

# Tri-state Catalysis Society

2023 Fall Meeting

1 September



National Energy Technology Laboratory

and

Erickson Alumni Center

Morgantown, WV

## Schedule

9:00 – 10:30	Labs Tour	Christina Wildfire – NETL
10:30 – 11:00	Travel	
11:00 – 11:30	Registration and poster setup	
11:30 – 12:50	Lunch	During lunch, we will conduct the club's business meeting, including the election for treasurer and president
12:50 – 1:00	Travel Awards Presentation	Will Shafer – Asbury University
1:00 – 1:15	1. Award Presentation	Hannah Pineault – OSU
1:15 – 1:30	2. Award Presentation	Jee-Yee Chen – OSU
1:30 – 2:00	3. Invited Presentation	Doo Young Kim – UK
2:00 – 2:30	4. Invited Presentation	Yuxin Wang – WVU
2:30 – 4:30	Coffee Break and Poster Session	<i>See program p. 13</i>
4:30 – 5:00	5. Invited Presentation	Rong Xing – Clariant
5:00 – 6:00	6. Keynote Presentation	Manos Mavrikakis – Univ. Wisconsin
6:00 – 6:01	Closing Remarks	Rob Hart – Shepherd Chemical

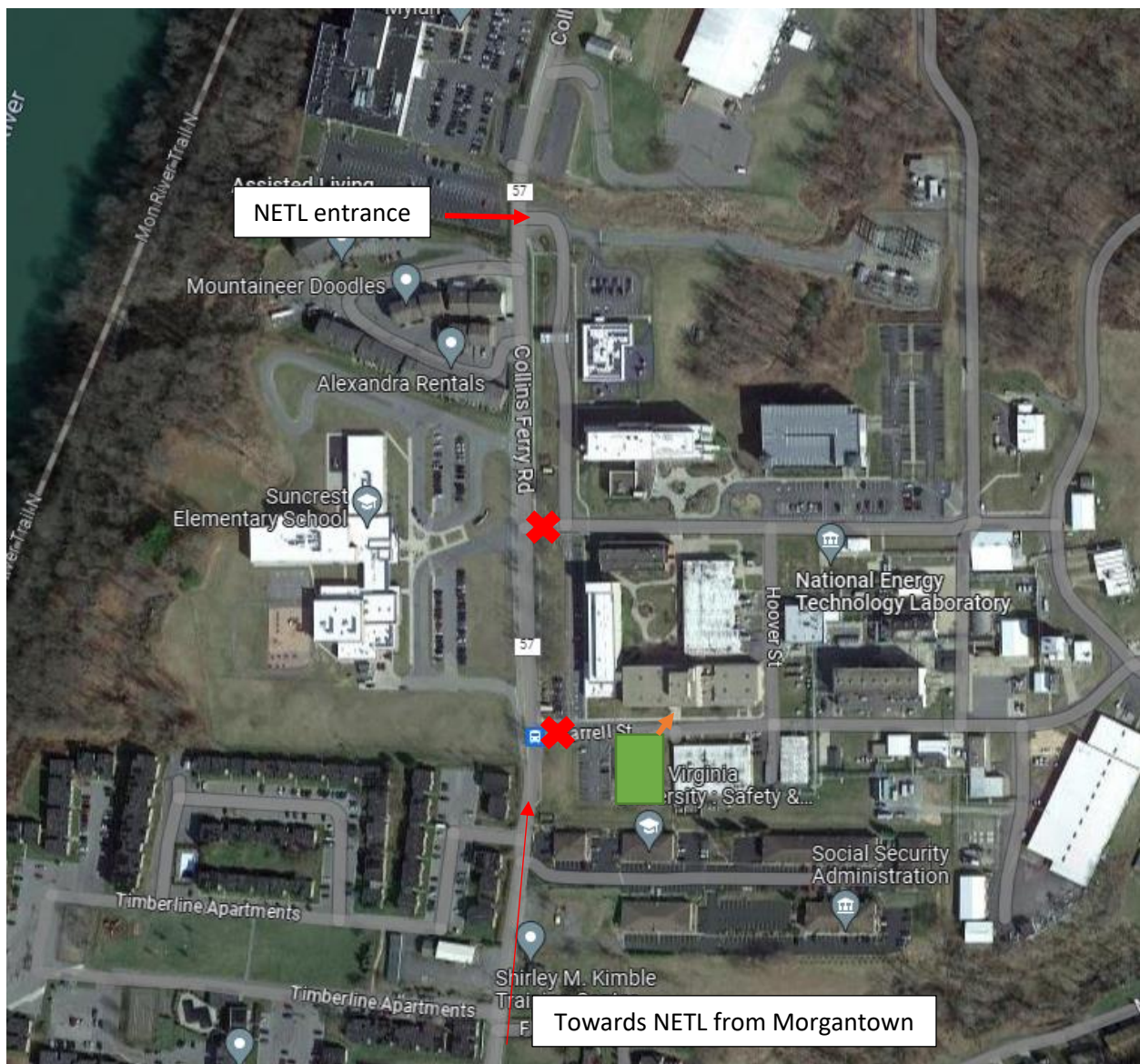
## Getting to NETL

The National Energy Technology Laboratory campus is at 3610 Collins Ferry Rd, Morgantown, WV.

