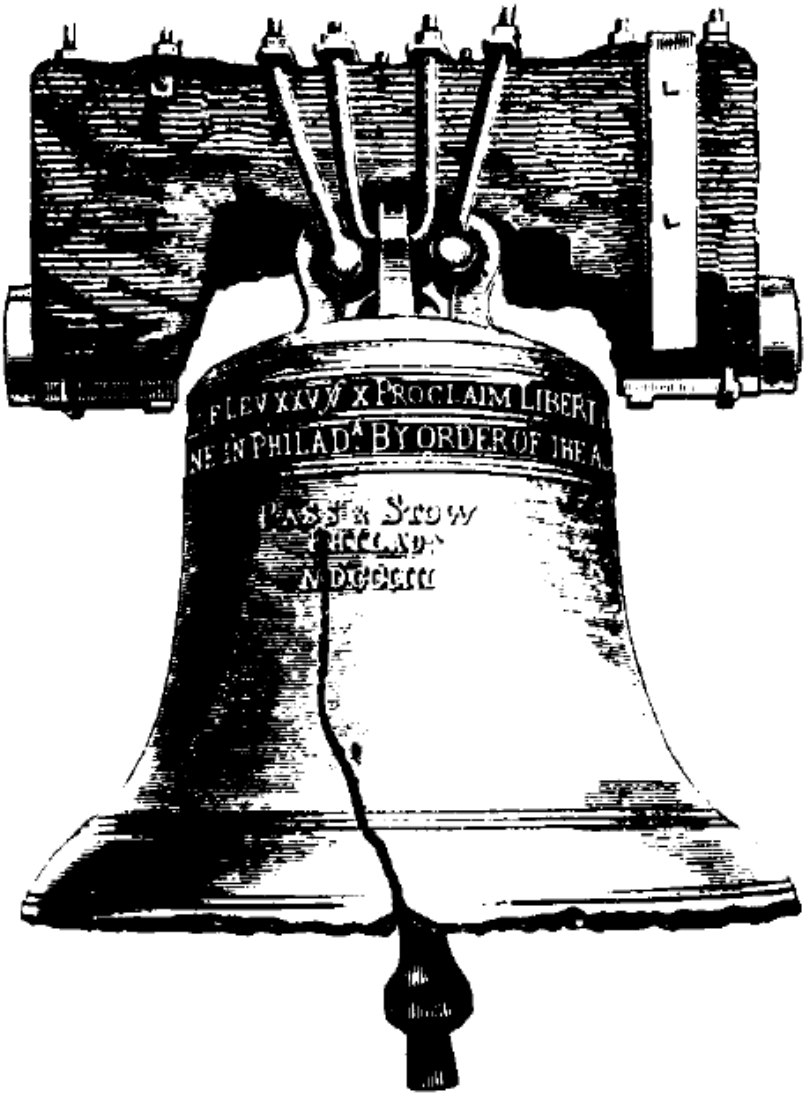
Catalysis Club of Philadelphia

2023 Spring Symposium Program



Promoting the science of catalysis since 1949

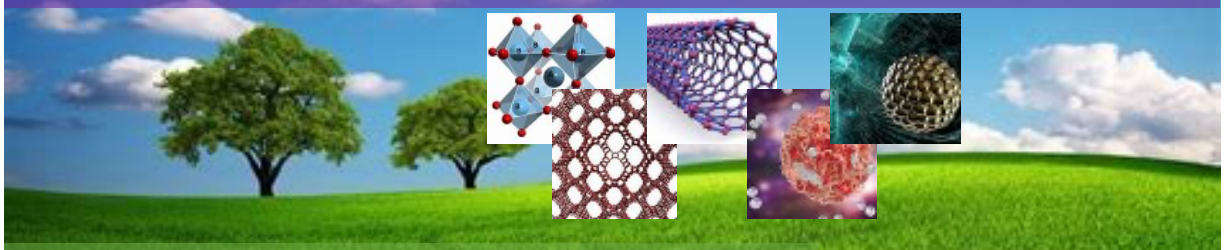
Wed, May 24, 2023

2023 Catalysis Club of Philadelphia (CCP) Annual Symposium-Student Poster Joint Conference

Catalysis for a greener future

***SAVE THE DATE:* Wed, May 24, 2023 @ Villanova University**

The Villanova Room at Villanova University, 800 Lancaster Ave, Villanova, PA 19085, USA



