity has significant implications. The ability to predict the space of possible enzymatic side reactions is crucial for elucidating underground metabolic networks in microorganisms, as well as harnessing novel biosynthetic capabilities of enzymes to produce desired chemicals. We have implemented reaction rule-based cheminformatics platforms to computationally enumerate possible promiscuous reactions, relying on existing knowledge of enzymatic transformations to inform novel reactions. We curated a set of 1224 most generalized reaction rules, automatically abstracted from atom-mapped MetaCyc reactions and verified to uniquely cover all common enzymatic transformations. We have developed Pickaxe, an open-source, flexible software that provides a user-friendly method to generate novel reaction networks that can accommodate the JN1224min ruleset or incorporate custom rules defined by users. As a second example of reaction network generation, the application of microkinetic modeling based on a detailed reaction mechanism to understand zeolite-catalyzed conversion, including oligomerization on bifunctional metal-zeolite catalysts, is demonstrated. First, plausible elementary reactions were considered and categorized into different types, and the reaction rules for each reaction type were formulated. Complex reaction networks comprising all possible elementary reactions were then constructed based on the reaction rules via an automated reaction network generator. To reduce the computational cost for estimating rate coefficients in Arrhenius form for all the elementary steps, the Evans-Polanyi relationship was used to relate activation energy to heat of reaction for each type of elementary reaction. The mechanistic models were able to capture the yields and selectivities to a wide range of major and minor products.

Biography: Linda Broadbelt is Sarah Rebecca Roland Professor in the Department of Chemical and Biological Engineering (ChBE) and Associate Dean for Graduate Research and Education of Engineering at Northwestern University. She was Chair of the Department of ChBE from 2009-2017. Her research and teaching interests are in multiscale modeling, complex kinetics modeling, catalysis, novel biochemical pathways, and polymerization/depolymerization kinetics. She served as the Past Chair, Chair, First Vice Chair and Second Vice Chair of the Catalysis and Reaction Engineering Division of AIChE, and also served on the Executive Board of the National Program Committee of AIChE and the Board of Directors. She is currently an Associate Editor for *Industrial &Engineering Chemistry Research* and *ACS Engineering Au*. Her honors include selection as the winner of the R.H. Wilhelm Award in Chemical Reaction Engineering from AIChE, the E.V. Murphree Award in Industrial Chemistry and Engineering from the American Chemical Society, the Dorothy Ann and Clarence Ver Steeg Award, a CAREER Award from the National Science Foundation, and an AIChE Women's Initiative Committee Mentorship Excellence Award, and selection as a Fellow of the American Association for the Advancement of Science, a Fellow of AIChE, a Fellow of AIMBE, and a Fulbright Distinguished Scholar. She was elected to the National Academy of Engineering in 2019. In 2021, she was elected to the American Academy of Arts & Sciences.

UOP Zeolitic Materials (UZM) in Aromatics, Derivatives and LAB Production

Deng-Yang Jan
Honeywell UOP

Benzene, toluene and xylene (BTX), derivatives (EB, Cumene) and detergent (LAB, Linear Alkyl Benzene) are important petrochemical intermediates used to produce a long list of consumer and engineering products with high CAGR (Compound Annual Growth Rate) demands. These aromatic molecules are primarily synthesized via aromatics ring formation (e.g., Reforming) followed by aromatics inter-conversion and separation unit operations to produce high purity benzene and individual xylene isomers, and further alkylation of benzene to derivatives and LAB with corresponding olefins. To meet the growing demands sustainably we are taking multipronged approaches for making the existing processes work at greater efficiency, developing solutions to address plastic circularity and developing processes from renewable feedstock such as biomass and CO_2. The emphases in improving the existing processes are placed on zeolite-catalyzed molecular transformation efficiency to the target molecules and the associated energy consumption. The process to bring about the advancement begins with constructing reaction networks, analyzing surface reaction chemistry and identifying material functional properties required to facilitate the molecular transformation leading to the target molecules at equilibrium or *most desirably above equilibrium levels* at the lowest possible energy consumption (and operating temperatures). The aforementioned functional properties comprise of distributions/structures of reaction centers (aluminum), adsorption properties and morphology (mass transport property) over a diverse array of zeolite topology and are attained in UOP Zeolitic Materials (UZM) via zeolite synthesis approach termed Charge Density Mismatch (CDM). By aligning the reaction centers and competitive adsorption with desired surface reactions under minimal mass transport resistance, greater efficiency is realized via lower feedstock and energy consumption.

Biography

Deng-Yang (DY) joined UOP in 1986 after earning a Ph.D. from the Ohio State University. He has taken positions in catalysis research, new product development and commercialization scale-up in refining, petrochemicals and renewables related technology. He is a Sr. R&D Fellow at Honeywell-UOP. DY is an inventor or co-inventor of more than 100 US patents and coauthor of 30 peer reviewed journal articles, a book chapter on “Processes on Industrial C-C Bond Formation” in Zeolites in Industrial Separation and Catalysis, Wiley-VCH of 2010, and the 2012 edition of Ullmann Encyclopedia on Zeolite, Wiley-VCH. He is a member of Catalysis Club of Chicago and American Chemical Society. DY’s research areas encompass material design for hydrocarbon conversions and separation and catalyst/process development. DY is the recipient of several awards including 2020 Recipient of Eugene Houdry Award of North American Catalysis Society, 2017 Honeywell Distinguished Technologist Award, 2016 Recipient of Herman Pines Award and 2007 Honeywell Fundamental Technology Development Award. He is also the president of 2016-2017 Catalysis Club of Chicago.

Accelerating Serendipity in Heterogeneous Catalysis

Ive Hermans

UW-Madison, Department of Chemistry, Department of Chemical and Biological Engineering,
Wisconsin Energy Institute, Madison Wisconsin, USA
KU Leuven, Molecular and Microbial Systems, Leuven, Belgium

In this talk I will elaborate on the discovery of new catalytic systems, illustrating how “luck favors the prepared”, and how the right tools allow us to establish molecular design principles to improve promising systems. For this we practice a convergence research approach, combining materials synthesis and characterization, kinetics and reaction engineering, *in situ* spectroscopy and computational description and prediction. I will illustrate this path for boron-based ODH catalysis, titanium-based epoxidations and CO_2 hydrogenation over mixed metal oxides. One powerful tool that I will highlight is Modulation Excitation Spectroscopy, a dynamic technique where the concentration of one of the reagents is periodically altered. By studying the response of the system to this perturbation we can filter out noise and signals stemming from spectator species and obtain kinetic insights in the activation and transformation of reagents at the fluid-solid interface.

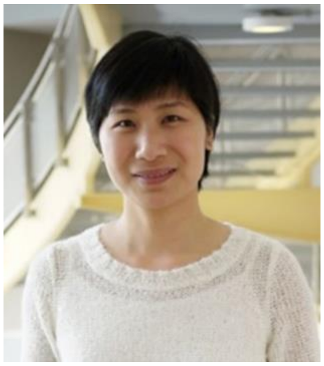
Biography

Ive Hermans obtained his Ph.D. under the supervision of Profs. Jacobs and Peeters (2006; KU Leuven, Belgium). In addition to his scientific education, Ive Hermans also holds a postgraduate degree in Business Administration (KU Leuven, 2006). After post-doctoral research on *in situ* spectroscopy and reaction engineering with Prof. Alfons Baiker, he became assistant professor (spring 2008) at the Institute for Chemical and Bioengineering of ETH Zurich in Switzerland. January 2014, Prof. Hermans moved to the University of Wisconsin-Madison, holding a dual appointment in the Department of Chemistry and the Department of Chemical and Biological Engineering. His group focuses on the development and understanding of catalytic technology using a variety of techniques. In 2009 he received the ExxonMobil Chemical European Science and Engineering Award, in 2014 the Emerging Researcher Award by the ACS Division of Energy and Fuels, the 2016 Postdoc Mentoring Award by the UW Postdoc Association, the 2017 Inaugural Robert Augustine award by the Organic Reaction Catalysis Society, the 2019 Ipatieff Price by the American Chemical Society and was selected as a 2021 Alexander von Humboldt Professor. Since 2021, Dr. Hermans also holds an honorary position as Extraordinary Visiting Professor at KU Leuven, Europe’s most innovative university, according to Thomson Reuters.

Membrane Reactor: Coupling Catalytic Reaction and Separation for Dehydrogenation of Light Alkanes

Dongxia Liu

Department of Chemical & Biomolecular Engineering, University of Delaware



Light alkanes, the main constituent of natural gas and shale gas, are deemed to be alternative sources to replace crude oil to produce chemicals and fuels. Direct non-oxidative alkane conversion has been recognized as a single-step technology that directly convert alkanes to olefins, higher hydrocarbons and hydrogen. Low alkane conversion, high energy input and low catalyst durability, due to endothermic reaction nature and coke formation, are main challenges. In this presentation, I would like to highlight our recent innovations in inorganic membrane reactors that solve the thermodynamic and kinetic challenges in alkane dehydrogenation to achieve high conversion, high product yield, negligible coke formation and system's long-term stability. These consequences originate from the removal of hydrogen co-product by hydrogen separation membranes to right shift the reaction towards high conversion. The elimination of coke formation achieved via design of subnanometer catalysts and lowering operation temperature in the membrane reactor, which enables alkane activation and suppresses the following secondary and following on reaction steps towards coke formation. The developed membrane reactors show great economic viability for practical industrial applications.

Biography

Dongxia Liu obtained her B.S. degree in Chemistry major from Shandong University in China in 2000. She won her M.S. degree from Institute of Chemistry, Chinese Academy of Sciences in 2003. In 2009, she received her Ph.D. in chemical engineering from University of Rochester. After graduation, she did 2.5 years of post-doctorate in University of Minnesota. In 2012, she joined the Department of Chemical and Biomolecular Engineering at the University of Maryland (UMD) as an assistant professor and was promoted to an associate professor in 2018 and to a full professor in 2022. In January 2023, she joined Department of Chemical and Biomolecular Engineering at the University of Delaware (UD) as a Robert K. Grasselli Professor. Dongxia is leading the Materials Synthesis and Catalysis Lab at UD, targeting for controlling composition and constitution of nanostructured materials for catalyst, membrane and reactor technologies to address the challenging issues in renewable energy and chemicals production. She has authored more than 80 peer-reviewed journal articles and 7 issued/pending patents on these topics and served on the program and organizing committees of various international workshops and conferences. Dongxia has won various awards including the UMD's Faculty-Student Research Award (FSRA) awards (2021 and 2013), Junior Faculty Outstanding Research Award in A. James Clark School of Engineering at UMD (2020), and the NSF CAREER award (2013).

