

Tri-state Catalysis Society

2022 Fall Meeting

21 September



The Faculty Club

at

The Ohio State University

Schedule

8:00 – 9:00	Registration and welcome	
9:00 – 9:10	Introductory remarks	Rob Hart – Shepherd Chemical
9:10 – 9:40	1. Invited presentation	Yeping Cai – Clariant
Travel Awards Presentation		Will Shafer – Asbury University
9:45 – 10:05	2. Presentation	Jee-Yee Chen – OSU
10:05 – 10:25	3. Presentation	Dishari Basu – OSU
10:25 – 11:00	Coffee Break	
11:00 – 11:20	4. Presentation	Robert Warburton – Case
11:20 – 11:50	5. Invited presentation	Christina Wildfire – NETL
11:50 – 1:30	Lunch	During lunch, we will conduct the club's business meeting, including the election for club secretary
1:30 – 2:30	Poster Session	<i>See program p. 17</i>
2:30 – 3:00	6. Invited presentation	Pamela Chu – NIST
3:20 – 3:50	7. Presentation	Zweli Hlatshwayo – OSU
3:50 – 4:10	8. Presentation	Jaesung Kim – OSU
4:10 – 4:30	Coffee Break	
4:30 – 4:50	9. Presentation	Jacek Pecyna – Shepherd Chemical
4:50 – 5:10	10. Presentation	Anagha Hunoor – OSU
5:10 – 6:10	11. Keynote Presentation	Abhaya Datye – UNM
6:10 -- 6:15	Closing remarks	Rob Hart




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Presentations



Yeping Cai, Ph.D.

Process Technology and Alternative Fuel Department Manager, Clariant

Yeping obtained his Ph.D. degree in Chemical Engineering from The Ohio State University. Prior to joining Clariant (United Catalysts Inc., Sud-Chemie Inc.) in 1996, he conducted three-year post-doctoral research at Lehigh University. Cai started his career in SynGas group, and advanced his professional growth from research engineer, group leader and R&D manager. Cai has managed Clariant's SynGas, Specialty and Catalyst Scale-up departments in his 25+ years of career journey. As an inventor, he holds 21 US patents in the field of heterogeneous catalysis.

1. Steam Methane Reforming with EARTH®

Abstract

SynGas, a mixture of CO and H₂, is a building block to produce many basic chemicals, including but not limited to ammonia, methanol, synthetic natural gas, and gasoline via Fischer-Tropsch process. Steam methane reforming (SMR) plays an important role in syngas generation. In steam methane reforming, methane reacts with steam under relatively high pressure and high temperature in the presence of a catalyst to produce a mixture of carbon monoxide, carbon dioxide and hydrogen. Steam methane reforming is a highly endothermic reaction requiring so much heat input that heat transfer typically limits overall reaction rate. Ni-based catalyst is commercially applied in SMR reaction where catalyst is shaped to maximize geometric surface-area to volume ratio so that the diffusion limited reaction can proceed at high enough rate without too much pressure drop.

The collaboration on Technip Energies' innovative technology solutions and Clariant's catalysis expertise has resulted in EARTH®, a breakthrough proven technology, that improves heat transfer rate and increases in catalyst's geometric surface area greatly. Details will be discussed during this talk.

Jee-Yee Chen, and Nicholas A. Brunelli

The Ohio State University

2. Upgrading biomass through the aldol condensation using cooperative interactions in aminosilica materials: Discovering the different types of catalytic sites in aminosilica materials

Abstract

Biomass upgrading of chemicals to fuels requires development of highly active and selective catalytic materials for important reactions such as the aldol condensation. The aldol condensation can be catalyzed by powerful enzymes that use cooperative interactions between simple acids and bases to catalyze challenging C-C bond forming reactions. It is highly desirable to translate cooperative interactions into heterogeneous catalysts such as aminosilica materials. Important structure-function behavior has been elucidated, including the structure of the aminosilane and the strength of the acid group. Previous work assumed that each amine site is equivalent, but this assumption has not been rigorously tested. In this work, we will demonstrate that multiple types of sites exist and that the relative amount of each site can be tuned through controlling the material synthesis.

We demonstrate that multiple types of sites exist in aminosilica materials through using site quantification experiments. For standard aminosilica material synthesis (REG-SBA-15), we have discovered that only 30% of the overall sites are active. Through reducing the micropore volume of the bare support before grafting (NMP-SBA-15), we are able to produce an aminosilica that has an increased fraction of active sites of 50%. This has important implications for the aldol condensation of furfural with acetone. We observe that the NMP materials had more than double the catalytic activity than the REG materials. Importantly, the difference can be attributed to the different fraction of active sites.

