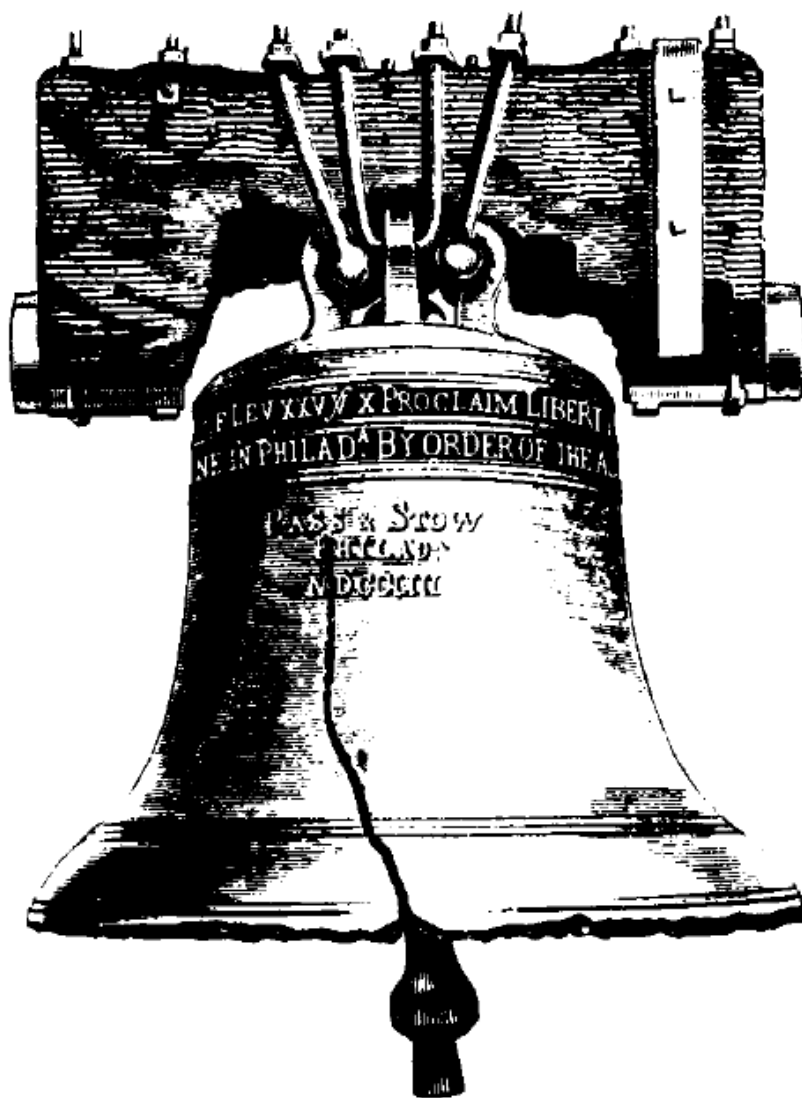


***Catalysis Club of Philadelphia***  
***2021 Spring Symposium Program***



***Promoting the science of catalysis since 1949***

**Thursday and Friday, May 20<sup>th</sup> and 21<sup>st</sup>, 2021**

# The Catalysis Club of Philadelphia

*Promoting the science of catalysis since 1949.*

## **Catalysis Club of Philadelphia 2020-2021 Officers**



<b>Chair</b> .....	Parag Shah, PQ Corporation
<b>Past Chair</b> .....	Jacob Dickinson, DuPont
<b>Chair-Elect</b> .....	Thomas Yeh, Johnson Matthey
<b>Treasurer</b> .....	Josh Pacheco, Zeolyst International
<b>Secretary</b> .....	Xinyu Mao, University of Pennsylvania
<b>Program Chair</b> .....	Angela Zheng, Johnson Matthey
<b>Arrangements Chair</b> .....	Jian Chang, University of Pennsylvania
<b>Director - Membership</b> .....	Udayshankar Singh, WR Grace
<b>Director - Poster Session</b> .....	Donna Liu, Johnson Matthey
<b>Director – Sponsorship</b> .....	Torren Carlson, Anellotech
<b>Webmaster</b> .....	Daniel DePuccio, Johnson Matthey
<b>Representative to NACS</b> .....	Michael Smith, Villanova University