Symposium chair: Dr. Qinghe (Angela) Zheng (Johnson Matthey)
Student poster chair: Dr. Donghua Zuo (Covation Biomaterials)

Symposium Program at a Glance

Keynote speakers

Prof. Robert Farrauto
Professor of Professional Practice of Earth & Environmental Engineering, Columbia University

Prof. Dionisios G. Vlachos
Unidel Dan Rich Chair in Energy Professor of Chemical & Biomolecular Engineering, University of Delaware

Seminar speakers

Dr. Haiying Chen
Distinguished R&D Staff Member, ORNL

Prof. Huiyuan Zhu
Professor of Chemistry, University of Virginia

Dr. Paulami Majumdar
Associate Research Scientist, Dow

Dr. John R. Lockemeyer
Chief Scientist, Shell

Dr. Basudeb Saha
CEO at RiKarbon

Kai Shen
PhD candidate, UPenn

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Spring Symposium 2023
Schedule of Events

Wednesday, May 24, 2023

8:00 AM **Breakfast and social hour**

9:00 AM **Opening remarks**

9:10 AM **Keynote, Prof. Robert Farrauto, Columbia University**.
"Dual Function Materials (DFM) for direct air capture of CO_2 and its' catalytic conversion to CH_4: Engineering a solution towards mitigating climate change"

9:55 AM **Dr. Haiying Chen, Oak Ridge National Laboratory.**
"Monolith Supported Multifunctional Catalysts for the Direct Conversion of CO_2 to Dimethyl Ether"

10:25 AM **Tea break**

10:40 AM **Prof. Huiyuan Zhu, University of Virginia.**
"Well-Defined, Atomically Precise Catalysts for Sustainable Chemistry"

11:10 AM **Dr. Paulami Majumdar, Dow.**
"Discovery of Novel Catalysts for the Selective Vapor-Phase Methoxycarbonylation of Ethylene"

11:40 AM **Lunch (Buffet).**

13:00 PM **Afternoon program opening remarks**

13:05 PM **Keynote, Dr. Prof. Dionisios Vlachos, University of Delaware.**
"Catalytic Upcycling Technologies for Sustainability and Circularity"

13:50 PM **Dr. John R. Lockemeyer, Shell.**
"The Shell Ethylene Oxide Catalyst Journey"

14:20 AM **Tea break**

14:35 PM **Dr. Basudeb Saha, Rikarbon.**
"Recycling Plastics for a Cleaner Planet"

15:05 PM **Student talk, Kai Shen, University of Pennsylvania.**
"Reversible perovskite-fluorite phase transition in alumina-supported CeFeOx films and their use as Pt support"

15:25 PM **Symposium closing remarks and Student Poster Session introduction**

15:30 PM **Student Poster Session and social hour**

17:00 PM **Conference closing**

Dual Function Materials (DFM) for direct air capture of CO_2 and its' catalytic conversion to CH_4: Engineering a solution towards mitigating climate change

Robert (Bob) Farrauto
Earth and Environmental Engineering, Columbia University in the City of New York.
RF2182@Columbia.edu

Abstract
Laboratory studies of dual function materials (DFM), for direct air capture (DAC) of CO_2 under simulated ambient conditions followed by its conversion to renewable CH_4 using "green" H_2 will be presented.