Driving from the Holiday Inn or elsewhere in Morgantown will take you out Collins Ferry Rd. There are several closed entrances to NETL (marked with red Xs on the map below). Proceed past the lab and take the driveway on the right to access the gate.

This link will direct you to the correct entrance: <https://goo.gl/maps/jtRyjGDYevQki8HQ8>

You will proceed to the security gate at the entrance and provide your Real ID and let them know you are there for the Tri-State Catalysis Tour. They will direct you straight through the fork and a parking area will be blocked off for our group (green area on map). Walk straight across road to building entrance for the safety briefing. The tour organizing group will be at the entrance to greet you.



## Getting to Erickson Alumni Center

The Erickson Alumni Center is 1.8 miles from NETL. Parking is available in lot ST-8 to the right as you pull into the Alumni Center.

Erickson Alumni Center: <https://goo.gl/maps/f2pW5eUPWgbRv6f58>

The 2023 Tri-State Catalysis Society  
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**CLARIANT** 

## Presentations



Hannah Pineault, and Nicholas A. Brunelli

The Ohio State University

### **1. 1:00: Tuning Aminosilica Catalysts for the Aldol Reaction and Condensation to Produce Bio-derived Surfactants**

#### **Abstract**

Designing catalysts to produce biomass-derived products is vital to society's transition away from fossil fuels. One intriguing target class of compounds is surfactants, including the recently discovered oleo-furan sulfonates (OFSs). OFSs are a bio-derived class of surfactants that are highly tunable compared to their conventional counterparts. Whereas synthesis methods to produce OFS have been identified, these tend to be costly. A potential low-cost synthesis route for OFSs is the aldol reaction and condensation between bio-derived furfural and linear ketones. A promising catalyst for aldol chemistry is aminosilica, which is highly active because of acid-base cooperativity. However, a key challenge for aldol chemistry is product selectivity, including both chemoselectivity (reaction vs. condensation product) and regioselectivity (linear vs. branched products). Here, aminosilica catalysts are tuned for OFS surfactant production to improve the selectivity for the linear condensation product. SBA-15 is post-synthetically grafted with a primary (1°) or secondary (2°) aminosilane. The catalysts are tested with a symmetric ketone (*i.e.*, acetone) to study chemoselectivity and unsymmetric ketones (*i.e.*, 2-butanone and 2-undecanone) to assess regioselectivity trends. We show that amine type impacts the activity and selectivity. For the reaction between furfural and acetone, the observed chemoselectivity for the condensation product is higher for 2° NMP SBA-15 than 1° NMP SBA-15. The regioselectivity of the catalysts for the reaction with butanone follows a similar trend. Counter to previous work, our kinetic results show that 1° NMP SBA-15 exhibits higher activity for reactions involving unsymmetric ketones, which is unexpected and will be investigated further. Ongoing work will elucidate the regioselectivity for the reaction with 2-undecanone and investigate temperature effects. Future work will leverage solvation and surface environment effects to improve the selectivity. Overall, this work develops a novel synthesis method for OFSs and establishes reactivity trends for aldol chemistry with unsymmetric ketones.



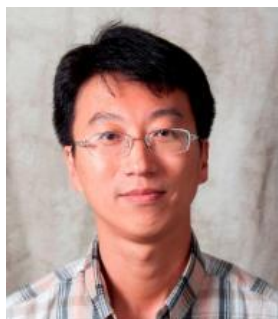
**Jee-Yee Chen**, and Nicholas A. Brunelli

**The Ohio State University**

## **2. 1:15: Biomass upgrading for aminosilica: stability and reactivation of different catalytic sites**

### **Abstract**

Research has shown that the high activity of heterogenous catalyst, and its easy separation benefits industry, such as biomass upgrading. Biomass upgrading to chemicals and fuels requires development of highly active and selective catalytic materials for important reactions, including aldol chemistry. Aldol chemistry can be catalyzed by powerful enzymes employing cooperative interactions between acids and bases to form C-C bonds. While obtaining the acid-base cooperative interaction, aminosilica materials have been used to reveal important structure-function behavior with its great catalytic performance. Next stage for the heterogenous catalyst is on investigating the sustainability. However, previous work assumed that each amine site is equivalent, but this assumption has not been rigorously tested. In this work, we demonstrate that multiple different types of sites exist and that the relative amount of each site can be tuned through controlling the material synthesis. Further investigation on recycle experiments reveals how the different types of catalytic sites of the material changes over time. The aminosilica (SBA-15 with amine) is applied in aldol condensation and reaction for the recycle test, and all the recycle materials are further applied with site quantification poisoning tests. Our results indicate that the highly active sites are transformed into lower activity sites where the active sites ratio remains. This observation indicates that the highly active sites are losing the cooperative interactions after reusing the catalyst. Two possible hypotheses are proposed for the site transformation: (1) silanol group dehydration, and (2) organic accumulation. Water treatment is applied to the recycled catalyst to rehydrate the silanol group on the surface. However, the treatment is not able to fully recover the catalytic activity for the recycled catalyst. On the other hand, dilute sodium carbonate solution treatment is used on the recycled catalyst to remove the organic accumulates. With elemental analysis and catalytic results, the treatment is able to fully recover the catalytic performance of the recycled catalyst. Overall, the work demonstrates the importance of a molecular understanding of cooperative interactions and the dynamic distribution of the catalytic sites during recycling.