# The Catalysis Club of Philadelphia

*Promoting the science of catalysis since 1949.*

---

***The Catalysis Club of Philadelphia is grateful for  
our 2020-2021 sponsors:***

**Gold Sponsors:**



**Silver Sponsors:**



# The Catalysis Club of Philadelphia

*Promoting the science of catalysis since 1949.*

---

## Spring Symposium 2021 Schedule of Events

### Thursday, May 20

- 8:50 AM Opening Remarks
- 9:00 AM Vladimiro Nikolakis, W.L. Gore & Associates, Inc.  
**Modeling of gas transport and adsorption considering liquid accumulation in the pore network of Sorbent Polymer Composite materials for mercury removal from flue gas**
- 9:40 AM Gold Sponsor Talk, Valerie Stephens, The Catalyst Group  
**The Catalyst Group (TCG) & The Catalyst Group Resources (TCGR) AT A GLANCE**
- 9:55 AM Crispin Cooper, Johnson Matthey  
**Perovskite Metal-Oxides for Automotive Three-Way Catalysis**
- 10:35 AM Break
- 10:55 AM Hongliang Xin, Virginia Tech  
**Interpretable Deep Learning for Accelerating Catalytic Materials**
- 11:35 AM Charles Mullen, USDA-ARS Eastern Regional Research Center  
**Catalytic pyrolysis of Biomass: Development and Demonstration**
- 12:05 PM Closing Remarks

### Friday, May 21

- 8:50 AM Opening Remarks
- 9:00 AM Keynote, Mark A. Barteau, Texas A&M University  
**A forty-year tour of surface acid-base chemistry: from solution to the gas phase and back again**
- 9:40 AM Gold Sponsor Talk, Josh Pacheco, Zeolyst International  
**Addressing the Challenge of Manufacturing Highly Siliceous Zeolites**
- 9:55 AM Krishna Janmanchi and Dimi Katsoulis, Dow Silicones Corporation  
**Two-Step Process for the Synthesis of Dimethyldichlorosilane using Copper Aluminate Catalysts**
- 10:35 AM Award Announcement
- 10:50 AM Break
- 11:10 AM William Medlin, University of Colorado  
**Controlling selectivity in reactions of complex oxygenates over metal catalysts**
- 11:50 AM Silver Sponsor Talk, Vladimiro Nikolakis and John Holcombe, W.L. Gore & Associates, Inc.  
 **Gore PTFE-catalyst composites: Enabling catalyst accessibility in challenging environments**
- 12:00 PM Bin Zhang, Lehigh University  
**Tuning the Surface Active Sites by Surface Modification of Supported ReOx/(SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) Catalysts for Olefin Metathesis**
- 12:40 PM Closing Remarks
- 12:50 PM Conference Adjourns

# The Catalysis Club of Philadelphia

*Promoting the science of catalysis since 1949.*

## **Modeling of gas transport and adsorption considering liquid accumulation in the pore network of Sorbent Polymer Composite materials for mercury removal from flue gas**

Uwe Beuscher and Vladimiro Nikolakis  
W.L. Gore & Associates, Inc.

Emissions of mercury, a toxic substance, from industrial flue gas stacks are regulated in many countries around the world. Several technologies are being developed to address the decreasing emission limits. W.L. Gore & Associates Inc. developed an innovative technology, called the GORE™ Mercury Control System (GMCS), for addressing this need. The GMCS is a unique fixed sorbent system that also provides SO<sub>2</sub> removal as a co-benefit. It is based on discrete stackable modules comprised of Sorbent Polymer Composite (SPC) materials with an open channel geometry. Hg is chemisorbed from the flue gas and bound into the SPC. On the other hand, SO<sub>2</sub> is converted to sulfuric acid filling a fraction of the SPC pores. However, due to the hydrophobic nature of the SPC, the liquid acid is expelled preventing the flooding of the entire pore network with liquid, which if it takes place it will have an adverse effect on Hg capture rates.

This paper describes the structure of the SPC material and introduces a simple model to describe the mechanisms to capture mercury by chemisorption and convert SO<sub>2</sub> to liquid sulfuric acid. Due to the generation of liquid sulfuric acid, it is important to understand the fraction of liquid inside the SPC tape pores. Characterizing the pore network of the SPC tapes is a challenging task not only because the pore sizes span several orders in magnitude, but also because measurements need to happen at dry and 100% relative humidity conditions. Emphasis will be placed on how we combined a set of complimentary techniques (Hg intrusion, N<sub>2</sub> & H<sub>2</sub>O physisorption, and X-ray computer tomography) to obtain a 3-D reconstruction of the dry and wet SPC pore network, and how this reconstruction was analyzed using diffusion calculations to get information about the porosity and tortuosity of wet and dry SPC tapes.