Sulfide catalysts for the selective vapor-phase methoxycarbonylation of ethylene

Beata Kilos, Ph.D.
DOW, Core Research & Development

Methyl methacrylate (MMA) is an important monomer in the production of acrylic polymers used for glass replacement acrylic sheets, surface-coatings, and emulsion polymers. Resins made from MMA are noted for their glass-like clarity, strength, and durability. Methyl methacrylate can be produced in diverse ways based on C2-C4 hydrocarbon feedstocks. The acetone cyanohydrin (ACH) route which is based on acetone and hydrocyanic acid is the most dominant one. Ethylene based routes have a potential advantage since it impart supply security of basic raw material and alleviate the environmental hazards associated with the ACH process. Carbonylation reactions to produce acids, esters, aldehydes are dominated by examples of homogenous catalysis based on Pd, Rh, and Co often with iodides as co-catalysts. There are very few examples of efficient vapor-phase heterogeneous catalysts for carbonylation reactions apart from the many attempts to anchor homogeneous catalysts on a support which results in few turnovers before loss of activity or selectivity. Vapor-phase syngas (CO+H_2) reactions on solid catalyst such as Fischer-Tropsch reactions and higher alcohol synthesis are well known however these transition metal catalysts all break the CO bond and eliminate the oxygen in H_2O and CO_2. The challenge for carbonylation reactions is that they require CO activation for insertion reactions without CO bond breaking. The present work describes very active and highly selective (98%) sulfide catalysts for ethylene methoxy-carbonylation to form methyl propionate a key intermediate for MMA synthesis and characterization of the unprecedented active site for selective vapor-phase carbonylation reactions.

Biography

Dr. Beata Kilos is a Senior Research Scientist and Technical Leader in Chemical Science, Core R&D at Dow. Beata began her career at Dow as a Senior Research Chemist in Core R&D in 2008 in Midland, MI. Over the course of her career Beata has defined, led, and contributed to R&D projects spanning multiple Dow businesses including Industrial Solutions, Consumer Solutions, Construction Chemicals, Coating Materials, Hydrocarbons, Polyurethanes. Beata's technical contributions and leadership have enabled the advancement of numerous R&D projects and technologies throughout her career at Dow. Beata's past R&D work at Dow has included contributions toward the commercialization of UNIFINITY™ fluidized catalytic dehydrogenation process technology for on-purpose propylene, which has been recognized with an ICIS Best Process Innovation Award and an R&D 100 Award. In recognition of her scientific achievements, Beata was named a 2017 ACS Rising Star award recipient and 2018 ACS Early Career Fellow of the Industrial & Engineering Chemistry Division. She is also a recipient of a 2017 Dow Chemical Engaged for Impact Award, 2017 WIN champion award and 2019 ACS WCC Encouraging Women in the Chemical Sciences Award.

Prior to joining Dow, Beata graduated from Adam Mickiewicz University in Poznan, Poland with a M.Sc. and Ph.D. in Chemistry. As one of a handful of scholars selected from across Europe's for the prestigious Marie Curie Fellowship, Beata completed work toward her Ph.D. at the Institut de Recherches sur la Catalyse et l'Environnement de Lyon in Villeurbanne, France. Beata followed this with a joint appointment at the University of California, Berkeley's Chemical Engineering Department, and the Lawrence Berkeley National Laboratory. Beata has 27 patents/patent applications, and over 80 external publications and presentations. Beata serves as treasurer of the North American Catalysis Society, sits on the advisory boards of the Reaction Chemistry & Engineering journal and the Journal of Catalysis, and is the first industrial topic editor for the ACS Catalysis journal.

Novel Materials and Chemistries for Carbon-Neutral Energy

Abdoulaye Djire
Department of Chemical Engineering,
Department of Materials Science and Engineering (Affiliated), Texas A&M University

The large-scale shift towards renewable energy technology requires the ability to reliably convert and store electrochemical energy. This technology is still limited in terms of performance, cost, and/or ease of utilization. In recent years, two-dimensional (2D) materials have been explored as low-cost, high-performing catalysts and electrodes for the reliable conversion and storage of electrochemical energy. Of these 2D materials, a special class of carbides and nitrides, known as MXenes, have gained popularity due to their high tunability, conductivity, and high surface area-to-volume ratio. From these MXenes, the carbide form has been the most vastly studied, but the nitride MXene has been theorized to perform better due to their higher electronic conductivity. In this presentation, I will present on the oxygen-assisted molten salt fluoride etching synthesis technique developed in my lab to produce phase-pure nitride MXenes. Along with this, I will provide evidence of the enhanced capabilities of the nitride MXenes compared to carbides, sulfides, and oxides, when applied in the nitrogen reduction reaction (NRR), hydrogen evolution reaction (HER), carbon dioxide reduction reaction (CO_2RR), and supercapacitor applications. In each of these fields, the enhanced performance is investigated using in-situ/operando spectroelectrochemical techniques. I will wrap up by discussing the future directions in the field of MXenes that require further attention for the advancement of 2D materials in electrochemical energy storage and conversion systems.

Biography

Dr. Abdoulaye Djire is an Assistant Professor in the Department of Chemical Engineering with an affiliated appointment in the Department of Materials Science and Engineering at Texas A&M University. Before joining Texas A&M, Dr. Djire was a Postdoctoral Researcher in the Chemistry and Nanoscience Center at the National Renewable Energy Laboratory (NREL). He received his Ph.D. in Chemical Engineering from the University of Michigan under Prof. Levi Thompson. Dr. Djire's group seeks to better understand how 2D materials catalyze the reactions of earth abundant feedstocks to value-added chemicals and fuels using renewable electricity. Dr. Djire has received numerous awards and recognitions including the 2019 DuPont GOLD Award, and the 2022 National Academies of Sciences, Engineering, and Medicine Frontier Award.

POSTER ABSTRACTS

1. Machine Learned Corrections to Transient Micro-Kinetic Models

Kenneth Kusima, Lars C. Grabow
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Transient mean-field micro-kinetic (MF-MK) modeling is a powerful approach to study, simulate, and forecast the reaction kinetics of heterogeneously catalyzed reactions. Using elementary steps to represent molecular-level interactions among chemical species allows for the exploration of the reaction mechanism to provide detailed kinetic information that aids in the interpretation of experimental findings. Typical MK models rely on the mean field approximation that disregards lateral interactions between surface adsorbates. In many cases, such interactions have significant effects on overall reaction kinetics [1].

Kinetic Monte Carlo (kMC) simulations produce coverage and reaction rate information that accounts for lateral surface adsorbate interactions. Nevertheless, kMC simulations are computationally expensive and require meticulous setup for accurate results.

Using machine learning (ML), we have been able to develop an improved MK model that uses a machine learned correction factor to obtain kMC-like results from the MF-MK model simulations at different coverages. The resulting ML-MK model appears to match closely with transient kMC simulation results. Consequently, our enhanced ML-MK model can predict the effects of surface adsorbate interactions that cannot be captured in a MF-MK model, while also maintaining an easy setup and minimal computational effort.

References:

(1) Tian, H. and Rangarajan, S. (2021) “Machine-learned corrections to mean-field microkinetic models at the Fast Diffusion Limit,” *The Journal of Physical Chemistry C*, 125(37), pp. 20275–20285. Available at: https://doi.org/10.1021/acs.jpcc.1c04495.

2. Non-Catalytic Direct Partial Oxidation of Methane to Methanol in a Microreactor

Kelly Cohen*, Justin Blancard Jr, James A. Dorman and Kerry M. Dooley,
Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA
*KCohen7@LSU.edu

This project uses an integrated mixer-reactor-heat exchanger microtube scalable module for the non-catalytic direct partial oxidation of methane in natural gas (NG) to methanol at elevated pressures (70-95 bar), reaction temperatures of 380-460°C, reactant CH_4:air ratios of 1.5-2.9 and reaction zone residence times on the order of 1 min.

While this project is not officially a catalytic one, the argument could be made that the microtubes that enable the high conversions of methane without the use of the use of more traditional catalyst are catalytic in nature. I acknowledge this lack of traditional catalyst, but most of the phenomena studied are similar to what would be found in a more traditional catalysis project.

Currently, methane in remote locations is often flared in large quantities rather than transported or converted to the more easily transportable methanol. However, if this gaseous methane were converted to liquid methanol at the wellhead, it could be transported in ways other than pipeline, or used onsite. For example, methanol is added to pipeline gas at remote locations to prevent hydrate formation in pipelines, and is a component used in water purification packages.

The microtube reactor/heat exchanger system for this process consists of a methane/air mixing, preheating and reaction section and a quenching section. In the quenching section, the heat transfer is from tubes to shell. The shell-side flow rate is controlled to attain the desired reaction and final (~250°C) process fluid temperatures. The entire reactor, tubes and shell, are made of Inonel 625 alloy. Alloy I625 is a high Ni-Cr steel (60 wt% Ni, 22 wt% Cr). To passivate the metal and reduce rates of total oxidation, the tubes are carbide-coated in a process based on the decomposition of propane at ~700°C. Several other coating schemes were tested along with several other potential tube metals (e.g., sulfiding instead of carbiding, and also metals C1010 mild steel, 304L, 904L, Nichrome and pure Ni) in coating experiments using coupons. The reasons for the choice of I625 and the carbiding process will be discussed.

For the current microreactor system, methane conversions of 12.5% have been achieved with a methanol selectivity of 80% at 417°C, 80 bar, 0.82 min space time and a CH_4:air molar ratio of 2.9. However, at 0.50 min and molar ratio 1.5 the methanol selectivity is only 16% (CH_4 conversion 14.5%, 417°C, 83 bar). So while methanol can be made selectively in the microtube reactor system, its selectivity can vary over a wide range depending upon certain reaction conditions.