Nadeesha L. Kothalawala, Tawabur Rahman, Manisha De Alwis Goonatileke, Nipun Chandrasiri, Beth S. Guiton, Aron Huckaba, and **Doo Young Kim**

**University of Kentucky**

**3. 1:30: Single platinum atom catalysts supported on exfoliated tungsten disulfide nanosheets for hydrogen evolution reaction**

Single-atom or clustered catalysts (SACs) have promise for electrochemical energy storage and conversion devices because of unique catalyst structure, ultrahigh metal utilization and strong electronic metal-support interaction (EMSI). Exfoliated, layered transition metal dichalcogenides (TMDs) serve as an ideal support material for SACs. In this geometry, TMDs stabilize SACs against agglomeration of catalyst atoms through an orbital interaction between catalyst and chalcogenide atoms. Furthermore, TMDs can facilitate the activities of SACs by tailoring EMSI. In this work, we report the synthesis and performance of platinum single-atom-catalysts (Pt-SAC) decorated tungsten disulfide ( $WS_2$ ) nanosheets for electrochemical hydrogen evolution reaction (HER). A green liquid-phase exfoliation was used to produce high-quality  $WS_2$  nanosheets (mono, bi- and few-layered). We found that single- or clustered Pt atoms were immobilized at the edges or on the basal plane of  $WS_2$ . Pt-SACs on  $WS_2$  have shown excellent HER activities in both acidic and alkaline electrolyte ( $\sim 40x$  higher Pt mass activity than Pt/C). This talk will present the synthesis, structure analysis, and activity of Pt-SAC on  $WS_2$ , including the results of high-resolution scanning transmission electron microscopy (HR-STEM), *in-operando* Raman spectroscopy, and electrochemical HER studies. As an attempt to probe active sites, CO stripping voltametric studies of Pt-SACs will also be presented.





**Yuxin Wang**, and Jianli (John) Hu

**West Virginia University**

#### **4. 2:00: Microwave-driven Catalysis in Decarbonization**

##### **Abstract**

Building a clean and equitable energy economy and addressing the climate crisis are top priorities of the Biden Administration. The administration aims to, "deliver an equitable, clean energy future and put the United States on a path to achieve net-zero emissions, economy-wide, by no later than 2050," to benefit all Americans. Decarbonizing is crucial for achieving this goal of net-zero emissions, economy-wide, by no later than 2050. The world produces more than 380 million tons of plastic every year, and 99% of plastics is made from fossil fuels sourced chemicals. By 2050 the plastic industry could account for 20% of the world's total fossil fuels consumption. The CO<sub>2</sub> emissions associated with plastic production are estimated to be around 14 million metric tons in 2022. However, 79% of plastics ends up in landfills or oceans. Over 200 billion ft<sup>3</sup>/year of natural gas at remote production sites is flared in the U.S. due to the limitations in pipeline transportation capacity. This wastes valuable resources, increases air emissions, and burns profits.

This presentation introduces the applications of microwave catalysis in decarbonization, the conversion of these energy resources/wastes (plastic waste, natural gas, and CO<sub>2</sub>) into valuable chemicals such as olefins, aromatics, ammonia, and hydrogen. Microwave irradiation has shown a profound impact on these reactions. In particular, it has been demonstrated that microwave-specific effects can manifest themselves through the enhancement of reaction rates, changes in the position of equilibria and the distribution of products.

Great efforts have been made to upcycle plastic wastes. Thermochemical technologies (*e.g.*, pyrolysis and gasification) enable the depolymerization of plastic wastes to produce small molecules that can be used as fuel or integrated into chemical refineries. However, these thermochemical processes suffer from high energy consumption and low product value. In this study, microwave catalysis was applied in plastic upcycling and demonstrated a high potential for producing high-value chemicals at a low cost.

Methane must be activated to a high-energy transition state before it can further react to produce stable products. The high reaction temperatures (>700°C) required to activate methane's strong C-H bonds usually result in rapid and extensive coke formation that blocks catalyst micropores, deactivating

the catalyst. The gaps in scientific understanding of the natural gas conversion process preclude the design of highly selective catalysts and reactors to make desired higher-value products. Technical hurdles include catalyst stability and thermodynamic limitations that constrain the desired product yields. In this study, the natural gas conversion reaction is enhanced with microwave irradiation to demonstrate microwave reaction chemistry at the catalyst-reactant interface for selective C-H bond activation, as well as CO<sub>2</sub>-assisted natural gas conversion.

Stranded electricity can be converted to liquid ammonia under ambient pressure and 320°C using water and air as feedstock. Conventional ammonia synthesis process, *i.e.* Haber-Bosch process, cannot be scaled down economically due to the high temperature and high-pressure operation and the intermittent nature of renewable electricity that requires frequent startup and shutdown. Other than selective activation of dinitrogen to metastable radicals, the most obvious advantage that microwave irradiation affords in driving a heterogeneously catalyzed reaction is the ability to locally heat the catalytic sites. Many industrial processes utilizing heterogeneous catalysts are high-temperature processes wherein both components of the reaction (*i.e.*, catalyst and medium) are heated to the temperature required for the reaction to occur. Specifically discussed in this presentation are the effects of electromagnetic properties of catalysts, microwave frequency and microwave energy absorbed on the conversion of nitrogen and ammonia yield.