Overall model results are compared to experimental observations from the lab environment to simulated flue gases to observations of pilot plants using actual flue gases. A comparison between the model results illustrates the shift in limiting process steps between these conditions. This insight can be utilized to optimize the structure and performance of the material under these conditions. Finally, the paper will conclude with illustrating the limitations of this simple model and the steps to improve the model description are described.

# The Catalysis Club of Philadelphia

*Promoting the science of catalysis since 1949.*

---

## Perovskite Metal-Oxides for Automotive Three-Way Catalysis

Crispin Cooper  
Johnson Matthey

Perovskite oxides have long been the subject of study and speculation as possible base-metal alternatives to precious metals in catalytic application. Here we present results and conclusions from a study of these materials for application to three-way emissions control catalysis (TWC) as well as wider catalytic functions. Key predictions are compared with experimental results.

The surface and defect chemistry of lanthanum first row transition metal oxide is described and surface oxygen vacancies identified as key active sites for both reduction reactions and production of reactive oxygen species which participate on oxidation. The adsorption and activation of a range of reactant molecules from the gas phase on to the perovskite surface has been calculated and adsorption modes described, this allows important trends with A- and B-site composition to be elucidated. In addition, the strong competitive adsorption of oxygen relative to the other components offers an important explanation for the poor nitric oxide reduction activity observed in realistic tests, despite the same materials showing great potential in tests using simple gas mixtures. This conclusion is the result of extensive agreement between experimental and theoretical studies and explains a significant limiting factor in the utility of these materials in TWC.

Traditional TWC materials are typically noble metals supported on redox-active supports such as doped ceria-zirconias. Noble and other metals can likewise be supported on, or incorporated in to, the perovskite oxides. The thermodynamic preference for a wide range of metals to segregate to the surface or dissolve in to the bulk of the supporting perovskite has been studied by application of theoretical methods and expands on the previously known literature results for these system. This includes the effects of reducing or oxidising environment on the segregation of components. The mechanisms of CO oxidation and NO reduction with and without supported metal particles are discussed. The effects of metal ad-atoms and larger supported particles are studied and results resented in terms of NO activation, competitive adsorption and effects on oxygen behaviour. We draw conclusions as to the potential and limits of these systems and briefly outline the scope for future study.



# The Catalysis Club of Philadelphia

*Promoting the science of catalysis since 1949.*

## Interpretable Deep Learning for Accelerating Catalytic Materials Discovery

Hongliang Xin  
Virginia Tech

The formation and breakage of chemical bonds at active sites is the molecular basis of catalysis. Being able to rapidly compute interaction strengths between bonding entities and understand their trends holds the key to the design of improved catalysts. Despite recent advances of data acquisition and algorithms development, machine learning (ML) faces tremendous challenges in catalyst design, largely due to its limited generalizability and poor interpretability. Here, we develop a theory-infused neural network (TinNet) approach<sup>1</sup> that integrates deep learning algorithms with the well-established d-band theory of chemisorption for interpretable reactivity prediction of transition-metal catalysts.

In this talk, we are going to use the electrooxidation of ammonia to dinitrogen as a specific case. The reaction plays an important role within the global nitrogen cycle. It has many applications including electrochemical sensing of ammonia, wastewater remediation, and direct ammonia fuel cells. While platinum (Pt) catalysts, specifically terminated with (100) facets, have shown promising activity. They still suffer from a large overpotential ( $\sim 0.5$  V) and surface deactivation. One approach that has been utilized to tackle these issues is the use of Pt-based alloys<sup>2</sup>. With adsorption energies of key intermediates, e.g.,  $\ast\text{N}$  species at bridge and hollow sites, as reactivity descriptors, we demonstrate that the TinNet outperforms the purely data-driven ML methods in prediction performance, especially for out-of-sample systems with unseen structural and electronic features. Incorporation of scientific knowledge of physical interactions into learning from data sheds further light on the nature of chemical bonding and opens up new avenues for ML discovery of novel motifs with desired catalytic properties.

(1) Wang, S.-H.; Pillai, H. S.; Wang, S.; Achenie, L. E. K.; Xin, H. Infusing Theory into Machine Learning for Interpretable Reactivity Prediction. arXiv [physics.chem-ph], 2021.

(2) Li, Y.; Li, X.; Pillai, H. S.; Lattimer, J.; Mohd Adli, N. Ternary PtIrNi Catalysts for Efficient Electrochemical Ammonia Oxidation. ACS **2020**.