3. Dynamically Excited Catalysts with Superior Oxidation Activity

<u>Surya Pratap S. Solanki</u>[1,2], *William S. Epling*[3], *Lars C. Grabow*[*1,2]
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Heterogeneous catalytic cycles involve the adsorption of reactants, followed by one or more activated surface reactions steps before products desorb. The presence of adsorbed reaction intermediates often results in a strong dependence of reaction rates on surface coverages. Furthermore, species with very high binding affinity may become overly abundant and poison the surface. Common examples of coverage sensitive performance are methane and carbon monoxide oxidation on platinum-based catalysts. Excess oxygen inhibits C-H activation and decreases the rate of CH_4 conversion, and CO binds so strongly that it is self-inhibiting during its oxidation to CO_2. To overcome this issue, we are investigating the behavior of catalysts under dynamic conditions which can result in surface coverages that differ from those encountered at steady-state. One approach is the use of modulated feed conditions to unlock surface coverage regimes that are inaccessible under steady-state operation, which has been shown to reduce the light-off temperature for methane oxidation by as much as 100°C. We are also developing the concept of a "Catalytic Condenser", a device that can manipulate the charge on a catalytic surface and alter adsorption energies or activation barriers at time scales commensurate with the frequency of a catalytic turnover.

Externally Applied Potential: The catalytic condenser is inspired by a transistor and concentrates charges on surface sites to affect the catalytic properties. Thus, through strategic periodic variation of the surface charge, a catalyst can be tuned towards the desired performance in terms of selectivity, yield, turnover frequencies, and more. We used DFT calculations to understand the changes in catalytic properties with surface charge modulation. Our results show that oxidizing the platinum surface results in stronger adsorption of CO, whereas the presence of excess electrons lowers the binding energy. Calculations predicted that accumulated charge of +/-0.10 e^-/surface-Pt-atom altered the binding energy by ~0.25 eV, TPD experiments also showed a change in ^{13}CO binding energy by 0.2 eV over the mentioned surface charge variation.

Methane Partial Oxidation: Given the abundance of methane the main component of natural gas, there is a growing interest in the scientific community to utilize methane in an efficient way rather than just burning it. Even though C-H activation is feasible on precious group metals, the selective conversion of methane to valuable products remains a 'Holy Grail' for chemical engineers. Dynamic catalytic operation can help in efficient conversion and has already gained attraction for a variety of reaction chemistries. Our results show that oscillatory feed conditions containing different amounts of oxygen result in increased hydrogen production compared to the equivalent steady-state measurements on Pt/Al_2O_3. We are also utilizing DFT calculations to understand the role of metal support interaction during feed modulation.

4. Choreographing Zeolite Crystallization: It is all Elementary

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Zeolites are composed of negatively-charged aluminosilicate frameworks balanced by counterions typically introduced as structure-directing agents. The crystallization of zeolites is governed by complex physicochemical interactions over a broad range of length scales. During hydrothermal treatment, anionic aluminosilicate oligomers interact with cations that can either be organic (e.g., tetraethylammonium) or inorganic (e.g., Na^+) species. Organic structure-directing agents (OSDAs) are generally governed by heuristics used to predict how molecular structures will influence resultant zeolite properties. Owing to the hazardous and/or costly nature of most OSDAs, it is preferable to instead use inorganic structure-directing agents (ISDAs) to generate zeolites; however, when using the latter, it is more challenging to predict how cation(s) selection will alter synthesis progress. Selection of elements as heteroatoms, which can be incorporated into the zeolite framework, is an additional topic of interest. During zeolite synthesis, charged heteroatom complexes interact in solution with (alumino)silicate species and can potentially accelerate, interrupt, or otherwise alter crystallization. Collectively, by understanding the effects of diverse elements forming cationic or anionic species in zeolite growth solutions, the rational design of zeolite crystals becomes a more attainable goal.

In this poster, we highlight various strategies for introducing additives or controlling composition to tune zeolite crystallization towards desirable outcomes. Examples include the promotion of certain zeolite frameworks using mixtures of inorganic cations, including some unconventional species (e.g., Li^+ and Ca^{2+}), wherein the judicious selection of composition can lead to dramatically reduced synthesis temperatures. Conversely, addition of zinc to zeolite growth mixtures is beneficial owing to its ability to suppress the formation of undesired impurity phases. We also observe that zeolites synthesized in the presence of germanium have smaller crystal dimensions, which demonstrate enhanced performance and greater longevity as catalysts with reduced diffusion limitations. Overall, elucidating the role of individual species present in zeolite growth mixtures assists in developing a more holistic picture of zeolite crystallization mechanisms. Our research provides several influential insights into the critical phenomena that should be considered for future advancements in zeolite engineering and design.

5. Zeolite Supported Pt for Depolymerization of Low-Density Polyethylene by Induction Heating

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The development of plastics over the past half century has led to rapid technological advances. Nonetheless, long-term negative environmental impacts of these materials compel new upcycling strategies. Worldwide production of polymers in 2015 reached 380 MMT. Despite the substantial amounts of polymers potentially available for reutilization, it has been estimated that of all synthetic polymers produced since 1950, only 7% have been recycled, compared to 60% which have been discarded (lifetimes > 20 yr). Currently, reconstituting these polymers into chemical products often requires high-temperature pyrolysis yielding unattractive product distributions. This work aims to address this issue by converting plastic waste into useful alkanes/alkenes oligomers, using rationally designed heterogeneous catalysts suitable for use in radio frequency (RF)-based induction heating.

Pt(0), either alone or in alloy form, is widely used for hydrocracking catalysis due to its high dehydrogenation activity leading to high rates of carbon-carbon cleavage of adsorbed alkene moieties. Four types of zeolites, decorated with Pt, were chosen to elucidate the role of crystal size, pore structure and acidity (as quantified, e.g., as Si/Al molar ratio). Zeolite-supported Pt catalysts mixed with Fe_3O_4 were inductively heated under inert atmospheres (no H_2) to depolymerize low density polyethylene. The depolymerization showed high concentrations of alkene/alkane hydrocarbons with a narrow product distribution that could be tuned between light gases to C14 hydrocarbons based on the zeolite structure. The addition of Sn as a promoter was found to increase activity with a preference for heavier products, and to reduce the coke formation. LDPE conversions up to 95% with minimal coke and light gas formation were obtained with Pt/LTL or SSZ-13 at 375°C estimated surface temperature and 2 h reaction time. Reaction kinetics show that the depolymerization process is diffusion limited across moderate temperature ranges (~280-500 C).

6. Expanding Surface Activity Limitations of MWW Zeolite Nanosheets via Boron Incorporation

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The design and development of 2D zeolites offers unique opportunities to tailor the formation of external surface materials that have demonstrated enhanced mass transport for improved catalyst lifetime and selectivity.[1–3] Typically, to achieve ultrathin 2D nanosheets, the use of harsh and complex post-synthesis methods (e.g., high pH, ultrasonic treatment, and silica dissolution) are needed to facilitate the exfoliation.[4,5] Recent studies have shown that the surfactant cetyltrimethylammonium (CTA) can be employed in a one-pot synthesis as a dual OSDA and exfoliating agent to generate 2D MWW-type layers with an average thickness of 3.5 nm (approximately 1.5-unit cells).[6] This approach eliminates the requirement for post-synthesis exfoliation. While this discovery represents a significant advancement, it is strictly limited to a silicon-aluminum ratio (SAR) of <15. In this presentation, we report the incorporation of boron during hydrothermal synthesis to enable SAR >15 MWW nanosheets. We show that by substitution aluminum with boron in the framework and keeping the silicon-heteroatom ratio (SHR) <15, the SAR of MWW nanosheets can be expanded up to 50 while maintaining high surface areas. Furthermore, we show that structural modification (i.e., chain length) of the surfactant used can have significant effects on the extent of exfoliation. Using various characterization techniques, we analyze the crystal structure and morphology of high SAR Al-B-MWW nanosheets relative to conventional low SAR Al-MWW nanosheets. Combined X-ray diffraction (XRD) and BET results confirm the formation of high surface area nanosheets with a high degree of layer disorder. Overall, this study presents a facile, efficient synthesis strategy to enable up to SAR 50 MWW nanosheets via the incorporation of boron for the design of robust zeolite catalysts.

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7. Effect of Proximity on Hydrocarbon Selectivity in the Tandem Hydrogenation of CO_2 Utilizing Zeolite-tailored Bifunctional Catalyst

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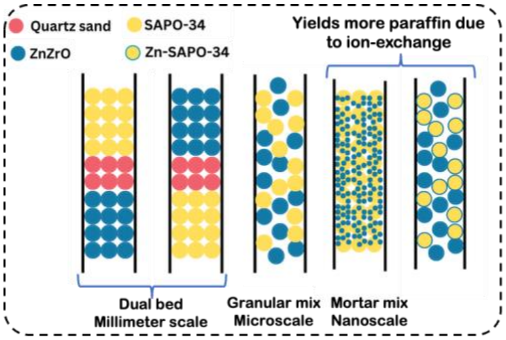
The direct conversion of CO_2 to C_{2+} hydrocarbons through tandem catalysis presents a promising solution for mitigating CO_2 emissions while producing value-added hydrocarbons and fuels. Recent studies corroborate that ZnZrO in tandem with zeolite converts CO_2 to C_{2+} hydrocarbons through CH_3OH intermediate.[1-4] However, the low conversion and selectivity to C_{2+} hydrocarbons demand a further understanding of the catalytic process to allow improvements in catalyst design. Herein, the effect of the proximity of ZnZrO and zeolites (HZSM-5 and SAPO-34) to catalyst activity is investigated. We control the proximity of interaction between the ZnZrO and zeolite by different integration manners, e.g., dual-bed arrangement (millimeter scale spacing), granular mix (microscale), and mortar mix (nanoscale). The ZnZrO/HZSM-5 system shows the highest selectivity for C_{5+} hydrocarbons (~40%) for granular mix while mortar mix exhibits the highest selectivity of short-chain paraffins (C_2-C_4) (~50%) at 400 °C. In the case of ZnZrO/SAPO-34, granular mix shows the highest selectivity for olefins ($C_2^{=}$-$C_4^{=}$) (~30%) while mortar mix exhibits the highest selectivity of short-chain paraffins (~80%). With microscale proximity, the chain length of end products is mostly affected by the pore size of zeolites. Interestingly, nanoscale proximity exhibits over-hydrogenation resulting in short-chain saturated hydrocarbons. Hence, we hypothesize that Zn sites could get ion-exchanged with protons of zeolite under reaction conditions. We investigate the ion-exchange effect of Zn^{2+} by using granular mix of ZnZrO and Zn-ion-exchanged zeolite (Zn-ZSM-5 and Zn-SAPO-34) that results in high paraffin selectivity, similar to mortar mix. We hypothesize that the ion exchange of Zn with HZSM-5 forms Lewis acid sites that increase zeolite acidity and causes the over-hydrogenation of olefins.[5] To conclude, proximity affects the hydrocarbon selectivity during CO_2 hydrogenation and migration of Zn^{2+} ions occurs at nanoscale proximity resulting in over-hydrogenation of products.