As multiple sites exist, we sought to investigate previous synthesis-structure-function behavior, including the effect of surface density. Interestingly, we have discovered that there are three types of active sites. At high surface densities, all of the active amines have low catalytic activity since the high surface density disrupts cooperative amine-silanol interactions. At moderate densities, we identify that some amines are highly active and contribute significantly to the overall observed catalytic activity. Through tuning the surface density, we can increase the fraction of highly active sites. Ongoing experiments are seeking to elucidate differences in the structure of amines.

Recycle experiments reveal that the catalytic activity of the material changes over time. Our results indicate that the highly active sites are transformed into lower activity sites. These results have important implications for material design. Overall, the work demonstrates the importance of a molecular understanding of cooperative interactions.

Deeksha Jain, Jonathan Hightower, **Dishari Basu**, Anne C. Co, Aravind Asthagiri, and Umit S. Ozkan

The Ohio State University

3. Electrocatalytic bromine evolution using nitrogen-doped carbon nanostructures: A combined experimental and DFT study

Abstract

Recently, electrochemical bromine evolution and halogen evolution reactions in general have become significant in the context of energy storage, wastewater treatment and large-scale halogen generation processes. Increasingly, electrochemical halide oxidation reactions are being tapped to replace commercial methods for halogen production. Currently, large-scale bromine manufacturing requires the transportation and handling of hazardous chlorine gas as the bromide oxidant making this process unsafe, thereby creating the need for a novel approach for bromine production. Traditionally, electrochemical bromine production involves the bromine evolution reaction (BER) on the anode while hydrogen evolution reaction (HER) occurs on the cathode. However, high energy requirements and expensive noble metal cathode catalysts make this process energy intensive and economically unattractive. Therefore, we propose replacing HER with oxygen reduction reaction (ORR) at the cathode i.e. using oxygen depolarized cathodes (ODC) to increase energy savings, based on the lowered thermodynamic cell potential. This requires active ORR electrocatalysts, tolerant to corrosive electrolytes and halide poisoning from ions which may cross over from the anode as well as robust BER anode catalysts. To that end, we report nitrogen-doped carbon nanostructures (CN_x) as highly active platinum group metal free electrocatalysts for ORR and BER in acidic medium.

Previously reported electrocatalysts for BER either include unstable graphite anodes or Platinum (Pt) based materials. In this work, we showed that CN_x outperformed 10% Pt/C and commercial vulcan carbon, resulting in higher BER current densities even at low bromide concentration at low overpotentials. CN_x has also been shown to be stable under high oxidative potentials up to 18 hours without carbon corrosion. Post reaction characterization using X-ray photoelectron spectroscopy, in conjunction with computational density functional theory (DFT) calculations are used to elucidate the nature of BER active sites and propose the BER mechanism occurring over CN_x. The high activity and stability of CN_x is attributed to several nitrogen-doped carbon sites in its graphitic matrix, which have been examined using DFT. These results demonstrate the applicability of CN_x as a promising noble metal free electrocatalyst for ODC technology assisted bromine production at room temperature eliminating the need for toxic chlorine gas as the oxidant.

Robert Warburton

Case Western University

4. Theoretical Modeling of Proton-Coupled Electron Transfer at Electrochemical Interfaces

Abstract

Proton-coupled electron transfer (PCET) is a critical elementary step involved in many electrocatalytic reactions. Theoretical modeling can be a useful approach to gain atomistic insight into the reactivity of electrochemical interfaces toward PCET. In this presentation, I will describe the application of first-principles periodic density functional theory (DFT) calculations to model systems that undergo electrochemical PCET. In the first part, DFT calculations are used to calculate electrode potential-dependent vibrational frequencies of a nitrile vibrational probe using a grid-based approach that accounts for anharmonicity and can capture the vibrational Stark effect. The theoretical modeling results are analyzed in the context of surface enhanced Raman measurements to describe different stages of PCET during the hydrogen evolution reaction. In the second part of the presentation, I will describe thermodynamic analyses of PCET reactions involving organic acids conjugated to graphite electrodes. These graphite-conjugated catalysts undergo heterogeneous PCET reactions where the molecular character of the surface site can be modified to tailor PCET thermochemistry. DFT calculations reveal the importance of interfacial fields in driving heterogeneous surface reactions, and thermodynamic modeling using constant-charge and constant-potential approaches achieves close agreement with experimentally measured redox potentials. These computational studies of electrochemical PCET provide atomistic insights into the mechanisms of electrochemical processes relevant to catalytic reactions.