# The Catalysis Club of Philadelphia

*Promoting the science of catalysis since 1949.*

## Catalytic pyrolysis of Biomass: Development and Demonstration

Charles A. Mullen

USDA-ARS Eastern Regional Research Center

600 E. Mermaid Ln.

Wyndmoor, PA 19038

Fast pyrolysis is an efficient biomass liquefaction process to convert biomass into an energy dense liquid (bio-oil) that can potentially be an intermediate for the production of advanced bio-fuels and renewable chemicals. However, bio-oil is a highly oxygenated mixture of organic compounds, including carboxylic acids, aldehydes, ketones, ethers, and phenolics thereby posing stability problems. This instability tends to produce an intractable solid upon heating during most refining processes including distillation or further refining via hydrotreating. Therefore, a significant amount of research has been undertaken to develop processes that produce a partially deoxygenated and stable bio-oil. Catalytic fast pyrolysis (CFP) over microporous ZSM-5 type zeolites has been the most cited and practiced method for pre-condensation deoxygenation of bio-oil, resulting in production of mostly aromatic hydrocarbons. More recently, various other catalysts and processes have been developed to increase the carbon efficiency of CFP.

The Agricultural Research Service, as part of a NIFA funded Biomass Research and Development project titled Distributed On-Farm Bioenergy, Biofuels & Biochemicals (FarmBio<sup>3</sup>) has developed a mobile pyrolysis unit, designed to demonstrate biomass fast pyrolysis and catalytic pyrolysis over zeolites at scale of 83.3 kg h<sup>-1</sup> (two metric tons per day, MTPD). The trailer-mounted pyrolysis apparatus is based on the combustion reduction integrated pyrolysis system (CRIPS), a patented, dual fluidized bed, biomass pyrolysis design developed by USDA and the University of Pretoria. The operation of the CRIPS was demonstrated for both fast and catalytic pyrolysis over HZSM-5 for conversion of switchgrass. Organic bio-oil yields for fast and catalytic pyrolysis were in the 45% and 5–10% ranges respectively, demonstrating production of large volumes of bio-oil on-farm. Bio-oil quality for catalytic pyrolysis was consistent over several hours on stream due to continuous catalyst regeneration that the design affords yielding high levels of BTEX compounds; however, deactivation due to alkali contamination was noticeable at cumulative biomass to catalyst ratios of > 6/1.

This presentation will cover zeolite catalyst property-activity relationships elucidated as part of the FarmBio<sup>3</sup> project and the operation and results of the demonstration scale tests described above. Other developments from our laboratory on biomass catalytic fast pyrolysis including use of bio-char based catalysts, development of renewable carbon materials and co-pyrolysis with waste plastics will also be discussed.