The DFM consists of low levels of a methanation catalyst and an alkaline adsorbent, both highly dispersed on γ-Al_2O_3. The renewable CH4 product is dried and lightly compressed for injection into the natural gas pipeline. High cell density monoliths, support the DFM/washcoat, providing high CO_2 capture with low pressure drop while allowing for rapid surface heating of the thin washcoat during temperature swing methanation. Scale up testing and process design studies are now in progress by our engineering partner.

Prof. Robert J. (Bob) Farrauto

Professor of Professional Practice
Earth and Environmental Engineering Department
Columbia University in the City of New York

Biography

Robert (Bob) Farrauto, PhD, utilizes his 40+ years of industrial catalysis experience to currently train graduate and undergraduate students in applied environmental catalysis. During his industrial career he commercialized a number of advanced materials for automotive emission control, specialty chemicals and hydrogen generation. His team invented, patented, and commercialized the first precious metal-free monolithic diesel oxidation catalyst first commercialized in 1994 for trucks in the US. In the early 2000s the technology was modified for passenger car manufacturers and commercialized in the Asia, Europe and the US.

Upon retiring from BASF (formerly Engelhard), Iselin, NJ as a Vice President of Research in 2012, he was appointed Professor of Professional Practice in the Earth and Environmental Engineering (EEE) Department of Columbia University in the City of New York. He teaches several graduate and undergraduate courses in catalysis for a sustainable environment.

The goal of his team's research is the development of new materials and catalysts for a sustainable environment. The group's current research focuses on advanced materials for direct capture of CO_2 from air and its' catalytic conversion to fuel. His team has published a number of advancements in aging performance and reduced Ru content for effective use. His research group and its engineering partner are now funded by DOE for engineering scale up for pilot plant studies.

Bob is the author (co-author) of 142 journal publications and 56 US patents. He is co-author of three catalyst textbooks *"Catalytic Air Pollution Control: Commercial Technology"* Third edition, Wiley and Sons, New York, NY, 2009. *"Fundamentals of Industrial Catalytic Processes"* Second

edition, Wiley and Sons, New York, NY, 2006 and *"Introduction to Catalysis and Industrial Catalytic Processes*" Wiley and Sons, New York, NY, 2016, He has a Google scholar rating of 50.

He is the recipient of a number of research awards, including the 2008 Ciapetta Lectureship Award sponsored by the North American Catalysis Society, the 2005 Catalysis and Reaction Engineering Practice Award from the American Institute of Chemical Engineers, the 2001 International Precious Metal Institute (IPMI) Award for Outstanding Contributions in the field of precious metal catalysis and the 1998 Cross Canada Lectureship Award sponsored by the Canadian Catalysis Society. He is a senior member of the National Academy of Inventors based on his 56 US patents.

He received a BS from Manhattan College, Bronx, New York and PhD from Rensselaer Polytechnic Institute, Troy, New York.

Catalytic Upcycling Technologies for Sustainability and Circularity

Dion Vlachos

Catalysis Center for Energy Innovation (CCEI), Center for Plastics Innovation (CPI) and Delaware Energy Institute (DEI), Harker Interdisciplinary Science and Engineering (ISE) Lab, 221 Academy St., Office 250 M, University of Delaware, Newark, DE 19716, USA

Abstract

Climate change demands a paradigm change in the chemical industry and waste stream valorization. Biomass provides a means to renewable products with potentially enhanced performance over current products. We report the production of bio-lubricant base oils from lignocellulosic biomass as an example of upcycling of renewable carbon. Next, we discuss plastic upcycling. Single-use plastics impose an enormous environmental threat, but recycling, especially polyolefins, has proven challenging. We report a direct method to selectively convert various polyolefins, including virgin materials, layered materials, and everyday plastics, to branched, liquid fuels, including diesel, jet, and gasoline-range hydrocarbons, with high yields and at low temperatures in the melt. We discover and discuss new mechanisms by which polyolefins depolymerize. Finally, we discuss electrification means, such as using plasmas, microwaves, and Joule heating, toward decarbonizing the chemical industry.