Christina Wildfire, Ph.D.

Research Scientist, National Energy Technology Laboratory

Christina Wildfire has served as a researcher at NETL since 2016 on the Reaction Engineering Team. Currently, she is leading the research for low pressure ammonia synthesis and CO₂ utilization using a microwave reactor. She also investigates the interactions and mechanisms of materials in a microwave field to aid in materials synthesis/processing and microwave reactions. Dr. Wildfire's research interests include: material synthesis, catalysis, microwave reactions, and scale-up. Dr. Wildfire received her BS and MS in Mechanical Engineering from Mercer University in Macon, GA and her PhD in Material Science from West Virginia University in Morgantown, WV.

5. Microwave Catalyst Design for Heterogeneous Reactions

Abstract

National Energy Technology Laboratory (NETL) is exploring microwave-assisted technologies for a wide range of chemical conversion processes such as ammonia synthesis, methane dehydroaromatization (DHA), CO₂ conversion, and coal conversion using heterogeneous catalysis. With the direct interaction of the electromagnetic field with the solid material, catalysis design has to be re-examined. However, the lack of a fundamental understanding of the underlying mechanistic and kinetic phenomena leading to the enhanced performance characteristics hinders the advancement of this technology and makes scaling from the laboratory-scale to commercialization difficult. R&D at NETL is devoted to understanding the fundamental microwave-material interactions, reaction chemistry, and kinetics, which will allow greater control over reaction mechanisms and lead to enhanced performance of microwave-assisted catalytic reactions. The lab is developing a one-of-a kind characterization facility to study these surface effects in-situ so that modeling of the materials can be improved and used in material and microwave cavity designs. In this talk, the application of microwaves to different reactions will be addressed to demonstrate the potential benefits. The research challenges for the MW-assisted reaction would also be addressed.



Pam Chu, Ph.D.

Leader, Carbon Dioxide Removal Program

Materials Measurement Laboratory, NIST

Pamela M. Chu, Ph.D., leads the Carbon Dioxide Removal Program in the Material Measurements Laboratory at the National Institute of Standards and Technology (NIST). This program is leveraging unique capabilities and expertise across NIST in sorption science and materials characterization to develop the critical metrologies and standards needed for scalable carbon dioxide removal (CDR) and carbon sequestration in building materials. Prior to this, Dr. Chu was the group leader of the Chemical Process and Nuclear Measurements Group, which focuses on developing state-of-the-art chemical and physical measurements to provide reference data, standards and models, and advance chemical measurement science and the fundamental understanding of chemical systems. Dr. Chu received A.B. degrees in Chemistry and Physics from Bryn Mawr College and a Ph.D. in Chemistry from University of California, Berkeley. She started at NIST as an NSF postdoctoral research fellow. As a NIST staff member, her laboratory research focused on the development and application of analytical spectroscopic techniques.

6. Tools to Help Enable Measurement Comparability

Abstract

To promote U.S. innovation and industrial competitiveness and assure the quality and comparability of measurement results, NIST conducts measurement science activities ranging from fundamental and applied research to the development and dissemination of analytical methods, reference materials, reference data, and documentary standards. NIST also provides guidance in best practices and resources which optimize the discoverability, usability, and interoperability of large information-rich data sets. To help identify stakeholders' needs, NIST actively engages the measurement communities through voluntary consensus standards development organizations, consortia, interlaboratory studies, and workshops. An overview of these approaches with an emphasis on specific areas most likely to address the catalysis research community needs will be presented.

Zweli T. Hlatshwayo, Jared G. Doremus, and Psaras McGrier

The Ohio State University

7. Porous Organic Polymer Catalyzed Carbon Dioxide Reduction: From Transition Metals to Main Group Elements

Abstract

Carbon dioxide (CO₂) is one of the primary greenhouse gases believed to be responsible for global warming on account of the world's continued dependence on the combustion of fossil fuels for economic growth. Thus, there is ongoing research geared towards new materials that can capture and transform CO₂ into alternative fuels like formic acid, methanol, ethanol, etc. The capture of CO₂ has been widely studied using various porous materials like covalent organic frameworks (COFs), porous organic polymers (POPs), etc. The catalytic transformation of CO₂ using homogenous transition metal catalysts and hydrogen (H₂) as a reductant has proven to be effective. However, this transformation is thermodynamically unfavorable, and relatively high pressures of H₂ are required. On the other hand, the hydrosilylative reduction of CO₂ to formates and methanol is a thermodynamically favorable approach. However, the development of heterogeneous catalysts that perform this chemical transformation with high catalytic efficiencies are rare.