# The Catalysis Club of Philadelphia

*Promoting the science of catalysis since 1949.*

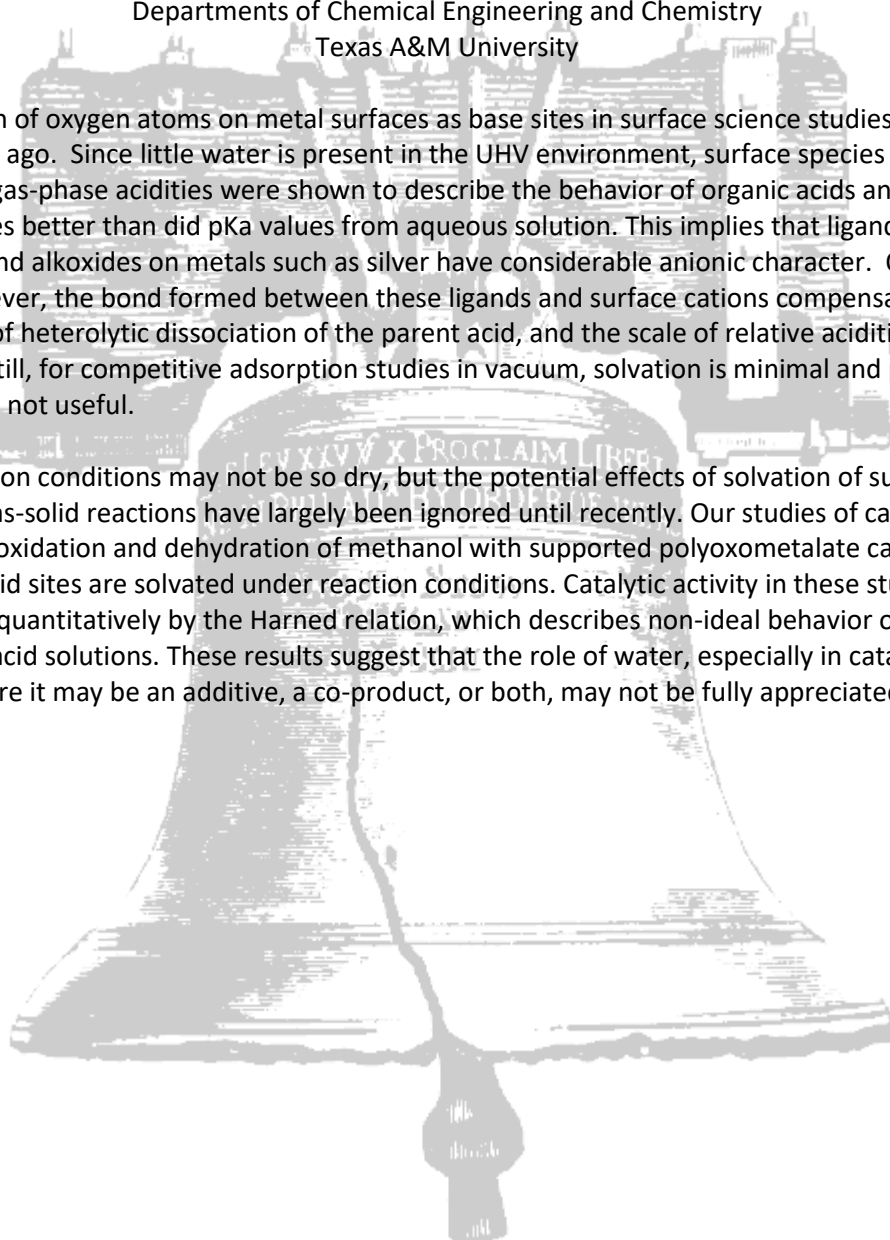
## A forty-year tour of surface acid-base chemistry: from solution to the gas phase and back again

Mark A. Barteau

Departments of Chemical Engineering and Chemistry  
Texas A&M University

The description of oxygen atoms on metal surfaces as base sites in surface science studies emerged about 40 years ago. Since little water is present in the UHV environment, surface species are not solvated, and gas-phase acidities were shown to describe the behavior of organic acids and their conjugate bases better than did pKa values from aqueous solution. This implies that ligands such as carboxylates and alkoxides on metals such as silver have considerable anionic character. On metal oxide surfaces, however, the bond formed between these ligands and surface cations compensates for much of the energy of heterolytic dissociation of the parent acid, and the scale of relative acidities becomes compressed. Still, for competitive adsorption studies in vacuum, solvation is minimal and pKa values of adsorbates are not useful.

Catalytic reaction conditions may not be so dry, but the potential effects of solvation of surface species in nominally gas-solid reactions have largely been ignored until recently. Our studies of cation exchange effects on the oxidation and dehydration of methanol with supported polyoxometalate catalysts suggest that surface acid sites are solvated under reaction conditions. Catalytic activity in these studies can be accounted for quantitatively by the Harned relation, which describes non-ideal behavior of highly concentrated acid solutions. These results suggest that the role of water, especially in catalytic processes where it may be an additive, a co-product, or both, may not be fully appreciated.