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8. Reactivity Investigation and Mechanistic Insights for the Hydrogenolysis of Polyethylene over Silica- Supported Earth-abundant Cobalt Catalysts

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Chemical repurposing of plastics, especially polyolefins, has emerged as a promising route to valorize the "end-of-use" plastic waste and mitigate its environmental release.[1] Hydrogenolysis with rare-earth metal catalysts, particularly Ru, has been shown to depolymerize polyethylene (PE) waste effectively.[2-4] However, the selectivity towards valuable liquid-range products remains a challenge.[5] Here, we show the ability of silica-supported, earth-abundant cobalt (5 wt % Co/SiO2) catalysts to produce liquid-range products (C5-C30) with high selectivity, having tested from 200-300°C, 20-40 bar H2, and 2-36 h. At an optimized reaction condition of 275°C, 30 bar H2, and 8 h reaction time, 55% yield towards liquid products on a carbon-mole basis was achieved, which comprised 75% of non-solid products, with gas yields limited to ~19%. By tracking the evolution of products over time, we infer a multi-pathway mechanism, including a dominant, non-terminal cleavage mechanism over the Co catalyst on the polymer chain, which drives the high liquid product selectivity. We demonstrate the viability of the catalyst in deconstructing various post-consumer polyethylene samples (HDPE jug, LDPE bag, and LDPE bottle) along with excellent recyclability and regenerability. The catalyst remained active over 4 reactions, but the selectivity of reaction products shifted heavily towards liquids after the first reaction. After regenerating the catalyst in air at 450°C, selectivity shifted back towards high gas yields. Post-reaction powder X-ray diffraction (PXRD) of the catalysts revealed that the cobalt phase shifted from the fully oxidized Co3O4 to CoO under reaction conditions but that the shift in selectivity is likely due to carbon deposition. N2 physisorption and thermogravimetric analysis coupled with mass spectroscopy (TGA-MS) confirmed the presence of a recalcitrant polymer substrate on the catalyst surface that likely causes catalyst deactivation, which is removed by calcination, thus restoring the activity. These results and insights move the field toward more sustainable and economically viable catalysts for the chemical upcycling of waste plastics.

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9. Shallow-Bed Reactor Design and Analysis for the Autothermal Oxidative Dehydrogenation of Ethane over MoVTeNbOx catalysts

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The oxidative dehydrogenation of ethane (ODHE) has gained increasing attention as an alternative method for producing ethylene from ethane. Despite various reactor designs that have been proposed in the literature for implementing ODHE, the impact of external and internal transport effects using large catalyst particles at an industrial scale have not been discussed thus far. Due to the high adiabatic temperature rise values associated with this system, ignition can occur at the particle level for larger catalyst particles (≥1 mm size) rather than merely at the bed level in the pseudo-homogeneous limit. In this work, we use a cell model with finite-size eggshell type catalyst particles to present a comprehensive ignition-extinction analysis of the oxidative dehydrogenation of ethane (ODHE) in an adiabatic shallow-bed reactor.

Our results reveal that external mass transfer can increase the ratio of ethane to oxygen on the catalyst surface, thereby improving ethylene selectivity but decreasing ethane conversion (at a fixed space time). We show that diffusion limitations in the catalyst reduce ethylene selectivity and shrink the region of multiplicity, highlighting the need for eggshell particles containing a thin active layer. We also examine the impact of ethane to oxygen ratio, feed dilution, space time, catalyst particle size, operating pressure, and active layer thickness on ignition and extinction behavior. A multi-layered bed with eggshell catalyst particles is proposed for near complete conversion of oxygen, enhanced ethane conversion and ethylene selectivity. Our results indicate the possibility of autothermal operation of the ODHE process with 20%+ per pass conversion of ethane (without dilution) and 90%+ selectivity to ethylene.

10. Recommended Best Practices for Gas Sorption Analyses

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Gas sorption analyses is an important technique for the characterization of porous solids and fine powders, and involves both adsorption and absorption. The gas used is referred to as the adsorbate, while the sample surface is the adsorbent. Adsorption can be physical or chemical (forming chemical bonds between the surface and the gas). In physisorption, the most common adsorbate gases used are nitrogen (N_2), argon (Ar), krypton (Kr) or carbon dioxide (CO_2). In chemisorption, the most common gases used are hydrogen (H_2), oxygen (O_2), ammonia (NH_3) or carbon monoxide (CO). However, with increased demands in today's ever-changing industrial landscape, where crucial decisions are based on experimental data, extra care is needed to achieve reproducible, relevant results.

In order to remind gas sorption technique users in today’s modern laboratories, best practices for gas sorption analyses are reviewed and summarized in a poster format. This which will not only help prevent operator errors and provide reproducible data, but also facilitate efficient evaluation of sample data with the right questions to be asked and discussed.

11. Improved Selectivity and Stability in Methane Dry Reforming by Atomic Layer Deposition onto Ni-CeO_2-ZrO_2/Al_2O_3 Catalysts

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The dry reforming of methane (DRM) is a potential route to convert greenhouse gases (CO2 and CH4) to syngas (H2 and CO) as building blocks for petrochemicals. Supported Ni catalysts are commonly employed to take advantage of the chemical activity and earth abundance. Still, most supported Ni catalysts, especially those using the rare-earth oxides, will eventually deactivate either due to coking at lower temperatures (<700°C) or sintering at higher ones. Such deactivation becomes more of a problem at total pressures higher than atmospheric, by multiple mechanisms. At the same time, the reducible nature of the CeOx or other rare earth oxide facilitates the reverse water gas shift reaction, lowering the H2:CO ratio. In this project, we are using hierarchical catalysts to try to limit deactivation mechanisms and inhibit the RWGS reaction by coupling reducible (CeOx) supports and more non-reducible (Al2O3, MgO, SiO2) thin overlayers.

For example, we have used a commercial Ce0.5Zr0.5O2 support (PIDC CZA-40) with 7 mol% Ni deposited on the surface. Next, atomic layer deposition (ALD) was used to deposit thin (<2 nm) porous layers of Al2O3 over the CZA-40 catalyst. The coating greatly improved the stability of the sample, with high activities present after over 100 h, whereas the uncoated catalyst quickly coked over 12 h. The hierarchical catalyst activity was dependent on the thickness of the films, with optimum performance achieved at between 5-7 layers, i.e., 70-80% methane conversion over 80 h. HRTEM and TPO analyses of the uncoated and coated samples indicated similar amounts of coking. However, Ni aggregation and filamentous coke were severely inhibited by the thin shell layers. Interestingly, the thin layers were also able to completely inhibit the RWGS reaction for some time before eventually H2:CO ratios above 1 and high coking rates were observed. Additionally, we will also discuss the significant induction period often observed with these catalysts.

12. Kinetic Studies of CO Oxidation over Highly Active, MOF-derived Cr_2O_3 nanoparticles

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Metal oxide nanoparticles derived from the controlled degradation of Metal-Organic Frameworks (MOFs) have gained extensive attention due to their porous structure, high surface area, as well as accessible, well-dispersed active sites compared to their bulk counterpart (1), thereby offering a unique opportunity for developing structure-property relationships for heterogeneous catalyzed reaction. A series of novel, porous chromium-materials were prepared through one-step calcination process using MIL-100(Cr) as metal precursor, and the effect of calcination temperature on pore structure, crystallinity, surface composition, metal oxidation states as well as surface oxygen mobility were systematically characterized through various in-situ and ex-situ techniques. Experimental results has shown Cr_2O_3 nanoparticles can be synthesized through calcining MIL-100(Cr) at 500 °C, and its exceptional high catalytic activity towards CO oxidation with 100 % CO conversion at 300 °C compared to bulk Cr_2O_3 is explained by its large surface area, improved adsorbed oxygen species capacity and increased surface reducibility. An Eley- Rideal reaction mechanism was also proposed for reactions measured between 240 and 280 °C.

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13. In Situ Characterization of Zeolite Surface Growth using Atomic Force Microscopy

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Zeolites are crystalline aluminosilicates with a network of pores that are useful for a broad number of commercial applications. In the area of catalysis, a constantly evolve energy landscape coupled with the changing of demands of different feedstocks requires more fundamental understandings of zeolite crystallization mechanisms as a means of developing more predictive protocols to tailor their physicochemical properties. One of the most widely-used commercial zeolites is faujasite (FAU), with applications spanning from ion exchange in detergents to catalysts in the (petro)chemical industry. The conventional sol gel media used to prepare zeolites such as FAU often leads to heterogeneous mixtures comprising both solution and solid states. These complex media contain diverse solute species, which evolve over the course of crystallization, making zeolite nucleation and growth pathways nontrivial to characterize. Despite tremendous efforts to understand the growth mechanism(s) of zeolite FAU, the pathways leading to its formation are generally not well understood. This is complicated by the fact that the harsh conditions of zeolite synthesis often make it difficult to perform *in situ* observations.

Here, we will discuss how we have been using high temperature atomic force microscopy (AFM) to characterize the growth of several zeolites, including silicalite-1 (MFI), zeolite A (LTA), and most recently faujasite (FAU). Our findings reveal diverse mechanisms involving both classical and nonclassical pathways. The latter include crystallization by particle attachment (CPA), either through amorphous precursors or via oriented attachment of nanocrystals. For the case of zeolite A, we observed that supernatant solutions with varying supersaturation could be used to switch growth from nonclassical pathways to classical growth involving 2-dimensional layer generation and spreading. Recently, we reported the use of AFM to monitor FAU surface growth *in situ* wherein we confirmed a pathway that markedly deviates from that of zeolite A, which is formed under similar conditions. Here, we will discuss how *in situ* AFM in combination with other state-of-the-art characterization techniques have been used in our group to provide a deeper understanding of zeolite surface growth under different crystallization environments; and how these conditions can be tailored to alter the physicochemical properties of the final zeolite materials.