POPs and COFs are a class of porous organic polymers that have emerged as promising platforms for heterogeneous catalytic applications due to their high surface areas and superior chemical stabilities. Herein, we report the hydrothermal synthesis, characterization, and hydrosilylative reduction of CO₂ to potassium formate (89% yield) and methanol (83% yield) using a benzobisthiazole(BBT)-linked Co(II)-porphyrin-based POP (Co-BBT-POP). The Co-BBT-POP is capable of CO₂ capture providing uptake capacities of 158 mg/g and 102 mg/g at 273 and 298 K respectively. Furthermore, we investigate the ability of two-dimensional (2D) cationic COFs to convert CO₂ to formic acid under metal free conditions using hydrosilanes as the reductant. Co-BBT-POP and the (2D) cationic COFs exhibits great recyclability up to five times without significant loss in catalytic activity for both catalytic systems (formate and methanol). Such systems are greatly needed to provide a practical design of functional POPs/COFs for sustainable CO₂ capture and conversion applications.

Jaesun Kim^a, Yu Jin Kim^b, Matthew Ferree^a, Seval Gunduz^a, Anne C. Co^a, Minkyu Kim^b, and Umit S. Ozkan^a

^a The Ohio State University

^b Yeungnam University

8. In-situ Exsolution of Bimetallic CoFe nanoparticles on (La,Sr)FeO₃ perovskite: Its effect on Electrocatalytic Oxidative Coupling of Methane

Abstract

Refinement of shale gas over the past several decades has produced an abundance of methane that is typically wasted by the practice of gas flaring. Research efforts have focused on identifying catalysts that can utilize this surplus methane by the production of ethane and ethylene. One strategy is to use a membrane reactor for OCM operating at low partial pressures of oxygen. A further advantage of solid oxide cells is that electricity can be spontaneously generated during OCM. Even with these advantages, however, it is still challenging for SOCs to develop mixed ionic and electronic conducting catalysts that selectively favor OCM over deep oxidation of methane to CO and CO₂.

The catalytic properties of the perovskite oxide surface can be modified by exposing it to CH₄ gas. We explored La_{0.7}Sr_{0.2}Co_{0.2}Fe_{0.8}O₃ (LSCF) catalyst as an anode for oxidative coupling of methane to ethylene and propylene. The in-situ exsolution of bimetallic CoFe nanoparticles and the resultant improvement on the electrochemical performance of the LSCF cell for OCM was supportively verified by analysis of surface and bulk characteristics as well as DFT calculations.

The reduced LSCF (Red-LSCF) was prepared by treating LSCF with 5% H₂/N₂ for 5 h at 800 °C. LSCF and Red-LSCF were characterized by TEM, XRD, in-situ DRIFTS, XPS, XANES, and TPR. For oxidative coupling of methane, the synthesized LSCF was screen-printed on the YSZ electrolyte as an anode and LSM-YSZ was deposited as a cathode on the opposite side of the YSZ electrolyte. The OCM reaction was conducted at 850 °C at different current densities (12.5–100 mA cm⁻²).

LSCF underwent the structural transformation under 5% H₂/N₂ at 850 °C as demonstrated by XRD. The main XRD peaks of LSCF remained after 1 h of reduction at 850 °C (H₂-Red-LSCF), but the additional features corresponding to bimetallic CoFe, LaSrFeO₄, and La₂O₃ also emerged. Moreover, XRD analysis showed that the CH₄-treated LSCF (CH₄-Red-LSCF) experienced the same structural transformation as H₂-Red-LSCF, displaying peaks present in CoFe alloy and LaSrFeO₄.

TPD-DRIFTS using CO₂ as a probe molecule were conducted on LSCF and Red-LSCF, and the results verified that the surface of Red-LSCF is more basic than that of LSCF and that reduction is an effective way of promoting the catalytic characteristics of LSCF for the activation of CH₄. Moreover, in order to

gain insight into the surface dynamics during CH₄ activation, in-situ CH₄-DRIFTS measurements were conducted on LSCF and Red-LSCF catalysts under CH₄ atmosphere at 450 °C. According to the results, CH₄ coupling reaction to C₂⁺ is competing with the oxidation of CH₄ and the controlled oxygen supply is a key parameter for a selective conversion of CH₄ on Red-LSCF.