# The Catalysis Club of Philadelphia

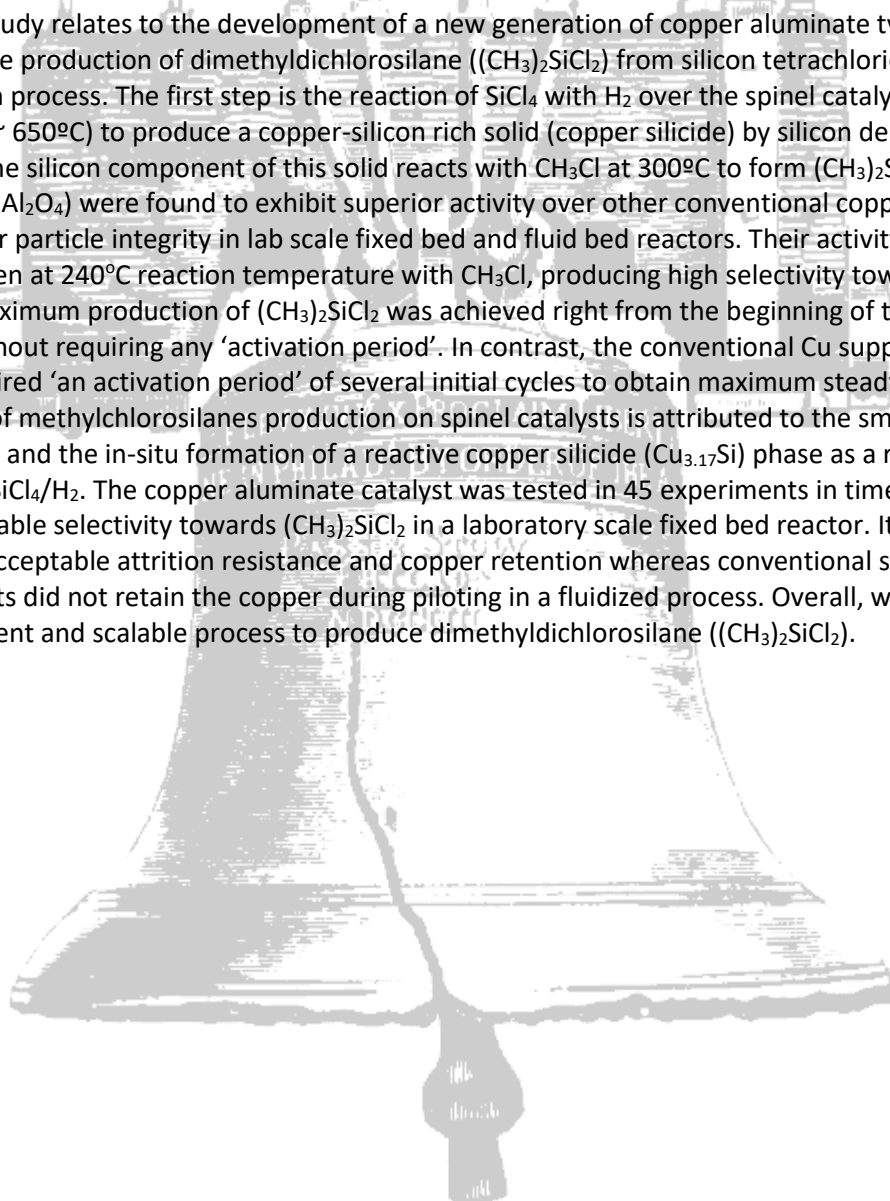
*Promoting the science of catalysis since 1949.*

## Two-Step Process for the Synthesis of Dimethyldichlorosilane using Copper Aluminate Catalysts

Krishna Janmanchi and Dimi Katsoulis

Process Research & Development, Dow Silicones Corporation, Midland, MI 48686

The present study relates to the development of a new generation of copper aluminate type spinel catalysts for the production of dimethyldichlorosilane ( $(\text{CH}_3)_2\text{SiCl}_2$ ) from silicon tetrachloride ( $\text{SiCl}_4$ ) in a 2-step reaction process. The first step is the reaction of  $\text{SiCl}_4$  with  $\text{H}_2$  over the spinel catalysts at high temperature ( $\sim 650^\circ\text{C}$ ) to produce a copper-silicon rich solid (copper silicide) by silicon deposition. In the second step, the silicon component of this solid reacts with  $\text{CH}_3\text{Cl}$  at  $300^\circ\text{C}$  to form  $(\text{CH}_3)_2\text{SiCl}_2$ . Copper aluminates ( $\text{CuAl}_2\text{O}_4$ ) were found to exhibit superior activity over other conventional copper catalysts and held better particle integrity in lab scale fixed bed and fluid bed reactors. Their activity was maintained even at  $240^\circ\text{C}$  reaction temperature with  $\text{CH}_3\text{Cl}$ , producing high selectivity towards  $(\text{CH}_3)_2\text{SiCl}_2$ . Maximum production of  $(\text{CH}_3)_2\text{SiCl}_2$  was achieved right from the beginning of the reaction with  $\text{CH}_3\text{Cl}$  without requiring any 'activation period'. In contrast, the conventional Cu supported catalysts, required 'an activation period' of several initial cycles to obtain maximum steady state activity. The high rate of methylchlorosilanes production on spinel catalysts is attributed to the smaller particle sizes of copper and the in-situ formation of a reactive copper silicide ( $\text{Cu}_{3.17}\text{Si}$ ) phase as a result of the reaction with  $\text{SiCl}_4/\text{H}_2$ . The copper aluminate catalyst was tested in 45 experiments in time on stream and showed stable selectivity towards  $(\text{CH}_3)_2\text{SiCl}_2$  in a laboratory scale fixed bed reactor. It demonstrated superior and acceptable attrition resistance and copper retention whereas conventional supported copper catalysts did not retain the copper during piloting in a fluidized process. Overall, we developed a low cost, efficient and scalable process to produce dimethyldichlorosilane ( $(\text{CH}_3)_2\text{SiCl}_2$ ).