**Rong Xing**, and Vladimir Fridman

**Clariant Corporation**

**5. 4:30: Application of  $\text{CrO}_x/\text{Al}_2\text{O}_3$  catalyst for Catofin Process: deactivation pathway**

**Abstract**

The  $\text{CrO}_x$ /alumina catalyst has been employed in commercial  $\text{C}_3$ - $\text{C}_4$  dehydrogenation technologies for several decades. The catalyst is operated in a cyclic dehydrogenation-regeneration (redox) mode with short time cycles and a steam purge after the dehydrogenation step, which creates stress on the catalyst leading to deactivation with time on stream. Due to its complexity, the catalyst deactivation pathway is still largely up for debate. In this work, we first prepared a series of industrial-like  $\text{CrO}_x$ /alumina samples at different aging levels, then evaluated their propane dehydrogenation performance. With increasing aging levels, the catalyst selectivity demonstrated very different behavior in response to temperature. To understand the catalyst deactivation pathway, the samples were systematically investigated by several techniques including X-ray diffraction,  $\text{H}_2$ -TPR,  $\text{O}_2$  chemisorption, Hg porosimetry, TEM, pyridine-FTIR, UV-vis, photoluminescence, and Raman. The results indicate that the  $\text{CrO}_x$ /alumina catalyst deactivation occurred through three major processes. The first process is related to the complex transformation of surface chromium species leading to reduced chromium oxide surface area. The second process refers to the phase transformation and/or sintering of alumina leading to the loss of texture integrity and the reduction of total surface area, and the third process involves the solid solution  $\alpha\text{-Cr}_x\text{Al}_{(2-x)}\text{O}_2$  formation leading to inactive sites.



**Manos Mavrikakis**

**University of Wisconsin**

**6. 5:00. Catalytic performance descriptors: An atomic-scale perspective**

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.

## Posters: 2:30 – 4:30

**1. Ashraf Abedin, Xinwei Bai, Mark Smith, and Pranjali Muley**

**National Energy Technology Laboratory**

**Microwave assisted catalytic cogasification of plastic-corn stover to produce clean H<sub>2</sub>**

### **Abstract**

Microwave co-gasification of plastics and biomass has numerous advantages over conventional gasification that includes higher H<sub>2</sub> yield and lower production of undesired char/tar. NETL Reaction Engineering Team carried out a catalytic optimization of an in-house microwave system to produce clean hydrogen from plastic-corn stover cogasification. Microwave enhanced the plastic-corn stover synergy and produced 30 mmol H<sub>2</sub>/g feedstock under air at 700°C as compared to 0.9 mmol H<sub>2</sub>/g feedstock at 700-950°C with conventional heating, which can be further enhanced with catalytic gasification. Microwave active catalysts have shown 30-70% more H<sub>2</sub> production compared to non-catalytic system, as the reduced metal oxides supply additional oxygen to the reaction that enhances cracking of intermediates to reduce tar and generate additional H<sub>2</sub>. TGA analysis suggests H-poor carbon formation resulting from the dehydrogenation of tar and carbon residue, plus light olefin decomposition, due to the external electric field generated by the microwave irradiation, allowing further cracking of the intermediate hydrocarbons to produce clean H<sub>2</sub>. Since microwave couples with carbon, addition of a microwave active catalyst further accelerates gasification by enhanced heating due to its surface carbon and results in additional H<sub>2</sub>.

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

**West Virginia University**

## **2. Investigation of the role of supports for Ni based CO<sub>2</sub> methanation.**

### **Abstract**

CO<sub>2</sub> conversion to methane is a potential strategy for utilization of atmospheric carbon. Nickel has been widely studied as a methanation catalyst because of its high activity, high availability, and low cost however there are challenges from coke formation and sintering. As one strategy to improve nickel catalysts, a variety of oxide supports are explored. Oxide supports may improve metal dispersion, basicity, and redox potential of the catalyst which have been shown to improve performance. Here, we have investigated the nature of metal-support interactions, characterized CO<sub>2</sub> adsorption, and explored potential reaction pathways to inform improved design of Ni based catalysts. We have prepared Ni catalysts on Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, TiO<sub>2</sub> by strong electrostatic adsorption and colloidal nanoparticle synthesis to produce different sized Ni particles on supports. The resulting catalysts were characterized using XRD, physisorption, H<sub>2</sub>-TPR, CO<sub>2</sub>-TPD, CO-chemisorption, and *in-situ* FTIR. Using *in-situ* infrared spectroscopy, we found that on TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supported catalysts with larger Ni particles, CO<sub>2</sub> methanation proceeds *via* a CO intermediate. For catalysts with smaller particles, however, no CO intermediates are observed, and catalytic activity is lower. The CeO<sub>2</sub> supported catalysts show the highest activity, which is attributed to the formation of oxygen vacancies and favorable basic sites. This observation leads to the direct participation of CeO<sub>2</sub> in CO<sub>2</sub> conversion, leading to an increased catalytic activity.