14. Kinetic Requirements for Non-Steady State Selectivity Enhancement of Ethane Oxidative Dehydrogenation

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Ethylene is a valuable commodity chemical traditionally produced through catalytic steam cracking of larger hydrocarbons. However, the endothermicity of catalytic steam cracking results in high energy demands to achieve desirable ethylene yields. Selective catalytic oxidative dehydrogenation (ODH) of ethane to ethylene has proven to be an attractive alternative due to its exothermicity and light alkane feedstock. It is speculated that CO_x is produced via reactions between gaseous ethane and oxygen, hence decreasing ethylene yields during ODH. It is proposed that higher ethylene yields are achievable by promoting reactions between ethane and selective oxygen stored within metal oxide catalysts as opposed to unselective gaseous oxygen. We demonstrate this, by comparing conventional steady state to concentration forcing (dynamic) operation of ethane ODH. Fig. 1a and b plots carbon selectivities versus ethane conversion over 3wt% VO_x and 7wt% MoO_3 Al_2O_3 catalysts respectively during dynamic and steady state operation. Fig.1a shows no significant difference between dynamic and steady state carbon selectivies over the 3wt% VO_x Al_2O_3 catalyst. However, fig. 1b demonstrates higher ethylene selectivities during dynamic operation over a 7wt% MoO_3 Al_2O_3 catalyst compared to steady state operation. We explain the differences during dynamic performances of supported VO_x and MoO_3 catalysts based the O_2 dependencies of unselective overoxidation reactions. More specifically, improvement via concentration forcing over MoO_3 catalysts were rationalized based on higher O_2 sensitivities of unselective overoxidation reactions compared to the selective ODH reaction. All reaction rates over the VO_x catalyst are independent of oxygen pressure, unlike the MoO_x catalyst over which selective and unselective rates are zero and positive fractional order in O_2, respectively. Our work presents a method for understanding dynamic enhancement during ethane ODH from the standpoint of apparent O_2 reaction orders of different steps in the overall reaction network, and could be used to provide kinetic criteria for improving selective catalytic oxidation processes through non-steady state operation.

15. Controlling Intrinsic Defects in Hierarchical Zeolite ZSM-5 Catalysts and their Impact on Methanol to Hydrocarbons

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ZSM-5 is a commonly used zeolite for catalytic applications such as methanol-to-hydrocarbons (MTH) and fluid catalytic cracking (FCC); however, the synthesis of ZSM-5 is prone to the generation of defects, which are attributed in part to non-framework Al species. Minimizing framework defects has been a study of interest since these defects are shown to be correlated to the onset of deactivation in various catalytic applications. One of the strategies employed by researchers to obtain defect-free crystals is synthesis in the presence of fluoride ions (using HF or NH_4F). Mild acid treatment using hydrochloric or oxalic acid has also been shown to reduce internal defects on ZSM-5 crystals.

Here, we show that defects are more prevalent in hierarchical ZSM-5 materials than previously reported. We present an alternate approach to reduce defects, referred to as annealing, wherein crystals are subjected to high-temperature thermal treatment in a saturated siliceous solution. The impact of annealing on catalyst performance is highly dependent on the Si/Al ratio and the nature of defects in ZSM-5 samples. The timescale of annealing is also a critical factor. For example, the protocol was used in the preparation of ZSM-5@silicalite-1 core-shell structures to obtain more crystalline shells; and the procedure was implemented in core-shell zeolite beta (*BEA) synthesis to introduce mesoporosity. In this presentation, we will discuss how annealing impacts the performance of several hierarchical ZSM-5 materials, including nanosheet, self-pillared, core-shell, and finned crystals.

16. Enhancing diffusion and catalytic performance on low-dimensional materials

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Reducing mass transfer limitations is critical to improving the catalytic activity and stability of zeolites in commercial applications such as hydrocarbon cracking and methanol-to-hydrocarbons (MTH) reactions. The pore structure of zeolites give rise to its well-defined shape-selectivity, which can result in highly selective products but they might not have long catalyst lifetime: for example one-dimensional zeolites such as MTT are highly selective to propylene in naptha-cracking, but they deactivate faster due to limited diffusion leading to extensive coking and pore mouth blockage. Such limitations can be overcome via simple post-treatment methods, such as growing rough protrusions on the external surface via secondary growth. This technique has been demonstrated so far for 3D (MFI) and 2D (FER) zeolites: both catalysts show faster diffusion (high D/R^2) and longer catalyst lifetime. Here we report our approach to designing one-dimensional material by growing “fins” on the external surface. Preliminary studies show better turnovers for finned MTT relative to conventional MTT materials.

Another secondary treatment being explored in our work is called annealing: where the zeolite crystals are subjected to high-temperature thermal treatment in a saturated siliceous solution. We have demonstrated this procedure so far with ZSM-5 crystals: nanosheet, self-pillared, core-shell, and finned crystals. In each case, an “optimum” exists in annealing time: too long annealing might result in detrimental performance (for e.g.: increase in extra-framework Al). But with optimum annealing, the catalyst show slower deactivation rates than their non-annealed counterparts.

17. Elucidating the Mechanism of Nanosheet Pillaring in MFI-type Zeolites

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Nanoporous aluminosilicates (zeolites) are used commercially as catalysts and sorbents for ion exchange and separation applications. Their tunable physicochemical properties make zeolites desirable catalysts for various chemical reactions; however, it is challenging to synthesize zeolite crystals with sizes smaller than 100 nm where the deleterious effects of mass transport limitations in confined pores can be limited, thereby improving the overall performance of zeolite catalysts for diverse applications. One strategy to address mass transport problems is the synthesis of hierarchical zeolites via the introduction of larger pore networks (e.g., mesopores and/or macropores). Here, we will discuss how such materials can be made through the generation of self-pillared pentasil (SPP) zeolites, which are comprised of intergrown nanosheets of five-membered ring zeolites (MFI and MEL types). The synthesis of these materials is accomplished using a seed-assisted technique that does not require costly organic structure-directing agents [1].

We will discuss diverse ways to tailor synthesis parameters to optimize the physicochemical properties of SPP zeolites. Parametric studies reveal the importance of zeolite synthesis composition, reagent selection, and the choice of the seed crystal structure. Our findings indicate that pillared nanosheets form within a relatively limited compositional space near the intersection of three zeolite phases: MFI, MEL, and MOR. Changes in growth conditions can markedly impact the degree of nanosheet pillaring and branching, as well as the kinetics of zeolite crystallization. Structural evolution from amorphous precursors to crystalline SPP products was tracked using state-of-the-art techniques, such as pair distribution function and solid-state NMR analyses. Collectively, these studies have improved our fundamental understanding of hierarchical zeolite crystallization, which is a rapidly growing area of research owing to the potential of these materials to replace conventional zeolites in numerous industrial applications.

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18. Incorporation of Ga in Zeolite Beta for Renewable Para-Xylene Production

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Para-xylene is an important precursor for the manufacture of polyethylene terephthalate (PET) among other commodity chemicals. Conventionally, p-xylene is produced from steam cracking of naphtha, which involves high energy consumption and results in relatively low aromatics selectivity. These drawbacks and the need for sustainable production of commodity chemicals have motivated research to develop alternative routes to produce p-xylene from biomass-derived feedstocks. One promising route is the Diels–Alder dehydration reaction, which includes the cycloaddition of biomass-derived dimethylfuran (DMF) with ethylene, and subsequent dehydration of the formed Diels–Alder adduct to p-xylene.[1] For this reaction, studies have shown that metal-substituted zeolite beta (*BEA) is an exception catalyst; thus, this framework was chosen as a parent catalyst for Ga incorporation.[2-3] By changing the Al/Ga ratio, the Lewis acid (LA) and BrØnsted acid (BA) densities can be controlled. Our findings reveal that Ga-*BEA with a specific range of Al/Ga ratio exhibits high DMF conversion and an increase in p-xylene selectivity from 40% with H-*BEA to 70% for the Ga-substituted analogue. This 30% higher yield of p-xylene compared to conventional zeolite outperforms other metal-substituted zeolites in literature using a more facile synthesis procedure. These results suggest that tuning the acidic property by optimizing the amount of heteroatom in the zeolite framework to tailor LA and BA densities is beneficial to maximize selectivity and yield of p-xylene using the Diels–Alder reaction of dimethylfuran and ethylene.

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19. Integrated Direct Air Capture and Methanation on Porous Transition Mixed Metal Oxides

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Low-cost direct air capture (DAC) technologies are urgently needed to mitigate CO_2 emissions and avert adverse effects of climate change. CO_2 capture and utilization has gained increased attention from offering alternative pathways of production of value-added chemicals. However, an integrated DAC and conversion process is not widely explored. We show herein that low-cost and highly tunable porous transition metal oxides (PTMOs) can capture CO_2 from simulated air at ambient temperature, with enhanced DAC capacity under humid environment. The CO_2 adsorption capacity of these materials can be tuned through aliovalent doping, with optimal adsorption capacities achieved at intermediate dopant loadings. Moreover, a subsequent methanation process after DAC is achieved under a diluted hydrogen flow at intermediate reaction temperature (200-300 °C). Overall, our findings reveal that PTMOs can serve as a new class of solid DAC sorbents that are significantly less expensive and more tunable. Furthermore, the feasibility to directly convert captured CO_2 from air into methane within a single component bed sets PTMOs apart from existing classes of sorbents.

20. Insights into the Mechanisms of Metal Incorporation in Zeolite Crystallization

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Metal-incorporated zeolites are promising materials due to their enhanced catalytic properties. Optimization of these properties requires unravelling the complex crystallization mechanism(s) of heteroatom incorporation in zeolite structures, which is still relatively elusive owing to the challenges of characterizing zeolite crystallization (including the disorder-to-order transition of amorphous precursors). The majority of zeolite crystallization studies rely on *ex situ* techniques given that *in situ* monitoring of zeolite formation is challenging. Our group has pioneered methods to probe zeolite growth *in situ* using solvothermal atomic force microscopy (AFM) to visualize zeolite surface growth at a near molecular level. We have shown that zeolite crystallization is predominantly a result of nonclassical pathways (e.g. crystallization by particle attachment) as well as classical layer-by-layer pathways involving monomer incorporation.

In this presentation, we report our recent observations of faujasite (FAU) growth mechanisms. FAU is one of the most widely commercialized zeolites with numerous industrial applications. We recently showed that FAU stability and corresponding catalytic performance is enhanced by the incorporation of zinc [1]; however, the mechanism of FAU formation in the presence of Zn remains unclear. Here we will present our study of Zn-FAU crystallization using *in situ* AFM to probe the inhibition effect of metal incorporation. We will also discuss studies of titanium incorporation in zeolite beta (BEA) catalysts. The Lewis acidity of Ti in large pores of zeolite BEA can be exploited for biomass conversion; however, its incorporation in zeolite BEA requires harsh conditions and long synthesis times. To overcome these limitations, we have developed seed-assisted methods to synthesize core-shell BEA catalysts for biomass conversion reactions [2].