# The Catalysis Club of Philadelphia

*Promoting the science of catalysis since 1949.*

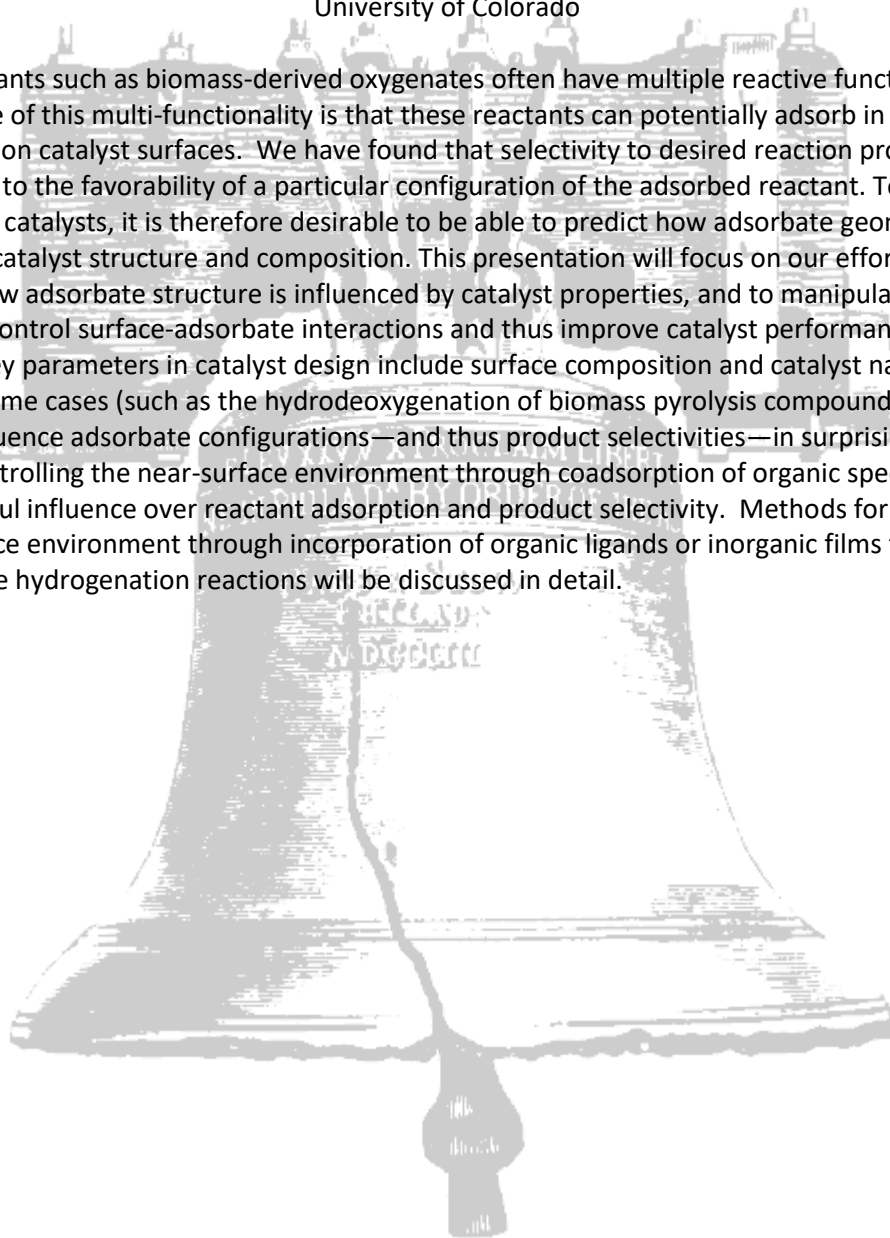
---

## Controlling selectivity in reactions of complex oxygenates over metal catalysts

Will Medlin

University of Colorado

Complex reactants such as biomass-derived oxygenates often have multiple reactive functional groups. A consequence of this multi-functionality is that these reactants can potentially adsorb in many configurations on catalyst surfaces. We have found that selectivity to desired reaction products is often closely related to the favorability of a particular configuration of the adsorbed reactant. To engineer more selective catalysts, it is therefore desirable to be able to predict how adsorbate geometry is influenced by catalyst structure and composition. This presentation will focus on our efforts to understand how adsorbate structure is influenced by catalyst properties, and to manipulate those properties to control surface-adsorbate interactions and thus improve catalyst performance. Not surprisingly, key parameters in catalyst design include surface composition and catalyst nanostructure. However, in some cases (such as the hydrodeoxygenation of biomass pyrolysis compounds) these properties influence adsorbate configurations—and thus product selectivities—in surprising ways. Moreover, controlling the near-surface environment through coadsorption of organic species is seen to exert a powerful influence over reactant adsorption and product selectivity. Methods for engineering the near-surface environment through incorporation of organic ligands or inorganic films for chemoselective hydrogenation reactions will be discussed in detail.



## Tuning the Surface Active Sites by Surface Modification of Supported $\text{ReO}_x/(\text{SiO}_2\text{-Al}_2\text{O}_3)$ Catalysts for Olefin Metathesis

Bin Zhang<sup>1</sup>, Soe Lwin<sup>1</sup>, Shuting Xiang<sup>2</sup>, Anatoly I. Frenkel<sup>2,3</sup>, Israel E. Wachs<sup>1</sup>

<sup>1</sup> Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical & Biomolecular Engineering, Lehigh University, Bethlehem, PA, 18015, United States

<sup>2</sup> Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY, 11794, United States

<sup>3</sup> Division of Chemistry, Brookhaven National Laboratory, Upton, NY 11973, United States