**Rachel Phillips, and Madelyn Ball**

**West Virginia University**

### **3. Development of Nickel Catalyst using Different Oxide Supports and Synthesis Methods**

#### **Abstract**

One approach to mitigate climate change is reducing the amount of CO<sub>2</sub> in the atmosphere *via* CO<sub>2</sub> conversion into useful chemicals. To carry out this reaction, we need to understand the effects that different catalyst supports have on performance so that we can design better catalysts. In this work, we developed Ni nanoparticle catalysts using different supports and synthesis methods to investigate how these parameters influence the structure and the effectiveness of the catalyst. From this study, we will be able to more effectively utilize support materials to improve catalysts for CO<sub>2</sub> conversion and other reactions. Catalysts were made by synthesizing nickel nanoparticles on oxide supports including silica, mesoporous silica, alumina, titania, and ceria. These catalysts were made by incipient wetness impregnation (IWI), strong electrostatic adsorption (SEA), and the direct addition of colloidal nickel nanoparticles. The catalysts were characterized by hydrogen chemisorption to measure the nickel active sites present on each support and TEM imaging was used to measure and understand how the colloidal nickel nanoparticles are adhering to the support. Through these, we found that the nickel on mesoporous silica (SEA) has largest dispersion from the studied catalyst. The colloidal nickel nanoparticles have an average size of 5 nm and were combined with the supports to create a more active catalyst.

**Paul Neff**, Nitish Deshpande, and Nicholas Brunelli

**The Ohio State University**

#### **4. Investigating the Effect of Micropore Content on Catalytic Activity and Selectivity for Glucose Isomerization to Fructose**

##### **Abstract**

An often-overlooked characteristic of common mesoporous silica catalytic supports lies in the specific details of their porosity. Though SBA-15 is known as a primarily mesoporous material, it contains a network of micropores within its mesopores that have been demonstrated to inhibit catalyst activity for various reactions. The micropore content of the material may be mitigated by a synthesis at 130°C, higher than a more commonly reported temperature of 100°C. Made in this way, the support is referred to as NMP (negligible micropore)-SBA-15, as compared to REG (regular)-SBA-15. Reactions of amine catalysts on NMP-SBA-15 have been shown to outperform REG-SBA-15 almost threefold in a general case of the isomerization reaction of glucose to fructose, which is considered valuable for various cost-related chemical applications including upgrading of biomass to plastics, solvents, and fuels.

With this said, the specific details of the application of NMP-SBA-15 to isomerization of glucose are not fully understood. Preliminary results indicate that tertiary amines placed at high loading on SBA-15 lead to higher rates of conversion, and that selectivity is positively influenced by initial concentration of glucose. As these ideas have not been fully applied to NMP materials, it has become necessary to do so. Here, tertiary amines on both NMP- and REG-SBA-15 will be tested across a range of surface loadings and initial glucose concentrations to determine the optimal reaction conditions for each and to deepen understanding of the effect of micropore content and the differences offered by NMP-SBA-15 supports.



Jungwon Yun, Dongjoon Kim, Minkyu Kim, Jason F. Weaver, and Aravind Asthagiri

The Ohio State University

## 5. Surface Chlorination of IrO<sub>2</sub> (110) and RuO<sub>2</sub> (110): Density functional theory study

### Abstract

The selective conversion of light alkane from shale gas into value-added products holds significant importance. Recently, we found that the selectivity of ethane oxidation to ethylene can be enhanced by surface chlorination of IrO<sub>2</sub>(110). In this study, we explore the surface chlorination processes on RuO<sub>2</sub>(110) versus IrO<sub>2</sub>(110) to enhance the selectivity of alkane reaction. Using first-principles calculations based on density functional theory (DFT), we investigate the structural, electronic, and energetic properties of chlorination process of IrO<sub>2</sub> (110) and RuO<sub>2</sub> (110). Surface chlorination on RuO<sub>2</sub>(110) has been extensively studied by others and serves as a reference for our work on IrO<sub>2</sub>(110). We have examined the elementary steps for HCl dissociative adsorption, water formation and desorption leading to bridge O (O<sub>br</sub>) vacancies, and Cl diffusion from surface metal sites (on-top sites) to O<sub>br</sub> vacancies. Furthermore, microkinetic modeling is being developed that can be compared directly with temperature programmed reaction spectroscopy (TPRS) and *in-situ* X-ray spectroscopy (XPS) of HCl on IrO<sub>2</sub>(110) as well. Such comparisons will be used to validate both the DFT energetics and the microkinetic model. The validated microkinetic model will be used to simulate different surface treatment procedures with the aim to controllably substitute O<sub>br</sub> atoms on the surface with Cl atoms. This study provides valuable insights and critical first step into the fundamental aspects of surface chlorination for alkane selectivity on the rutile transition metal oxide surfaces.