Jacek Pecyna^a, Rob Hart^a, Mohammed Sifat Hossain^b, and Sheima J. Khatib^b

^a The Shepherd Chemical Company

^b Virginia Tech University

9. Incorporation of metals into ZSM-5 zeolite for methane dehydroaromatization process

Abstract

Benzene is an important building element of polymers, pharmaceuticals, dyes and other materials.

Current methods of synthesis of benzene include catalytic reforming, steam cracking and toluene dehydroalkylation, among others. These methods, however, require harsh reaction conditions such as high pressure, high temperature, and the use of expensive catalysts.

Here, we report on synthesis of molybdenum pre-catalyst on zeolite support for converting natural gas, mainly methane, into benzene and other aromatics. The catalyst precursor is prepared via acid-base mediated ion exchange. A solution of metal precursor and a slurry of zeolite are mixed simultaneously under strict pH control to ensure optimal deposition of metal on the zeolite surface. For example, a highly alkalized solution of ammonium molybdate is mixed with low pH slurry of zeolite to yield catalyst precursor with good metal loadings. The precursor is then calcined to give ZSM-5 zeolite doped with molybdenum trioxide. The material is characterized by ICP-OES, SEM, EDS, XRD and TGA. Activated precursors have shown good catalytic activity compared to catalysts prepared by other routes.

Anagha A. Hunoor^a, Saurabh A. Ailawar^a, Benjamin Rudzinski^a, Gokhan Celik^a, Yehia Khalifa^a, Laurence Burel^b, Jean-Marc Millet^b, Jeffrey T. Miller^c, Paul L. Edmiston^d, and Umit. S. Ozkan^a

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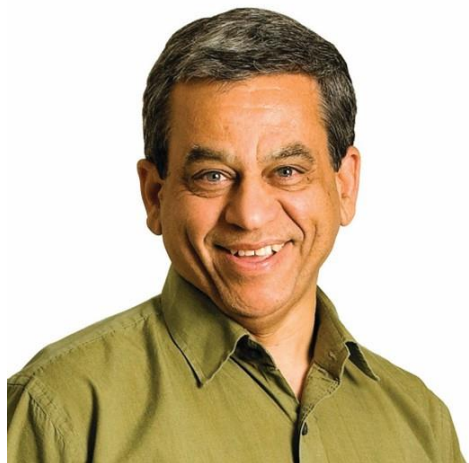
^c Purdue University

^d The College of Wooster

10. Aqueous phase hydrodechlorination of trichloroethylene (HDC of TCE) using Pd supported on swellable organically modified silica (SOMS): Role of aminated nature

Abstract

Trichloroethylene (TCE) is one of the major contaminants found in groundwater. Exposure to TCE even in trace quantities is known to impact human health adversely. Hence, the concentration of TCE in groundwater has been strictly regulated by US EPA to be lower than 5 ppb. Hydrodechlorination (HDC) using Pd catalysts has been demonstrated to be an effective approach to convert TCE into benign products, ethane and HCl. However, deactivation of conventional catalysts such as Pd/Al₂O₃ due to HCl formed during the reaction has prompted researchers to develop strategies for enhancing the deactivation resistance of HDC catalysts. Our group has demonstrated the superior deactivation resistance of Pd supported on a novel aminated material known as swellable organically modified silica (SOMS). SOMS is a hydrophobic mesoporous material which possesses a high affinity for organics and swells on exposure to organics. The swelling ability of SOMS was found to influence the accessibility of TCE to Pd sites. In this work, during HDC, swelling of SOMS induced by ethanol led to faster removal of HCl formed during the reaction from the pores thereby, protecting the catalyst from product inhibition. We also investigated the role of TCE, both as a reactant and as a swelling agent during HDC. Experiments with ethanol were used to describe the extent of TCE-induced swelling comparatively. Pre-soaking Pd/SOMS with TCE prior to the batch reaction led to 45% higher conversion than dry Pd/SOMS. Additionally, similar steady-state activities obtained in flow-mode experiments with and without ethanol indicated that TCE acts as a reactant as well as a swelling agent. Along with the dual role of TCE, flow experiments coupled with in-situ characterization by time-resolved X-ray absorption near edge spectroscopy (XANES) exhibited rapid reduction of Pd(2+) to Pd(0) under reaction conditions. Thus, performing HDC of TCE in flow mode enhanced the economic viability of the process by eliminating the need for an external swelling agent and a pre-reduced catalyst.



Abhaya Datye, Ph. D.