Prof. Dionisios (Dion) G. Vlachos

Biography

Dionisios (Dion) G. Vlachos is the Unidel Dan Rich Energy Chaired Professor of Chemical and Biomolecular Engineering, a Professor of Physics at the University of Delaware, and the Director of the University of Delaware Energy Institute (DEI) and of the Catalysis Center for Energy Innovation (CCEI), an Energy Frontier Research Center (EFRC). He has also been a lead in the Process Intensification Fundamentals of the RAPID Manufacturing Institute. Professor Vlachos is the recipient of the R. H. Wilhelm Award in Chemical Reaction Engineering from AIChE, the Philadelphia Catalysis Club Award, the Irving Wender Award for Excellence in Catalysis from the Pittsburgh-Cleveland Catalysis Society, Exceptional Achievements in Catalysis Award of the Catalysis Science & Technology Division (CATL) of the ACS, an ExxonMobil Visiting Chair Professorship at the National University of Singapore, and an AAAS Fellow. He also received an NSF Career Award and an Office of Naval Research Young Investigator Award. His current research interests include catalysis and reaction engineering for a circular economy, renewable fuels and chemicals, plastics recycling, modular and distributed manufacturing, process intensification and electrification, multiscale modeling, data science, uncertainty quantification, and in silico prediction of catalysts.

Monolith Supported Multifunctional Catalysts for the Direct Conversion of CO_2 to Dimethyl Ether

Hai-Ying Chen
National Transportation Research Center, Oak Ridge National Laboratory
2360 Cherahala Blvd, Knoxville, TN 37932, USA
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Abstract

Direct conversion of CO_2 to dimethyl ether (DME) can improve energy utilization efficiency as well as reduce the capital and operational costs of the system. This requires bifunctional catalysts that integrate metal oxide components, such as $CuO/ZnO/ZrO_2$ (CuZnZr), for the CO_2 hydrogenation to methanol and acid components, such as Ferrierite (FER) zeolite, for the subsequent methanol dehydration to dimethyl ether in a well-designed fashion. Although conventional catalysts with the two components intimately mixed exhibit good synergistic effects, the catalysts exhibit poor long-term durability because of the detrimental interactions between the components.

In this presentation, a monolith supported bifunctional catalyst for the direct conversion of CO_2 to dimethyl ether will be presented. The catalyst consists of a layer structured configuration, in which CuZnZr and FER components are washcoated onto the channel surfaces of a metallic monolith substrate as two consecutive layers. The metal substrate provides heat conduction to regulate the catalyst bed temperature. The layered configuration significantly improves the synergistic effects of the two components, resulting in a 20% increase in the productivity for dimethyl ether at 240 ℃ as compared with the conventional catalysts with the two components being blended in various levels of proximity. Additionally, the layer structured design minimizes the undesirable interaction between the two components and drastically improves the on-stream durability of the catalyst. No activity decline was observed in a 146-h performance test.

Dr. Hai-Ying Chen

Biography

Dr. Hai-Ying Chen is a Distinguished R&D Staff Member at Oak Ridge National Laboratory. His research interest is in advancing catalysis science and technologies to enable internal combustion engines to meet near-zero pollutant emission standards, and in developing energy-efficient catalytic processes to accelerate the decarbonization of the transportation sector. Before he joined ORNL in April 2021, Dr. Chen was a Global Technology Fellow at JM with more than 21 years of industrial catalysis experience in exhaust emission control technologies. Dr. Chen has published more than 60 technical papers and holds more than 400 granted patents in various jurisdictions around the world. Dr. Chen is a Fellow of the Society of Automotive Engineering. He received numerous awards, including the Catalysis Club of Philadelphia Award in 2014.