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

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There is growing interest in the design of zeolite catalysts with tunable composition using a combination of framework or extra-framework Lewis acids as sole active sites or in tandem with traditional Al Brønsted acid sites. Replacing framework Si and Al by other elements can lead to improvements in zeolite acidity or adsorption capacity, while potentially influencing properties such as crystal size and shape. Several elements like B, Ge, V, Sn, Ti, and Ga, among others, have been introduced into different zeolite frameworks as heteroatoms. Notably, Ti-based zeolites have garnered much interest in recent years due to their acidic properties that are ideal for oxidation reactions, such as olefin epoxidation. One of the most frequently studied zeolitic materials is TS-1 (titanium silicalite-1) where Ti sites are distributed homogeneously throughout the zeolite crystal. TS-1 is an excellent catalyst for hydrogen peroxide olefins epoxidation reactions; however, overcoming the low epoxide selectivity on traditional bulk TS-1 is a major challenge. Here, we discuss alternative design schemes of TS-1 catalysts wherein the distribution of Ti sites is altered to increase access to active sites while minimizing mass transport limitations within zeolite pores. We designed TS-1 crystals with both core-shell (silicalite-1@TS-1) and egg-shell (TS-1@silicalite-1) configurations using secondary growth protocols that were previously established with ZSM-5. Tests of egg-shell samples reveal an improved selectivity of olefins epoxidation compared to traditional bulk TS-1. We also produced a series of finned zeolites where nanosized protrusions of TS-1 (30 - 50 nm in average dimension) were epitaxially grown on the surface of catalytically inactive silicalite-1 seeds. Our findings reveal interesting trends in structure-performance relationships, which we compare against previous work with ZSM-5 showing that fins enhance the internal diffusion of molecules, thereby reducing external coking and extending the lifetime of the catalyst. The egg-shell architecture of TS-1 functions as a pseudo nanosheet with enhanced mass transfer, whereas the reverse core-shell configuration presents a passivated exterior rim that eliminates non-selective reactions at external surface sites.

22. Optimizing One-Dimensional Zeolite Catalysts for Hydrocarbon Upgrading Reactions

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One-dimensional (1D) medium pore zeolites, such as ZSM-22 and ZSM-23, are promising catalysts for naphtha cracking owing to their high olefin (propylene) selectivity. However, diffusion limitations pose significant limitations for their broad commercial use. In this presentation, we report recent findings where we explore alternative synthesis of ZSM-23 that employ techniques such as interzeolite transformation. We have discovered methods to prepare ZSM-23 catalysts with much higher surface area at reduced synthesis temperature. Given that the restricted channels of 1D zeolites accelerate deactivation, thereby decreasing catalyst lifetime, methodologies to synthesize materials with reduced diffusion limitations is crucial for improving their activity and stability in commercial applications. Nanosized zeolites have been explored in this regard, but preparation of such materials requires either complex organics or nontrivial synthesis techniques that have been demonstrated for relatively few zeolite framework types.

In this presentation, we will also report an alternate approach to achieve nanosized zeolites via the growth of small protrusions (or "fins") on the external surfaces of zeolite seeds. Finned zeolites for three-dimensional (3D) zeolite structures, such as ZSM-5 and ZSM-11, has been reported by our group [1]. It was observed that finned zeolites exhibit enhanced mass transport properties relative to conventional materials in the methanol to hydrocarbons (MTH) reaction. Notably, we showed that finned zeolites are superior catalysts with respect to lifetime and total turnovers. Finned ferrierite (2D zeolite) also exhibit enhanced catalyst lifetime and selectivity [2]. Here we show for the first time how the concept of *fins* can be extended to a 1D zeolite framework (ZSM-23) to investigate the changes in diffusion properties and assess improvements in catalytic performance for the MTH reaction.

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23. Design of a novel Ru-based NRR catalyst using a framework integrating DFT and kMC

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Ammonia (NH3) production through nitrogen reduction is a crucial chemical reaction[1] with significant implications for green energy and sustainable fertilizer development[2]. The Haber-Bosch process, currently responsible for large-scale ammonia production, operates at high pressure and temperature due to the inert N2 triple bond, leading to severe environmental challenges. As an alternative, the nitrogen reduction reaction (NRR) under ambient conditions has gained considerable interest; however, challenges related to low ammonia production selectivity and rate persist.

For the above-mentioned reason, we newly designed diverse Ru-based catalysts (i.e., RuTi, RuV_2, Ru_3W, $RuZn_3$, and RuZr) and identified the ideal candidate (RuV_2) surpassing conventional noble Ru. Further, to gain a comprehensive understanding of their NRR performances, we combined Density Functional Theory (DFT) and kinetic Monte Carlo (kMC) approaches to assess diverse catalytic properties, with each method complementing the other. DFT method was utilized to delve deeper into the mechanistic aspects of the catalytic reaction, examining thermodynamic factors such as reaction potentials, activation barriers, and electronic characteristics of catalyst materials. Nonetheless, DFT alone has limitations in explicitly capturing the spatiotemporal evolution of site distributions and concentrations of adsorbates. This is because DFT typically considers only a small portion of the reaction system and not accounting for the influence of the surrounding environment on reaction kinetics. To address these limitations, we integrated the obtained DFT parameters into a high-fidelity surface reaction kMC model. This integrated approach enabled the analysis of surface-level kinetics and realistic environmental factors, providing a thorough evaluation of catalyst materials. Additionally, to explore the effect of surface degradation on activity over long-time scales, we developed a data-driven Long-short-term memory (LSTM) model that allows us to predict surface degradation in reasonable time.

Specifically, we analyzed N_2 selectivity for NRR initial reaction of designed structures and their overpotentials based on the thermodynamic Sabatier analysis. Additionally, based on the kinetic reaction rates available from the kMC simulations, we investigated adsorbent localization, surface coverage, reaction turnover frequency (TOF), and I-V curve as a function of time, temperature, and pressure. Here, our systematic investigations clearly reveal that the newly designed RuV_2 material has superior NRR catalytic activity to other conventional Ru-based catalysts by decreasing H poisoning, overpotential, and increasing TOF, current density.

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24. Subsurface Oxygen Reduction Reaction Activity on Ti_2N MXene Revealed by In-situ Raman Spectroelectrochemistry

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The multistep oxygen reduction reaction (ORR) in the cathodes of fuel cells and metal-air batteries is sluggish and requires a large overpotential.[1] Pt-based catalysts are used to catalyze ORR, but due to their high price, low abundance, and poor durability, recent trends in materials science have shifted towards noble metal-free catalysts.[2] Nitride MXenes, a subclass of two-dimensional (2D) transition metal carbides and nitrides, can lower the ORR overpotential because of their high electronic conductivity and low activation energy barrier for oxygen adsorption.[3-5] However, they are yet to be experimentally studied for this system. In this poster, I will report on the electrocatalytic ORR activity of Ti_2N nitride MXene in alkaline medium. alkaline medium. The Ti_2N MXene is first synthesized via molten salt etching and delaminated using tetramethylammonium hydroxide (TMAOH). XRD spectra shows clear exfoliation of the parent MAX phase with a shift in the (002) peak to lower 2θ angles. SEM images depict accordion-like morphology in the clay and lateral flake sizes of roughly 5 μm. The Ti_2N MXene catalyst undergoes a four-electron ($4e^-$) ORR, has an onset potential of 0.70 V vs. RHE, and exhibits significantly better ORR stability compared to Pt/C with 81.97% current retention over 15 hours of chronoamperometry. We use in-situ Raman spectroelectrochemistry to corroborate our findings and uncover the ORR mechanism in real time. We found the subsurface to be active for ORR and the adsorption of O_2 on the basal plane to be the rate determining step. These results expand the applications of MXenes in electrocatalysis, which will accelerate the discovery of cost-effective and efficient catalysts for green energy technologies.

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25. Theoretical methods for assessing the feasibility of PFOA oxidation on photo-catalyst surfaces

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Removing the pervasive, persistent and harmful water contaminant, perfluorooctanoic acid (PFOA) efficiently is a concerning topic in water treatment. Working with collaborators, we found that hexagonal boron nitride (hBN) is an excellent photocatalyst for PFOA degradation under UVC illumination, which outcompetes TiO_2 under the same conditions (see Environ. Sci. Technol. Lett. 2020, 7, 8, 613–619). We applied density functional theory (DFT) to examine the feasibility of the initial oxidation step of PFOA degradation cycle over hBN: $C_nF_{2n+1}COO^- + h^+ \rightarrow C_nF_{2n+1}\bullet + CO_2$. We computed the redox potential of the PFOA oxidation, and found the redox potential is less positive than the valence band maximum (VBM) of hBN, which suggests that the photo-generated holes can oxidize PFOA thermodynamically. We also calculated the explicit reaction free energy and activation barrier of the surface reaction as a function of surface charge density in a grand canonical (GC) formalism and found the reaction is exothermic with a surmountable barrier. Also, Marcus theory was applied to calculate the electron transfer rate. This further implies the kinetic feasibility of the electron transfer between the anion and the hBN surface. The excellent photocatalytic performance of hBN under UVC illumination is unexpected because of its wide bandgap. By analyzing the density of states of the defective surface models, we found the nitrogen-boron substitutional defect (N_B) on hBN surface can generate mid-gap states that promote the UVC light absorption. Furthermore, the presence of N_B does not change the VBM of hBN and thus does not affect the feasibility of oxidation reaction. Therefore, we propose that introducing more N_B defects can further enhance the performance of hBN on PFOA degradation.

26. Tuning the Electrocatalytic Activity of Nitrogen Reduction Reaction on Ti_2N MXene Through pH Selection

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Electrochemical nitrogen reduction reaction (NRR) is used to convert atmospheric nitrogen (N_2) to ammonia (NH_3) at ambient temperature and pressure. In general, acidic electrolytes are used to provide protons (H^+) for the reduction process. However, this leads to a low NH_3 selectivity because of H_2 by-product formation via the hydrogen evolution reaction (HER). Recently, we showed that a Ti_2N MXene is active and selective for NRR in acidic electrolyte. We demonstrated that this catalyst works through a Mars-van Krevelen (MvK) mechanism instead of the conventional associative/dissociative mechanisms. However, the effect of pH and electrolyte on its catalytic activity and selectivity was not well understood. Here, we investigate these effects by performing experiments in varying electrolytic conditions and develop relations between pH, electrolyte choice, and performance. The Ti_2N nitride MXene was synthesized via an oxygen-assisted molten salt fluoride etching technique and characterized through XRD and Raman and FTIR spectroscopies. Our findings showed that changing pH does not affect the NRR onset potential. However, it was found that as pH increases, selectivity towards NH_3 increases due to a lack of free H^+ available to participate in HER. Also, it is found that smaller cations with smaller solvation shells suppress HER activity, while smaller anions prevent catalyst poisoning during the NRR process, as evidenced by cyclic voltammetry before and after experimental conditions. We are expanding these findings to other materials and systems. The knowledge from these systems will help to design optimal electrolytic conditions for the production of NH_3 through NRR.