Snehal Patil<sup>1</sup>, Anagha Hunoor<sup>1</sup>, Umit S. Ozkan<sup>1</sup>, and Paul L. Edmiston<sup>2</sup>

<sup>1</sup> The Ohio State University, <sup>2</sup> The College of Wooster

## 6. Bridged polysilsesquioxane as catalyst scaffolds for aqueous hydrogenation of phenol: Role of aromatic content of bridged polysilsesquioxane

### Abstract

Bridged polysilsesquioxanes are highly versatile silica-based organic-inorganic hybrid (OIH) materials derived from precursors consisting of an organic bridging group and at least two trifunctional silyl groups. Chemical and textural properties of the material can be modified by appropriate choice of precursor. This offers a great scope for synthesizing catalyst scaffolds with tailored morphologies and functionalities suitable for a particular reaction. In this research, we have used bis(trimethoxysilyl) ethane (BTE) as a precursor to synthesize the OIH material. This is used as a support for a palladium (Pd) catalyst for aqueous phase hydrogenation of phenol to cyclohexanone and cyclohexanol. The mixture of cyclohexanone and cyclohexanol, known as ketone-alcohol (KA) oil, is used as starting material for manufacturing of nylon and esters. These are also used as solvents in several processes. While conventional methods rely on fossil-derived crude oil to produce these chemicals, we aim to use phenol, that can be derived from lignocellulosic biomass.

In this research, we have studied the effect of aromatic content in the bulk of the support, on the activity of the supported Pd catalyst. To alter the aromatic content, ethane-bridged organosilane-bis(trimethoxy silyl) ethane (BTE) is blended along with the phenylene-bridged precursor (BTEB). Characterization techniques such as N<sub>2</sub> physisorption, infrared spectroscopy, <sup>29</sup>Si and <sup>13</sup>C NMR were used to analyze the structural changes to the modified supports. Binding of phenol with the supports was determined by static vapor phase adsorption of phenol. To study the effect of aromatic content on hydrophobicity of the supports, acetone and water vapor adsorption experiments were performed. The ratio of amount of adsorbed acetone/water decreased with decreasing aromatic content of the support. This suggested that the hydrophobicity of the supports decreased with decreasing aromatic content. Aqueous phase phenol hydrogenation was performed in a batch reactor at 50 bar H<sub>2</sub> and 150 °C. All the OIH supported catalysts outperformed conventional mesoporous SBA-15 supported catalyst at the given reaction conditions. Activity of the catalyst increased as the aromatic content of the support decreased from 100% to 60%. <sup>29</sup>Si and <sup>13</sup>C NMR revealed that the extent of crosslinking decreased with decreasing the aromatic content of the support. This resulted in an increase in the Si-OCH<sub>3</sub> groups present on the surface which could improve adsorption of phenol and thus, improve the catalytic activity. Further reduction of the aromatic content of the samples to below 60% led to a decrease in phenol conversion.

This could possibly be due to higher hydrophilicity of these materials. To deconvolute the interactions of the polar hydroxyl group of phenol and the aromatic ring of phenol with the supports, a non-polar probe molecule, toluene was used to study the interactions with the support. At lower aromatic content,  $\pi$ - $\pi$  interaction between toluene and the phenyl group of the support showed a significant effect on toluene adsorption. Thus, this study shows that an optimum amount of aromatic content of the support is necessary to obtain good activity of the catalyst in phenol hydrogenation reaction.

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

The Ohio State University

## 7. High-temperature electrocatalytic NH<sub>3</sub> production on strontium iron molybdate-type double perovskite oxynitride cathodes

### Abstract

The demand for ammonia has been continuously increasing due to its widespread use in several industrial sectors including agriculture, transportation, pharmaceuticals, explosives, as well as the energy sector as a promising indirect hydrogen storage medium. The conventional Haber-Bosch (HB) process is operated continuously at 380-520°C and 150-250 bar of pressure and is not efficient or economical at smaller scales. A promising alternative electrochemical process can be augmented with intermittent availability of wind, light or solar thermal energy without major disruption to current infrastructure and it can be engineered for small-scale processes that has the potential to enable on-site, sustainable, scalable and energy-efficient ammonia production. In the high-temperature electrocatalytic production of ammonia, nitrogen reacts with water to form ammonia, hydrogen and oxide ions at the cathode side. Oxide ions are then conducted through the solid oxide electrolyte and reach anode side where they recombine and form gaseous oxygen. In order to achieve high activity, the cathode material should possess high electrical and ionic conductivity and high selectivity towards nitrogen activation and ammonia production. Although perovskite-type oxide materials are promising cathode catalysts due to their tunable electrical and ionic conductivity, they do not provide high activity for ammonia production. Nitrides are considered promising ammonia production catalysts due to the presence of lattice nitrogen in their structure which, in presence of hydrogen, can be converted to ammonia and nitrogen vacancies but they do not have any ionic/electrical conductivity.

In the present study, double perovskite oxynitride-type materials which possess the benefits of both perovskite oxide and nitride materials were synthesized, characterized *ex-situ/in-situ/in-operando* and tested in a single-chamber solid oxide electrochemical cell (SOEC)-type reactor for ammonia production from nitrogen and water at 500-600°C.

Dishari Basu, **Vennala Niharika**, and Umit S. Ozkan

**The Ohio State University**

## **8. Effect of Electrochemically Doped Bromine on Oxygen Reduction Activity**

### **Abstract**

PEM fuel cells are efficient energy conversion devices which may help with a more sustainable future. In PEM fuel cells, the major power loss happens due to slow kinetics of the oxygen reduction reaction (ORR) on the cathode. The state-of-the-art catalysts for PEM fuel cell cathodes are Pt-based. However, their cost is a major obstacle in wide-spread commercialization of the PEM fuel cells. Nitrogen-doped carbon nano-structures (CN<sub>x</sub>) have emerged as potential alternatives to Pt catalysts as first reported by Ozkan and co-workers [1-3], although they are not as active. They have been reported to have improved activity when doped with a halogen such as Cl or Br. Although there are techniques for incorporating these halogen atoms into CN<sub>x</sub> catalysts, these are usually quite involved and often hazardous. In this work, we present a facile electrochemical method of incorporating Br into CN<sub>x</sub> structure. Bromine, being an electronegative atom, is expected to improve the activity of the CN<sub>x</sub> catalysts for ORR. Results from synthesis, characterization and activity measurements will be presented.