Distinguished Regents' Professor & Emeritus Department Chair, Department of Chemical & Biological Engineering, University of New Mexico

Abhaya Datye has been on the faculty at the University of New Mexico since 1984 after receiving his Ph.D. in chemical engineering from the University of Michigan (advisor Johannes Schwank). He has authored 250 publications, 7 patents and has presented 166 invited lectures around the world. His published work has received 22,221 citations with an *h-index* of 77 (Google Scholar). He is a fellow of the AIChE, the Microscopy Society of America and the Royal Society of Chemistry. He has been actively involved in the North American Catalysis Society, serving as co-chair for the Denver NAM 2017, program co-chair for the Snowbird NAM 1995 and Vice Chair for the International Catalysis Congress 2020. He was the Chair of the Gordon Research Conference on Catalysis in 2010. He has served on the American Chemical Society Petroleum Research Fund Advisory board (2014 – 2020) and on the Frontiers of Catalysis board at Haldor Topsoe in Denmark. He was elected as a board member for the North American Catalysis Society (2017-2021 & 2021 – 2024) and he is serving on the Department of Energy Basic Energy Sciences (BESAC) advisory committee.

His research group has pioneered the development of electron microscopy tools for the study of catalysts. His current work involves fundamental studies of catalyst sintering, especially the stabilization of isolated single atoms on supports for high temperature catalytic applications such as exhaust catalysis and alkane dehydrogenation. His research has been recognized through numerous awards, including the Robert L. Burwell Lectureship of the North American Catalysis Society (2019), Walter J Weber Distinguished Lectureship from the University of Michigan Chemical Engineering (2019), Eastman Lectureship from the University of South Carolina (2019) the John Matthews Lectureship from the Microscopy Society of South Africa (2012) and the 2008 Award for Excellence from the NSF IUCRC program, In 2016, the ACS publication Chemical & Engineering News included his research on single atom catalysis as one of the top 10 stories for the year.

11. Single atom catalysis: from an academic curiosity to industrial applications

Abstract

Over the past decade, single atom catalysis has evolved from being an academic curiosity to one of the most widely studied methods for the synthesis of novel catalytic materials [1]. The promise of single atom catalysts is to lower the requirements for platinum group metals by utilizing these metals more efficiently and to create novel catalytic pathways. For industrial applications, single atom catalysts need to be stable under reaction conditions and demonstrate durability during accelerated aging. Recent research shows pathways for scalable synthesis of single atom catalysts that might deliver catalysts meeting the thermal durability requirements of industry while yielding reactivity improvements over conventional supported metal nanoparticle catalysts [2]. Since mobile single atoms constitute the dominant mechanism for catalyst sintering via Ostwald ripening, improving the stability of single atoms could help improve the durability of all heterogeneous catalysts used in industry. In this presentation we will describe recent work on an approach which we termed atom trapping [3]. Our initial work focused on trapping volatile metal oxides such as PtO₂, to improve the durability of Pt catalysts, but we are now learning how this approach can be more broadly applicable. We will describe how fundamental understanding of the stabilization of single atoms and sub-nanometer particles and clusters can be helpful in applications ranging from emission control to hydrocarbon conversion.

1. A.K. Datye and H. Guo, Single atom catalysis poised to transition from an academic curiosity to an industrially relevant technology. *Nature Communications*, 2021. 12(1): p. 1-3.
2. Regalbuto, J.R. and Datye, A.K., All the lonely atoms, where do they all belong? *Nanotechnol*, 2022. 17(2): p. 110-111.
3. Jones, J., Xiong, H.F., Delariva, A.T., Peterson, E.J., Pham, H., Challa, S.R., Qi, G.S., Oh, S., Wiebenga, M.H., Hernandez, X.I.P., Wang, Y., and Datye, A.K., Thermally stable single-atom platinum-on-ceria catalysts via atom trapping. *Science*, 2016. 353(6295): p. 150-154.

Posters

1. Hannah Pineault, and Nicholas A. Brunelli

The Ohio State University

Tuning aminosilica catalysts for the aldol condensation reaction to produce bio-derived surfactants

Abstract

Surfactants are a key ingredient in everyday products like soap, detergents, and coatings. Oleo-furan sulfonates (OFSs) are a new type of surfactant that are bio-derived and highly tunable compared to their conventional petroleum-derived counterparts. A potential synthesis route for OFSs is the aldol condensation reaction between furfural and long-chain linear ketones. This route reduces the steps in the synthesis and has the potential to be low cost. A key challenge for the aldol reaction is the selectivity, regarding both chemoselectivity and regioselectivity. Aminosilica catalysts are highly active for the aldol condensation reaction because of cooperative acid-base interactions on the catalyst surface. The goal of this work is to tune the selectivity of amine-functionalized negligible micropore (NMP) SBA-15 for the linear aldol condensation product to produce OFSs. Different amine types (primary and secondary) and the reaction temperature will be investigated.