Due to the global shortage of propylene, the chemical industry is turning to metathesis of ethylene and 2-butene to produce on purpose propylene. Heterogeneous supported  $\text{ReO}_x/\text{Al}_2\text{O}_3$ ,  $\text{MoO}_x/\text{Al}_2\text{O}_3$  and  $\text{WO}_x/\text{SiO}_2$  catalysts have been found to be most efficient for metathesis of olefins. Although the supported  $\text{ReO}_x/\text{Al}_2\text{O}_3$  catalyst has received much attention for olefin metathesis, the effect of the oxide support on olefin metathesis by supported  $\text{ReO}_x$  catalysts is still not well understood. For the most common  $\text{Al}_2\text{O}_3$  support, not all rhenia anchoring sites lead to activation of rhenia for olefin metathesis. Mixed oxide  $\text{Al}_2\text{O}_3\text{-SiO}_2$  supports are highly effective supports for promoting surface  $\text{ReO}_x$  sites for olefin metathesis. The improved metathesis performance of the  $\text{Al}_2\text{O}_3\text{-SiO}_2$  mixed oxide supports has been attributed to the modified surface Lewis and Brønsted acidity, but supporting data have not been provided in these studies because the nature of the surface  $\text{AlO}_x$ ,  $\text{SiO}_x$  and  $\text{ReO}_x$  sites present in these mixed oxide supports are still unknown. The objective of the present study is to determine the origin of the enhanced performance of the surface  $\text{ReO}_x$  sites on  $\text{Al}_2\text{O}_3\text{-SiO}_2$  mixed oxide supports.

Modern in situ molecular spectroscopy (UV-Vis, Raman, IR and XAS) and chemical probe studies (ammonia chemisorption,  $\text{C}_2^-/\text{C}_4^-$ -titration,  $\text{C}_3\text{H}_6$ -TPSR and steady-state propylene self-metathesis) of the surface  $\text{ReO}_x$  sites on  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and surface modified mixed oxide supports (5%  $\text{SiO}_x/\text{Al}_2\text{O}_3$ , 5%  $\text{AlO}_x/\text{SiO}_2$ , and ZSM-5 ( $\text{Si}/\text{Al}=15$ )) were applied to address the origin of the promotional effect. The characterization studies of the supported rhenia catalysts demonstrated that the enhanced activity on  $\text{Al}_2\text{O}_3\text{-SiO}_2$  mixed oxide supports is due to the anchoring of rhenia at acidic surface hydroxyls ( $\text{Al}_3\text{-OH}$  and  $\text{Al}(\text{OH})^+\text{-Si}$ ) that results in a greater number of activated surface  $\text{ReO}_x$  sites. These findings demonstrate that the olefin metathesis activity of supported rhenia catalysts are tuned by modifying the nature of the anchoring surface hydroxyls present on the oxide support.

# The Catalysis Club of Philadelphia

*Promoting the science of catalysis since 1949.*

---

**Notes:**