Well-Defined, Atomically Precise Catalysts for Sustainable Chemistry

Huiyuan Zhu

University of Virginia

Abstract

At the core of the pursuit of energy and environmental sustainability is the management of carbon and nitrogen cycles to provide high-value carbon-based fuels and nitrogen-based chemicals through new catalytic processes with high efficiency and minimal environmental impact. Fortunately, the rapid growth of renewable electricity (*e.g.*, solar-, wind-, hydro-electricity) and the emergence of new materials have offered unprecedented opportunities to advance clean and sustainable production of chemicals and fuels. For example, electrochemical reactions, driven by solar/wind electricity, allow the conversion of CO_2, N_2, and nitrate, into chemicals and fuels. However, the costs and efficiencies of these reaction schemes have to be substantially improved before the large-scale implementation, which is to a large extent dependent on the understanding and optimization of catalysts in these schemes. Nevertheless, the structural complexity of heterogeneous catalysts makes the design rule elusive, limiting our capability of developing high-performance catalysts. Meanwhile, finding electrocatalytic materials with desired properties, i.e., moderate adsorption energies of descriptor species underpinned by the Sabatier principle, is a highly complex, multidimensional optimization process. Due to the ubiquitous adsorption-energy scaling relations that impose limits on attainable catalytic performance, it remains a grand challenge to design highly efficient electrocatalysts beyond such scaling relations.

Well-defined, atomically precise materials allow us to bridge the knowledge gap between conventional single-crystal bulk materials and powder catalysts to achieve new understandings of structure-catalytic property relationships. In this talk, I will highlight our recent progress in developing well-defined catalysts for sustainable chemistry with a specific focus on electrochemical CO_2 conversion and nitrate reduction. A new mechanism of breaking adsorption-energy scaling relations through Pauli repulsion that originates from orbital orthogonalization of the metal d-states with frontier orbitals of surface intermediates will be highlighted. Extending the design concept of active sites to heterogeneous thermal catalysis will also be covered.

Prof. Huiyuan Zhu

Biography

Huiyuan Zhu is an Assistant Professor of Chemistry at the University of Virginia (UVA). Before joining UVA, she was an Assistant Professor of Chemical Engineering at Virginia Tech (VT). Her research focuses on tailoring multi-functional nanostructures for catalysis, energy conversion, and chemical transformation. She received her B.S. in Chemistry from the University of Science and Technology in China (2009), and her Ph.D. from Brown University (2014). From 2014 to 2018, she was one of the inaugural Liane B. Russell Fellows and then a staff scientist in the Nanomaterials Chemistry Group, Chemical Sciences Division at the Oak Ridge National Laboratory. She has received the 2023 Sloan Research Fellowship, 2022 NSF CAREER Award, 2021 Class of Influential Researcher from *Industrial and Engineering Chemistry Research,* and 2022 *Nanoscale Horizons*, 2021 *Nanoscale* Emerging Investigator awards. She is also a recipient of the 2020 Jeffress Trust award, the 2020 Ralph E Powe Junior Faculty Enhancement Award, 2020 Doctoral New Investigator Award of the ACS Petroleum Research Foundation, and the 2020 *Journal of Materials Chemistry A* Emerging Investigator award, in addition to the recognition for her contributions as a teacher and advisor.

The Shell Ethylene Oxide Catalyst Journey

John Lockemeyer - Chief Scientists Catalysis Shell Global Solutions (US) Inc.

Abstract
This presentation will offer an overview of some of the significant contributions by Shell scientists, engineers, and technical staff to the field of ethylene oxide (EO) production. Starting with Shell's involvement in silver based EO catalysts dating back to the 1930's and culminating in the deployment of our most recent achievement in the High Performance EO Process, the journey through the approximately 90 inventive years will be described.