The completed synthesis and characterization of amine-grafted NMP SBA-15 confirms its mesoporous structure and the presence of catalytic sites. Preliminary kinetic tests of both materials confirm that they are catalytically active for the aldol reaction. Future work will focus on tuning the selectivity of the catalysts. More specifically, a reaction with a symmetric ketone will be used to study the chemoselectivity between the addition and condensation product. Likewise, an asymmetric ketone will be used to determine the regioselectivity between the linear and branched products. Overall, tuning furfural aldol chemistry for the linear condensation product will enable feasible synthesis of bio-mass derived surfactants.

Matthew Ferree, Seval Gunduz, Jaesung Kim, Anne C. Co, and Umit S. Ozkan

The Ohio State University

2. Electrocatalytic synthesis of ammonia on composite bimetallic nitride-perovskite oxide SOEC cathode

Abstract

In the past century, the human population has become increasingly dependent on commercial NH_3 production to grow food, but the technology has evolved very little to keep up with the accelerating demand. In the conventional Haber-Bosch process, N_2 and H_2 are reacted at high temperatures and pressures, but the H_2 production and pressurization steps can be bypassed by using N_2 and H_2O in a solid-oxide electrolysis cell (SOEC). Perovskite oxides are known to be active cathode materials for high-temperature electrolysis of H_2O , but certain transition metal nitrides may be more capable of activating N_2 .

In this study, a composite SOEC cathode of the perovskite $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.95}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) and the nitride $\text{Co}_3\text{Mo}_3\text{N}$ was fabricated, and its activity for NRR was studied. During NRR, 3% $\text{H}_2\text{O}/\text{N}_2$ was supplied to the cathode at 500–600°C with applied current densities of 0–2 mA/cm^2 . The composite cathode performed significantly better than the pure perovskite cathode or pure $\text{Co}_3\text{Mo}_3\text{N}$ cathode, indicating a synergistic relationship between the two materials. These results imply that $\text{Co}_3\text{Mo}_3\text{N}$ increases the rate of nitrogen activation, while the ionic/electronic conduction properties of LSCF improve the overall cell performance.

$\text{Co}_3\text{Mo}_3\text{N}$ was characterized by in-situ XRD, NAP-XPS, XANES, DRIFTS, and temperature-programmed experiments to study the mobility of lattice nitrogen, stability under humid conditions, and adsorption behavior.

Few non-noble metal materials have been identified as effective electrochemical NRR catalysts for the high-temperature range. The activity of $\text{Co}_3\text{Mo}_3\text{N}$ and its compatibility with proven perovskite catalysts allow for this unique composite cathode approach to high temperature NH_3 production.

Leah Ford, and Nicholas Brunelli

The Ohio State University

3. Quantifying active catalytic sites in Lewis acidic zeolite Sn- β

Abstract

Sn- β is a promising catalyst for numerous reactions involved in biomass upgrading and fine chemical production. Interestingly, Sn- β is proposed to have two distinct catalytic sites: open and closed sites. The quantification of these different sites is important, as previous investigations suggest a correlation between specific types of sites and improved activity for certain reactions. Common techniques to quantify the fraction of open and closed sites in Sn- β include solid-state MAS NMR and diffuse-reflectance FTIR with probe molecules, but these methods do not provide insight into the activities associated with the different sites for a given reaction. This information can be obtained from site quantification experiments that involve the addition of a catalyst poison. Here, four Lewis bases are tested as poisons in site quantification poisoning experiments: triethylamine, pyridine, 2,6-lutidine, and trimethylphosphine oxide. The poisoning solution is introduced to the Sn- β to deactivate a certain fraction of the Sn metal sites prior to catalyzing the ring opening of epichlorohydrin by methanol. Results of the site quantification poisoning experiments using triethylamine indicate that approximately 80% of the catalytic sites in Sn- β are active for this reaction. As demonstrated experimentally, the results are robust with little to no effect of diffusion limitations on the data. Triethylamine and pyridine are able to distinguish catalytic sites with different levels of activity by preferentially deactivating sites with higher activity, evidenced by multi-slope decreases in turnover frequency. 2,6-lutidine and TMPO, however, are unable to make this distinction, likely because of steric hindrance and solvent effects, respectively. Ongoing work is demonstrating how the crystallization time impacts the fraction of active catalytic sites that are formed in Sn- β . The identification of appropriate poisons will contribute to the establishment of robust procedures for Sn- β site quantification, which in turn will enable the determination of effective Sn- β synthesis parameters.