27. What is the Second Most Stable Fe-N-C Structure?

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Fe-N-C is a promising material to catalyze the oxygen reduction reaction (ORR) due to its two-dimensional architecture and single-atom active site[1]. Two moieties of Fe-N-C have been experimentally identified, namely pyridinic and pyrrolic structures[2]. DFT calculations have demonstrated that the pyrrolic moiety is more active for ORR than the pyridinic site[3]. This observation agrees with experiments that observe an active site with higher activity. However, the exact structure of pyrrolic Fe-N-C is not yet known. In our work, we construct several structural variations of Fe-N-C through carbon dimer deletions, insertions, and bond rotations. We then examine the formation energies of these structures to elucidate the most prominent pyrrolic candidates. Our structures are validated by calculating the Mössbauer spectroscopic parameters and comparing with experiments[4]. These findings illuminate the precise architectures of pyrrolic Fe-N-C and expedite catalyst development.

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28. Unraveling Metal-Support Interactions in Catalysis with Density Functional Theory and Statistical Learning

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Transition metals supported on oxide materials are commonly used as catalysts in the chemical industry. Single atom catalysts (SACs) are particularly effective as they utilize all the metal atoms. Strong interaction between the transition metals and oxide supports is essential for synthesizing SACs, as weak interaction can lead to sintering and the formation of metal nanoparticles on the oxide substrate. Electronic metal-support interactions (EMSI) also play a crucial role in tuning the oxidation state of the transition metals, which affects catalytic reactivity and selectivity. In this study, we utilized density functional theory (DFT) and a statistical learning (SL) algorithm called iterative Bayesian additive regression trees (iBART), developed by our group, to derive physical descriptors that predict hydrogen binding energy on doped oxide supports [1]. Our findings show that iBART can generate models that capture the binding strength of hydrogen in response to substituent dopants or surface adsorbates, providing insights into EMSI and contributing to real catalyst design.

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29. The role of surface environment in catalytic methane partial oxidation

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Most hydrogen produced today is made via catalytic steam reforming of methane, a strongly endothermic reaction for which high-temperature steam is required. As an alternative route, methane partial oxidation does not require additional energy input and produces syngas with a H_2/CO ratio of about two, which is suitable for gas-to-liquids technology. While methane steam reforming, (partial) oxidation and other methane conversion processes share many elementary steps in their underlying reaction networks, methane partial oxidation over Pd stands out as the only reaction that proceeds faster as the particle size increases. All other methane conversion processes follow the usual requirement of small, high-surface area nanoparticle catalysts allowing for efficient utilization of metal atoms.

To investigate the abnormal size dependence of Pd nanoparticles for methane partial oxidation, we have analyzed the facet-dependent catalytic performance of Pd nanoparticles by multi-scale simulation including density functional theory, kinetic Monte Carlo Simulation and microkinetic modeling. The multi-scale model reveals the origin of increased methane activation rates with increasing particle size to be surface oxygen concentrations, which affect the dominant reaction pathways. We predict that oxygen poisoning can be mediated by passivating the edges of small Pd particles to inhibit diffusion without any significant loss of specific surface area or by periodically altering the CH_4/O_2 ratio. We validated our predictions against experiments using Ag-decorated Pd nanoparticles. Alternatively, we propose that the concentration of surface oxygen can be dynamically tuned by charging the Pd nanoparticle using the novel catalytic condenser design[1]. Overall, our results provide fundamental insights into Pd-catalyzed partial oxidation of methane, which can be leveraged for the design of improved catalysts in combination with dynamic process conditions.

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30. Reaction Engineering and Process Development for Large-Scale Production of Semiconductor Nanocrystals

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Semiconductor nanocrystals, also known as Quantum Dots (QDs), are a new class of highly fluorescent nanoparticles whose emission wavelength can be tuned by size. Their superior optical properties and stability in comparison to organic fluorophores makes QDs ideal materials for applications in color displays, medical imaging, biosensors, and solar cells (1). Commercial development of QDs is presently hampered by difficulties in scaling up existing synthetic approaches, and substituting the expensive and pyrophoric organometallic precursors with air-safe, inexpensive metal salts, without sacrificing nanocrystal quality. Our research focuses on addressing these problems by developing new reactor concepts, and discovering new chemistries and methods for large-scale synthesis of highly fluorescent nanocrystals.

Template-assisted synthesis of semiconductor nanocrystals, with precise control over particle size and shape, has been demonstrated by exploiting the dispersed aqueous domains of microemulsions and liquid crystals formed by self-assembly of p-xylene, an amphiphilic block copolymer, and water as individual nanoscale reactors (2). In particular, the synthesis of zinc selenide nanocrystals has been templated by reacting zinc acetate dissolved in the dispersed aqueous phase of microemulsions with hydrogen selenide gas. The particle size is controlled by the concentration of zinc acetate in the aqueous phase and the size of the dispersed domains. In an effort to maximize the utilization of all reactants, a novel counterflow reactor has been developed that can be scaled up for industrial production and modularized for parallel synthesis of QDs with different sizes. In another effort, new chemistries and synthetic methods are being developed to replace the widely used QD synthesis approach, which relies on the injection of expensive and pyrophoric organometallic precursors in a hot coordinating solvent, with new approaches that employ inexpensive salts and carefully selected co-solvents, all without sacrificing nanocrystal quality. Optical characterization of the QDs is performed by fluorescence spectroscopy and structural/morphological characterization by transmission electron microscopy.

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31. Kinetic Mechanism of Oxygen Reduction Reaction on Fe-N-C Catalysts

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Understanding electrocatalysis at solid/water interface is critical to addressing challenges in energy and environmental technologies. Although the thermodynamics of electrocatalysis has been extensively studied, the complexity of the kinetic mechanism has limited its investigation. In this study, we employ an advanced atomistic model (constant-potential hybrid-solvation dynamic-model; CP-HS-DM) to investigate the kinetic mechanism of Oxygen Reduction Reaction (ORR) catalyzed by a Fe single atom embedded in nitrogen-doped graphene (Fe-N-C).[1] Fe-N-C catalysts have been shown to be a promising alternative to Pt catalysts for ORR. Our findings provide insights into the importance of kinetic studies in ORR mechanisms, which can facilitate the design and optimization of more efficient electrocatalysts for energy and environmental applications.

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32. Cu-SSZ-39: Copper exchanged zeolite for partial methane oxidation

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The direct conversion of methane to methanol using molecular oxygen as the oxidant is a grand challenge in the chemical sciences. Many catalytic materials have been investigated for this reaction. Copper-containing zeolites have emerged as one promising class of materials. Here we describe our efforts in using copper exchanged SSZ-39 zeolite for this chemistry and show that it is very promising material for this reaction and more active in our hands than the small-pore zeolite copper exchanged SSZ-13 under similar conditions.

Initial testing at 225°C showed Cu-SSZ-39 with superior activity to the current zeolite literature benchmark catalyst for methane partial oxidation, Cu-SSZ-13. We have focused on 1) mapping out the catalytic behavior of this material over a range of operating conditions and metal loadings, and 2) understanding whether there are multiple types of active sites in this material. Maximum methanol productivity, both in terms of a mass catalyst basis and copper basis was observed at a Cu/Al ~ 0.2 with specific activity of 9.82 ± 0.23 mmolCH3OH.gcat-$^{1.}$h and site time yield of 26.9 ± 0.8 molCH3OH.molCu-1.h *10^{-3}. We should note that this site time yield significantly exceeds our prior work with Cu-SSZ-13. The lab also followed up on running this reaction in the *absence* of oxygen, per our prior work with SSZ-13. Results for the different catalysts with similar Cu/Al ~0.2 showed different behavior in the presence and absence of O2. The reason why, is not clear at the moment but hints towards the possibility of different copper sites in SSZ-39 compared to SSZ-13 or that their different shaped cages lead to different copper speciation. We are initiating a collaborative effort to perform X-ray absorption spectroscopy (XAS) to better understand this, and the data will be reported at a future time. Ongoing work also focuses on using NO binding using DRIFTS to study probe-molecule metal interactions.

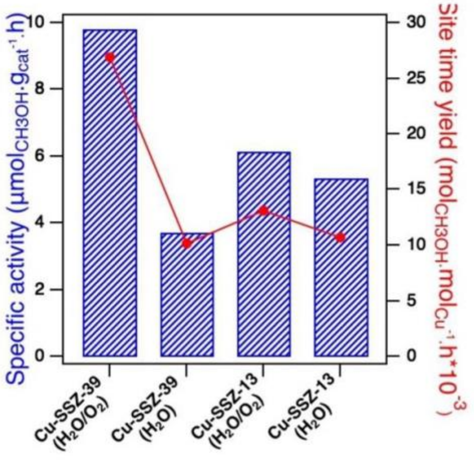

Figure 1. Specific activity and site time yield of Cu-SSZ-39 and Cu-SSZ-13 with water as oxidant in presence/absence of O_2 at 225 °C

33. DFT Investigation of PFAS Adsorption on Metal Surfaces

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Per- and polyfluoroalkyl substances (PFASs) are a growing environmental concern.[1] Efficient methods for degrading PFAS are urgently needed.[2] PFAS degradation via catalytic hydrogenation on transition metal surfaces is a promising strategy to achieve high defluorination rate. Since the adsorption step is the first step in the catalytic process, we systematically investigate the adsorption of PFAS molecules on different metal catalyst surfaces. We find that the PFAS molecule adsorption configuration is strongly influenced by the presence of adsorbed hydrogen by blocking the formation of metal-oxygen bonds between the surface and the PFAS head-group. Thus, the PFAS species prefers to bind parallel on the fully hydrogenated metal surface via van der Waals interaction, which favors the following defluorination step. Furthermore, adsorbate-adsorbate interactions between co-adsorbed PFAS molecules can promote PFAS adsorption through van der Waals forces among the tail groups of adjacent PFAS molecules, which can lead to the enhanced co-removal of different PFAS molecules. This mechanistic insight provides strategies for improving catalyst design to maximize PFAS uptake and degradation.