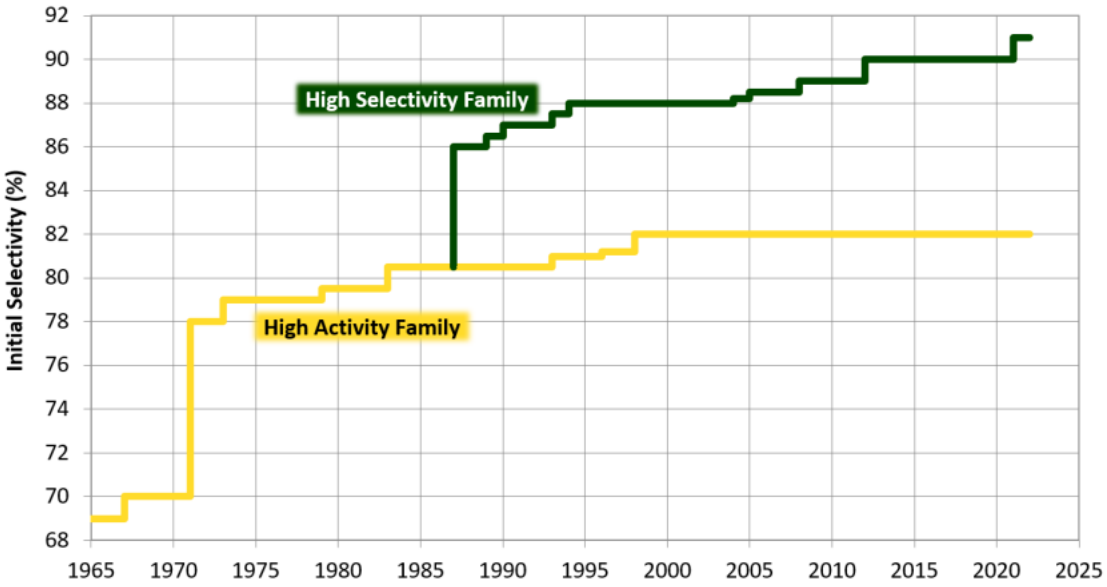

Figure 1. A Historical representation of modern Shell EO catalyst performance progression.

Dr. John R. Lockemeyer
Shell Chief Scientist Catalysis

Biography

John was appointed Shell Chief Scientist for Catalysis in 2020 to provide technical leadership and advise on strategy in areas involving catalysis and related fields.

Passionate about inventions that help solve the world's chemical and energy challenges, John enjoys collaborating globally with scientists in Shell and at universities and technical organizations on projects ranging from fundamental R&D to world scale deployment. Since joining Shell in 1989 his career has focused on catalyst development programs including hydrocracking, olefin epoxidation, acetoxylation, Fischer-Tropsch, and a variety of other systems at locations in USA, Europe, and India. He is the recipient of the 2018 Southwest Catalysis Society Award for Excellence in Applied Catalysis and is a listed inventor on 36 issued US Patents, 35 issued European Patents, and numerous patents in international jurisdictions.

John's academic career started with a B.S. in Chemistry at Villanova University (1982), a Ph.D. in Inorganic Chemistry at the University of Delaware (1987), and was capped by a postdoctoral appointment at the University of Illinois at Urbana Champaign (1987-'89). In 2010 he served as the elected Chair of the Gordon Conference on Inorganic Chemistry.

Recycling Plastics for a Cleaner Planet

Basudeb Saha
RiKarbon Inc, 550 S. College Ave, Ste 107, Newark, Delaware 19713

Abstract
Plastics are ubiquitous in modern life. Global production of plastics has reached over 400 million tons annually and is estimated to grow to 700 million tons by next 10 years. Over 10% of used plastics ends up in the ocean. Ocean vortices form "garbage patches" or "stomach-size colorful plastic piles" of disposed plastics and attracts seabirds. Slow photo-degradation of plastics forms microscopic pieces, creating waterborne pollutants and leaching toxins, and causing health risks to ocean life and humans through the food chain. The challenges of plastics and increasing sustainable feedstock demand can be simultaneously addressed by proper characterization of ocean plastics and their selective depolymerization into plastics' building block chemicals to produce upcycled polymers.