Majed Alam Abir, Joseph Z M. Harrah, Rachel Phillips, and Madelyn R. Ball

West Virginia University

4. Investigation of the role of supports of Ni based catalyst for CO₂ methanation

Abstract

Carbon dioxide (CO₂), a potent greenhouse gas, is the main component of industrial effluents and automobile emissions. The strategies for CO₂ emission reduction mainly cover capture-storage as well as capture-conversion such as hydrogenation. Methane is an attractive target of CO₂ hydrogenation. For CO₂ methanation, metal catalysts such as nickel have been widely studied due to their promising activity for CO₂ methanation.¹ However, these catalysts have low stability because of carbon deposition (coke formation) and sintering of the nanoparticles. To improve the stability of these materials, researchers are trying to design improved catalysts using promoters, bimetallic catalysts, supports, etc.² We are particularly interested to investigate the role of oxide supports as supports improve metal dispersion, change the basic properties, and tune the redox potential of the catalyst. Through modification of these properties, we hypothesize that the adsorption strength of intermediate species can be tuned and catalyst stability improved.³ In this project, we investigate how different supports change the CO₂ conversion, selectivity to methane, active sites, metal dispersion, and intermediate species. We have prepared Ni catalysts on Al₂O₃, CeO₂, SiO₂, and mesoporous SiO₂ (SBA-15) by strong electrostatic adsorption. Using a fixed bed flow reactor, we have investigated the CO₂ methanation performance over these catalysts, including CO₂ conversion and selectivity to methane. Additionally, we have compared the active site density and metal dispersion from H₂ chemisorption on Micromeritics instrument. Studies thus far have found the Ni dispersion increases from 9.7% for Al₂O₃ to 24% for SiO₂ and 26% for SBA-15. Ongoing work is investigating the performance and metal dispersion of Ni/CeO₂. In addition, continued work will identify variations in intermediate species using in situ FTIR under CO₂ methanation conditions for these Ni-based catalysts on different supports.

Reference:

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5. Tunable palladium catalyst using swellable organically modified silica as a scaffold for aqueous phase phenol hydrogenation

Abstract

Limited availability and harmful environmental impacts of fossil sources has created a need for development of sustainable technologies using renewable feedstocks for fulfilling the ever-growing demand for energy and chemicals. Manufacturing of indispensable commodities such as nylon and ester require cyclohexanone and cyclohexanol as starting materials. These are also used as solvents in several processes. While conventional methods rely on fossil-derived crude oil to produce these chemicals, we are focusing on the selective production of cyclohexanone and cyclohexanol using bio-derived feedstock. To this end, we have developed a palladium (Pd) catalyst using a novel aminated organic-inorganic hybrid support, swellable organically modified silica (SOMS), for aqueous phase hydrogenation of phenol to cyclohexanone and cyclohexanol. SOMS has a selective affinity towards organics and an ability to swell in the presence of organics. These properties impart SOMS, a high adsorption capacity which enhances the local concentration of the reactant near the active sites and hence, promote the reaction kinetics. As SOMS is hydrophobic, it preserves the mechanical integrity of the catalyst during aqueous phase reaction and protects the active metal sites, unlike conventional supports like Al₂O₃. SOMS is synthesized using sol gel method from organically modified precursor, bis (trimethoxysilyl) ethyl benzene, followed by capping of the hydrophilic Si-OH groups with hexamethyl disilazane. The active metal, Pd, was deposited on the support samples by incipient wetness impregnation and reduced in solution, by NaBH₄. The synthesis procedure of SOMS and parameters were varied to modify the surface properties of SOMS. Activity experiments performed in a batch reactor under 50 bar H₂ at 200 °C, showed the dependence of cyclohexanol and cyclohexanone on the surface hydrophobicity of SOMS. Structural changes and the resulting effects on metal dispersion, caused by the modification in the synthesis procedure was characterized by techniques such as N₂ physisorption, Fourier transform infrared spectroscopy, pulse CO chemisorption and transmission Electron Microscopy (TEM). Thus, this work provides a unique and facile approach of synthesizing a tunable and selective catalyst for phenol hydrogenation, using SOMS.