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34. Mildly acidic electrolytes can optimize reactant utilization in CO_2 reduction electrolyzers to scale up carbon conversion

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Electrocatalytic reduction of carbon dioxide (CO2R) is a pathway to synthesize fuels and chemicals using captured CO2, water, and renewable electricity. In most electrolytes, excess loss of CO2 to crossover makes electrolyzers energy- and carbon-wasting devices. Acidic electrolytes suppress conversion, but strong acids can increase side reactions. Preliminary results in an in- house test electrolyzer show that selectivity towards CO2R is improved in mild conditions and that crossover is entirely suppressed.

Future decades will see rapid growth in low-carbon renewable energy sources, but renewables are unlikely to displace our dependence on fossil fuels enough to prevent catastrophic climate change. Electrocatalytic reduction of carbon dioxide (CO2R) can provide a pathway to utilize CO2 to synthesize carbon-based fuels and chemicals using renewable electricity. Synthetic fuels like ethanol and ethylene can be stored for long periods of time, transported, and used to power sectors that cannot be electrified easily. CO2R can hence provide an integrated solution to enable carbon drawdown, store renewable electricity, and close the carbon cycle for chemicals and fuels. To access industrially relevant CO2R yields, reactor engineering is urgently needed.

Most CO2R electrolyzers are carbon- and energy-wasting devices because of carbonate ion crossover. In typical alkaline and neutral electrolytes, acid-base equilibria convert CO2 into carbonate ions that migrate away from the catalyst and cross into the anode. The resulting gas separation to recycle unreacted CO2 back to the reactor inlet would require ¼ of the system energy. Depending on the operating conditions, especially pH and water management, selectivity can also be limited by competing hydrogen evolution. To scale up CO2R, it is critical to simultaneously address carbonate crossover and selectivity loss.

Acidic electrolytes can eliminate carbonate crossover by neutralizing hydroxide produced by reduction reactions at the cathode. Operating zero-gap CO2R electrolyzers at mildly acidic pH could overcome crossover while maintaining selectivity to CO2R. Mild acids would also be less corrosive, improving process safety and reducing the prohibitive cost of stack replacement. To date, there are no reports of zero-gap electrolyzers operated at pH 2-7. Preliminary testing of mildly acidic electrolytes shows that selectivity to CO2R is improved as the pH is increased from 2 to 5. Carbonate crossover is entirely suppressed even at pH 5, suggesting that mildly acidic electrolytes have great promise to improve reactant utilization in zero-gap electrolyzers.

35. Growth Studies of Zeolite SSZ-39

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Zeolites, microporous materials whose frameworks are comprised mainly of silicon, aluminum, and oxygen, are an industrially important class of materials whose use spans the petrochemical sector, gas purification, detergents, and environmental remediation. Zeolite SSZ-39, as a particular example, is viewed to be a next-generation material for the selective catalytic reduction (SCR) of nitrogen oxides from diesel truck exhaust systems. Thus, developing a more fundamental understanding of how this zeolite forms should lead to the ability to tailor properties such as framework composition and active site density/spatial arrangement.

I will provide an overview of my work on the nucleation and growth of SSZ-39. This work involves the interconversion of one zeolite, faujasite (FAU), into SSZ-39 in presence of the organic structure directing agent (OSDA) under alkaline medium. The OSDA used exists in two isomeric forms: cis and trans. We investigated the effect of the trans isomer on the growth of SSZ-39 by varying trans/cis ratios in the synthesis gel by using different characterization techniques including X-ray powder diffraction (XRD), Nuclear Magnetic Resonance spectroscopy (NMR) and scanning electron microscopy (SEM) over the synthesis period. Crystalline SSZ-39 is first detected by XRD after four hours for samples made with 14% trans OSDA content. SEM results appear to indicate that SSZ-39 nucleates of the FAU surface. For the case of 14% trans OSDA, the synthesis appears complete by XRD after 30 hours. i.e., no FAU is detected by diffraction. In contrast, for the case of 80% trans OSDA, the synthesis appears complete by 24 hours of heating. Consistent with prior work increasing the trans content of organic structure directing agent (OSDA) in the synthesis increases the rate of SSZ-39 formation. NMR of the synthesis liquors show that the trans OSDA is selectively depleted from solution during synthesis, potentially indicating that the trans OSDA is more efficient at nucleation the material. Ongoing work is investigating intermediate trans contents between 14 and 80% and will also be described.

36. Mixed Metal catalysis of Methane to methanol reaction

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Methane to methanol conversion is an important reaction to help upscale methane to a more versatile industrial chemical, methanol. Methanol is a preferred product because it is easier to transport and store and helps to reduce unwanted emission of methane which is a potent greenhouse gas. Copper exchanged zeolites have been heavily investigated as a great catalyst for partial oxidation of methane to methanol in the presence of oxygen and water. Partially ion exchanged Copper SSZ13 (CuSSZ13) has been shown to be a great catalyst due to its microporous structure, ability to form metal-oxo sites, and presence of Brönsted acid sites needed for this reaction. However, the site time yield of this catalyst is not high enough for industrial application. Mixed metal catalysts have been used for various reactions to help promote the positive effects of one metal, as a sacrificial metal in reactions, and for their redox properties. To help improve the site time yield and the selectivity of CuSSZ13, Zinc was ion exchanged in small amounts into CuSSZ13 to help promote the catalytic activity of copper in the reaction. The duration of the ion exchange was used to control the amount of Zinc loaded into the CuSSZ13. The data from the mixed metal, CuZnSSZ13, catalysts were compared with monometallic, CuSSZ13 catalysts with the same Copper loading to allow proper comparison. Result shows that keeping the catalyst's Zinc/Copper ratio between 0.22 and 0.35 gave the optimum results with increased yield of 20%. Catalysts with Zn/Cu ratio <0.25 showed little to no difference from the pure Copper catalysts, while catalysts with Zn/Cu ratio >0.4 had less yield which indicated that the zinc starts to occupy the Brönsted acid sites.

37. CO_2 uptake with CuSSZ39

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Carbon dioxide, CO2, is a greenhouse gas that exists in nature as a trace gas and helps to trap heat on earth to make earth habitable. However, due to the industrialization and advances in technology, the amount of CO2 emitted into the atmosphere has been on the steady rise since the industrial age which has caused earth to start experiencing global warming. Different measures have set out to help reduce the emission and more importantly, capture some of the CO2 in the atmosphere. A lot of solid materials, such as Metal Organic Frameworks, silica gels, and activated carbon have been used to capture CO2 via physisorption and/or chemisorption, but due to their sensitivity to water and high energy requirement, there is need for better adsorbents. In this work, we set out to uncover the prospects of copper ion exchanged SSZ39 zeolite structures (CuSSZ39) for CO2 capture mainly because of its high thermal stability and moderate water tolerance. The CO2 adsorption process was carried out using a Thermogravimetric Analysis (TGA) device, the temperature for adsorption of CO2 was set to 35°C, and desorption temperature using Nitrogen gas was done at 120°C. The CuSSZ39 was shown to capture CO2 at low temperatures and via the two methods, physisorption and chemisorption. CO2 absorbed using parent SSZ39 catalyst was compared to CuSSZ39 with various loading of copper. The amount of CO2 captured went from 2.7614mmol/g of material for parent SSZ39 to 2.9616mmol/g of material for CuSSZ39 at optimum loading of 2.45 weight%. Copper loading above this optimum weight% leads to blocking of the pores of the zeolite, this results to a slight reduction in the amount of CO2 uptake by physisorption. CuSSZ39's ability to capture and trap CO2 is important as it hold future applications in CO2-to-methanol reaction.

38. Developing a Diagnostic Tool for the Determination of MXenes's Stability in Various Solvents

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Two-dimensional transition metal nitride and carbide MXenes have attracted increasing attention for various applications, including optoelectronics, sensing, and energy storage and conversion, due to several unique properties including high conductivity, high surface area and tunable electronic structure. Nonetheless, the reliable evaluation of stability for these MXenes, which is a crucial factor for their applications, has been a source of debate, primarily due to the lack of a consistent and reliable diagnostic tool. Herein, we report on the stability of delaminated $Ti_4N_3T_x$ (d-$Ti_4N_3T_x$) which was obtained via an oxygen-assisted molten salt fluoride etching technique. We use spectroscopy techniques such as UV-Vis, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, to study the stability and optoelectronic properties of the d-$Ti_4N_3T_x$ MXenes dispersed in ethanol, N-N dimethylformamide (DMF), water, dimethyl sulfoxide (DMSO), hexane and acetonitrile (ACN). Raman spectroscopy was also utilized to show photoluminescent-like behavior of the synthesized materials. We employ the energy band gap (E_g), an inherent characteristic of a material, as an accurate diagnostic tool for examining the stability of $Ti_4N_3T_x$ MXenes. Classical theoretical models such as Kubelka-Munk model and Tauc plots have been adopted in determining the E_g. Our findings show that the high-quality d-$Ti_4N_3T_x$ flakes are reasonably resistant to oxidation and retain their optical properties (optical energy band gaps, absorption coefficient, optical conductivity) over time in solution. Both Tauc and Kubelka Munk methods reveal a direct E_g irrespective of the solvents used.

39. Zeolite Catalysts for Low-Density Polyethylene Cracking

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Almost half of the global polymer production stands for polyolefins and low-density polyethylene (LDPE) takes significant amount of this portion. As only a small amount of consumed polymers are recycling, to find a mature technology for recycling is utmost important. Traditional polymer recycling methods require high process temperature which limits product selectivity, so in this research, it is investigated the recycle of LDPE into valuable gases at low temperatures using solid-acid zeolite catalysts via a catalytic cracking process.

Low temperature catalytic cracking of LDPE was studied with various zeolite catalysts and the impact of copper loading on catalytic activity of different zeolites are investigated. ZSM-5 was chosen as a base catalyst for this project because of its high Bronsted acidity, simple synthesis procedure, and resistance to coking. It was found that while protonic form of regular H-ZSM-5 (Si/Al=25) gives only 29% conversion value, presence of copper ions in framework helps to achieve high LDPE conversion with 71%. Furthermore, some commercial zeolites with different Si/Al ratio values are investigated and it was supported that high external surface area of catalyst particles results in high LDPE conversion values. In conclusion, it is clear that catalytic cracking process is more energy-efficient and effective than other processes for recycling of LDPE, and presence of an extra-framework metal cation in the framework of ZSM-5 zeolite helps to improve catalytic ability of zeolite.

A Brief History of the Southwest Catalysis Society

As recounted by ***Joe W. Hightower***, Professor Emeritus, Rice University (April 2009)

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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” though 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 C_4 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).**