Currently a small fraction of post-consumer plastics is recycled through mechanical processing. The mechanical recycling causes a loss in the properties of plastics. Thus, the recycled materials are used for low value applications, which is often referred to as ***'carbon downcycling'***.

RiKarbon is commercializing an enabling technology, RiPURPOSE®, to capture higher value for post-consumer polyethylene terephthalate (PET) plastic waste. The technology enables hydrolytic depolymerization of low cost and unprocessed mixed PET plastic in the presence or absence of other form of end-use polymers into the plastic's building block oligomers (trade name: RiPurpose®Olig) with up to 70% carbon emissions reduction (compared to incumbent technologies). This product has unique functionalities to produce upcycled PET, adhesives, polyurethanes, polyamines and others.

This presentation will provide a glimpse of non-confidential information of the technology platform and our upcycled polymer innovation. It will (1) mitigate environmental challenges of waste plastics, (2) '***upcycle***' plastic's carbon value, (3) decarbonize polymer industry, (4) reduce our dependence on petroleum, (5) improve future energy security, (6) reduce global CO_2 footprint, and (7) create a circular economy.

Dr. Basudeb (Basu) Saha

Biography

Basudeb Saha is currently serving as the CEO at RiKarbon Inc. He served as an Associate Director in Catalysis Center for Energy Innovation at the University of Delaware, as a tenured faculty at the University of Delhi and worked as a research scientist at Dow Chemical Company. He received the Technology Center award from the Dow Chemical Company, the Team award from Purdue University, STE (Save the Environment) international achiever award, and served as a Technical Advisory Committee member for the U. S. Biomass Research and Development Initiative, an honorary position appointed by the Secretaries of the U.S. Department of Energy and the U.S. Department of Agriculture. He published over 150 peer-reviewed journal articles and patents, an edited book, and book chapters. His research focus includes catalysis, bioproducts and biofuels, plastic recycling and upcycling, clean energy, Green chemistry, and chemical kinetics.

Discovery of Novel Catalysts for the Selective Vapor-Phase Methoxycarbonylation of Ethylene

Paulami Majumdar, Beata Kilos-Reaume, David G. Barton, David Yancey
Core R&D, DOW, Midland, Michigan USA

Abstract
Methyl methacrylate is a specialty monomer to produce polymethylmethacrylate (PMMA), used for coatings and emulsion polymers. MMA can be produced in diverse ways based on C2-C4 hydrocarbon feedstocks. Exploring more ethylene-based routes are of growing importance owing to the abundant ethylene from shale gas feedstock. The dominant commercial process for MMA production utilizes acetone and hydrogen cyanide to produce MMA (ACH route). However, hydrogen cyanide and the acetone cyanohydrin intermediates are highly toxic and present an environmental hazard. Heterogeneous processes based on C2 carbonylation are commercially attractive technologies for MMA manufacture. While the literature on catalytic systems for hydroxy- and methoxy-carbonylation focuses mainly on homogeneous catalysis, we instead focus on heterogeneous catalytic pathways that facilitate separation. There are very few examples of efficient vapor-phase heterogeneous catalysts for carbonylation reactions with the exception of the many attempts to anchor homogeneous catalysts on a support which results in few turnovers before loss of activity or selectivity. The challenge for carbonylation reactions is that they require CO activation for insertion reactions without CO bond breaking. We will discuss the synthesis and characterization of novel heterogeneous catalytic systems for ethylene methoxy-carbonylation and the relationships between catalyst properties and catalyst performance. Remarkable catalysts were studied that facilitated significant steps forward in both the advancement of catalysis science and establishing the basis for new technologies.

Dr. Paulami Majumdar

Biography

Dr. Paulami Majumdar is an Associate Research Scientist in Core R&D, Chemical Science organization at Dow. She earned her Bachelor's in Chemical Engineering from Jadavpur University, India, and her Ph.D. in Chemical Engineering from Purdue University, USA. During her Ph.D., she worked on atomistic modeling using Density Functional Theory (DFT) simulations for heterogeneously catalyzed reactions. As a graduate student, Paulami was awarded with the prestigious Bilsland Fellowship from Purdue University and the Kokes award from the North American Catalysis Society.