### REFERENCES:

[1] Matter, Paul H., Eugenia Wang, Maria Arias, Elizabeth J. Biddinger, and Umit S. Ozkan. "Oxygen reduction reaction catalysts prepared from acetonitrile pyrolysis over alumina-supported metal particles." *The Journal of Physical Chemistry B* 110, no. 37 (2006): 18374-18384.

[2] Matter, Paul H., Eugenia Wang, and Umit S. Ozkan. "Preparation of nanostructured nitrogen-containing carbon catalysts for the oxygen reduction reaction from SiO<sub>2</sub>-and MgO-supported metal particles." *Journal of Catalysis* 243, no. 2 (2006): 395-403.

[3] Matter, Paul H., and Umit S. Ozkan. "Non-metal catalysts for dioxygen reduction in an acidic electrolyte." *Catalysis letters* 109 (2006): 115-123"

Katherine Stanley<sup>1</sup>, Chris Benmore<sup>2</sup>, Jincan Jin<sup>3</sup>, Rob Hart<sup>4</sup>, Wilson Shafer<sup>1</sup>

<sup>1</sup> Asbury University, <sup>2</sup> Argonne National Lab, <sup>3</sup> University of Georgia, <sup>4</sup> Shepherd Chemical

## 9. Characterization of a Molybdenum Carboxylate Catalytic Precursor for Hydrodesulfurization

### Abstract

This report focuses on the characterization of a molybdenum 2-ethylhexanoate. This material is a precursor for hydrodesulfurization catalysis. It has been the subject of several studies, but a convincing molecular structure model has remained elusive.[1] Several experiments were done to gain insight about the molecular structure, including: pair distribution functions (PDF) *via* high energy x-ray diffraction (HEXRD), simultaneous thermogravimetric analysis and differential thermal analysis (TGA-DTA), chemical analysis, Fourier transform infrared (FTIR) and Raman spectroscopy, and electrospray ionization mass spectroscopy (ESI-MS). From these data, initial guesses at the structure were made by geometrical reasoning and chemical rationalization. The guessed-at structures were compared to the diffraction data. Good candidates were geometrically minimized with density functional theory (DFT) electronic structure calculation with the metal ions fixed. Those structures that achieved a stable minimum were re-assessed against the PDF. The best models had 3 to 4 molybdenum ions and were either neutral or dicationic. These models were allowed to geometrically relax with no constraints for comparison to the FTIR data. Overall, the strongest evidence is for predominantly neutral molecules containing four Mo ions and four 2-ethylhexanoate ions in the presence of some free acid.

1. Qiu, He and Bing Zhou; Headwaters Heavy Oil, LLC. Highly Stable Hydrocarbon-soluble Molybdenum Catalyst Precursors and Methods for Making Same. US9403153 B2, 2 Aug. 2016.

Xinwei Bai, Swarom Kanitkar, and Daniel Haynes

National Energy Technology Lab

## 10. Microwave-assisted conversion of natural gas into aromatics

### Abstract

Natural gas flaring has two major drawbacks: significant greenhouse gas emissions and wasting valuable domestic resources. Recently, many routes have been developed to utilize and upcycle methane and other light alkanes into value-added chemicals *via* direct nonoxidative reactions. However, thermodynamic limitations and poor catalyst stability remains challenging in the conventional thermal reactor systems. Microwave-assisted reactions could offer a novel non-traditional approach in catalyst activation and product selectivity compared to a traditional thermal approach. Moreover, microwave reactors can be developed into compact, modular systems for flare gas conversion at the well site. This work investigated the performance of molybdenum- and gallium-doped HZSM-5 catalysts under non-traditional reaction conditions using microwaves, and a simulated real-world natural gas blend was applied to evaluate catalyst performance. The catalyst deactivation mechanism under microwave irradiation was studied experimentally and computationally. Different catalyst regeneration strategies were also reviewed. The results showed a higher catalytic performance compared to the conventional thermal method. Meanwhile, the addition of ethane and propane further improved the benzene yield, and the gallium catalyst performed better in converting liquid natural gas components to aromatics. Compared with the same reaction carried out in the conventional reactor, deactivation was observed faster in the microwave reactor. The numerical simulation demonstrated that the coke on the catalyst surface and pores would lower the overall electric field intensity, which could be essential for hydrocarbon conversion. Therefore, coke removal is crucial to restoring the catalyst activity for this microwave-assisted process. By using appropriate regeneration conditions, the catalyst activity could be fully recovered. To conclude, this work investigated different aspects of microwave-assisted natural gas conversion, and more future work is necessary to improve the catalyst stability in the microwave reactor.

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## **11. Scalable manufacturing of inorganic nanomaterials using Jet Mixing Reactors**

### **Abstract**

Typical laboratory batch reactors for inorganic nanoparticle synthesis can be difficult to scale since rapid particle nucleation and growth require efficient mixing to produce monodisperse particle size distribution (PDI). As the size of the reactor increases, it becomes increasingly difficult to achieve uniform temperature and concentration, leading to variations in the size, shape, and composition of the nanoparticles. These factors limit the use of inorganic nanoparticles in commercial applications ranging from energy to healthcare. Continuous microreactor-based synthesis is an attractive alternative, providing a uniform particle size distribution with mixing times of a few milliseconds. This work explores a novel jet-mixing reactor (JMR) design consisting of an axial flow with two jets impinging on the mainline, resulting in a single stream that exits the reactor. Previous work in our laboratory successfully synthesized metal nanoparticles and inorganic nanocatalysts like Pd@TiO<sub>2</sub> in JMR at room temperature using Palladium nanoparticles pre-synthesized in batch. The current ongoing research builds on this by integrating batch methods into a single continuous process using JMRs in series to produce Pd@TiO<sub>2</sub> which requires balancing flow rates and heating/cooling rates. Because Palladium nanoparticles are sensitive to reaction temperature, we are investigating the construction and characterization of the jet mixing reactor at high temperatures through nanoparticle synthesis and scaling analysis. Palladium-catalyzed reactions for biomass upgrading will then be further studied to quantify the yield of these heterogeneous nanocatalysts. Mixing time and size distribution studies will then be further explored to address scalability issues.



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## 12. Tuning of Charge density for Programmable Catalysis in the Water Gas Shift reaction

### Abstract

Most catalytic processes are limited by the Sabatier principle, *i.e.*, the faster a material is to promote the rate determining step(s), the slower it is to desorb the products. The result of this is the typical “volcano plot” which illustrates the theoretical maximum rate, which is an optimum typically formed between the rate of the rate determining surface reaction and the rate of desorption of the most important product. One way to break this relationship is to operate the catalyst under two regimes: one which focuses on promoting the rate determining surface reaction(s), and the other which focuses on promoting product desorption. A recently developed approach for doing this is programmable catalysis. In programmable catalysts, a material property is altered at a frequency, and if the material property is chosen properly, the catalytic properties are altered as well. Our work focuses on altering the charge at the catalyst interface using a “catalytic condenser”. A catalytic condenser is a concept based on programmable catalysis where a catalytic layer is deposited over a conductor/insulator/conductor layer; this stack of layers can condense at the catalyst surface. Specifically, a frequency is applied, allowing the condensed charge to oscillate between positive and negative. This charge condensation is reversible and can be tuned using applied voltage/ electron charge. Hypothetically, this oscillating charge should impact the binding energies, which should influence both the rates of the surface reactions and the rates of desorption. If applied correctly, this oscillating charge should create the two operating regimes described above and hence maximize catalytic performance. In this work, we examine the influence of oscillating charge on the Water Gas Shift (WGS) reaction. Through this work, we explore how the oscillating charge influences the rate of WGS using a combination of density functional theory and microkinetic modeling. We identify intermediates that are particularly influenced by charge and make hypotheses about how to tune catalyst properties to maximize the rate of WGS using charge condenser catalysts.

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**13. Investigation into the Activation of Molybdenum and Iron Catalysts towards Non-oxidative Coupling of Methane**

**Abstract**

Methane, a major component of natural gas, needs next generation manufacturing processes that will convert into high value products such as ethylene. Challenges in non-oxidative coupling of methane, an equilibrium limited reaction, are attributed to the high activation energy and low conversion rate due to the high stability of the methane molecule. To overcome these challenges and enable a feasible methane conversion process, we aim to develop catalysts that can be operated at lower temperatures with higher stability and selectivity. In this study, supported molybdenum and iron catalysts are synthesized and studied in a fixed bed flow reactor for non-oxidative coupling of methane. The catalysts are characterized using techniques H<sub>2</sub>-TPR, CO chemisorption, N<sub>2</sub> physisorption to understand the surface properties. Reactions are performed at 700°C and the reaction conditions optimized viz. pretreatment step, temperature, gas flows, catalyst mass, and time for kinetic investigation. The aforesaid tests will probe the effectiveness of these catalysts for future catalytic modifications aiming to obtain higher selectivity towards desired products on an industrial scale benefiting economically as well as reducing the waste generated from the reaction.

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#### **14. Modeling the structure of molten and glassy silicates from X-ray and neutron diffraction studies**

##### **Abstract**

Silicate melts corrosion of ceramic coating materials applied on the hot section components of military and commercial aircraft turbines is still a major durability challenge. The corrosiveness of silicate melts is governed by high temperature chemical reactions at molecular level. It is important to understand the nature of these interactions at molecular level to mitigate the corrosion of ceramic coatings. To that end, Calcium-Magnesium-Aluminosilicate (CMAS) compositions were designed to be similar to those deposited on hot section components of the aircraft engines operated in various environments. High energy x-ray diffraction and neutron diffraction data on molten and glassy CMAS samples have been modeled using Empirical Potential Structure Refinement (EPSR). Here we report the cation-oxygen coordination numbers and determine the degree of polymerization in the melt *via* the average number of bridging oxygens. These results will allow for a greater understanding of the reactivity of silicate melts.