In her current role at Dow, Dr. Majumdar continues to investigate the fundamental design principles for heterogeneous and homogeneous catalysts using DFT and explore tools and workflows to bridge the gap between atomistic models and industrial catalysts. At Dow, she has contributed to diverse technical areas such as olefin oxidation, alkoxylation, carbonylation and silicone chemistries. She has authored/co-authored 8 external publications and 1 patent filing. She holds leadership positions within Dow as a steering committee member in the Young Researchers Community – a professional networking platform for new hires within Dow and is a mentor for new hires. She is active in the local ACS Diversity and Inclusion team at Midland, MI. Dr. Majumdar currently serves as a peer reviewer for manuscripts in various catalysis journals and is a member of the Early Career Editorial Board of the Journal of Catalysis. She is also active in academia-industry engagements and sustainability and leads a collaborative project on plastic pyrolysis with University partners.

Reversible perovskite-fluorite phase transition in alumina-supported $CeFeO_x$ films and their use as Pt support

Kai Shen, Raymond J. Gorte, John M. Vohs
Department of Chemical and Biomolecular Engineering, University of Pennsylvania

Abstract

Ceria-based oxides in which a portion of the Ce^{4+} cations in the fluorite lattice have been substituted with a second +4 or +3 metal cation have a range of interesting properties. One example of this kind of materials is $Ce^{+3}FeO_3$, which is not easily formed, especially under oxidizing conditions, since +4 is the most stable oxidation state for cerium in the bulk oxide. While some bulk synthesis approaches are useful for obtaining samples for characterization of the bulk properties of $CeFeO_3$, the high-temperature calcination steps that are required generally result in a material with a relatively low surface area (< 1 m^2g^{-1}). Furthermore, bulk $CeFeO_3$ is unstable under oxidizing conditions at high temperatures and tends to irreversibly separate into CeO_2 and Fe_2O_3 phases upon oxidation.

In this talk, thin films with a stoichiometry of $CeFeO_x$ were conformally deposited on high-surface-area γ-Al_2O_3 by Atomic Layer Deposition (ALD). The 2-nm-thick films exhibited a perovskite structure after reduction at 1073 K but converted to a fluorite phase upon oxidation at 1073 K. It was demonstrated that Ce has +3 valence in the perovskite phase and +4 valence in the fluorite phase, while Fe is mixed +2 and +3 valence in the reduced perovskite phase and +3 valence in the fluorite phase. The transition between the fluorite and perovskite structures was reversible for at least five oxidation and reduction cycles.

These $CeFeO_x$ films were then used as support for Pt, which was deposited onto the films by ALD. The produced 3.3-wt% Pt/$CeFeO_x$/γ-Al_2O_3 catalyst showed large (~10-nm) Pt particles after oxidation at 1073 K. However, the Pt dispersed uniformly over the support after reduction at 1073 K. The rates for CO-oxidation and the Water-Gas-Shift (WGS) reaction were measured on Pt/$CeFeO_x$/γ-Al_2O_3, which were found dependent strongly on the pretreatment conditions. Based on these results, the potential implications of support composition and structure were discussed.

Kai Shen

Biography

Kai is currently a fourth-year Ph.D. Candidate in Chemical and Biomolecular Engineering at the University of Pennsylvania. His work focuses on preparing thin-film cerium-based perovskite oxides onto refractory high-surface-area supports by Atomic Layer Deposition. He investigates the structural and redox properties of these materials and their uses as oxygen carriers in chemical looping processes and support materials for transition metal catalysts. Prior to UPenn, he obtained his B.S. in Chemical and Biochemical Engineering at Rutgers University, where he investigated the behavior of naphthenic acids at the interface of an n-heptane-toluene mixture using Molecular Dynamics simulations.