Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room A213 - Session HC+OX+SS-WeA

Metal-Support Interactions Driving Heterogeneously-Catalyzed Reactions

Moderators: Aravind Asthagiri, The Ohio State University, Jason Weaver, University of Florida

2:20pm HC+OX+SS-WeA1 Yittria-stabilized Zirconia (YSZ) Supports for Low Temperature Ammonia Synthesis, *Z. Zhang, S. Livingston,* Colorado School of Mines*; L. Fitzgerald,* University College Dublin*; J.D. Way, **Colin Wolden**,* Colorado School of Mines

The use of renewable hydrogen for distributed synthesis of ammonia requires the development of efficient catalysts and processes that operate under mild conditions. Here we introduce yittria stabilized zirconia (YSZ) as a more active Ru catalyst support for NH_3 synthesis than traditionally used supports such as Al_2O_3. The addition of Cs promoter increased rates an order of magnitude higher by reducing the apparent activation energy from 103 kJ/mol to 65 kJ/mol. The rate enhancement is largely insensitive to the amount of promoter addition, with Cs outperforming Ba and K by a factor of 2. At 400°C under 1.0 MPa, the synthesis rate was comparable with that of most active oxide-supported Ru catalysts. The rate becomes inhibited by H_2 absorption at low temperature (< 350°C), but the use of lower H_2:N_2 ratios enables the rate to remain comparable to what is observed in stoichiometric mixtures at temperatures > 400°C. A detailed microkinetic model was developed that successfully captures the observed behavior, revealing that adsorption is coverage dependent. These results provide insight and direction into developing alternatives to Haber-Bosch for distributed synthesis of green ammonia.

2:40pm HC+OX+SS-WeA2 Operando PTRF-XAFS Technique for 3D Structure Determination of Active Metal Sites on a Model Catalyst Surface under Working Conditions, *Satoru Takakusagi, L. Bang, D. Kido, Y. Sato, K. Asakura,* Hokkaido University, Japan

Polarization-dependent total reflection fluorescence (PTRF)-XAFS is a powerful technique which can determine 3D structure of highly dispersed metal species on a single-crystal surface by measuring polarization-dependent XAFS of the metal species. To obtain atomic-level understanding of metal/oxide-support interaction in heterogeneous catalysis, we have determined the precise 3D structures of single metal atoms and metal clusters deposited on single-crystal oxide surfaces such as TiO_2(110) and Al_2O_3(0001) by UHV PTRF-XAFS apparatus.[1]

Recently we have constructed a new apparatus which enables us to measure PTRF-XAFS of active metal species dispersed on a single-crystal oxide surface under working condition. A compact vacuum chamber which works both as PTRF-XAFS cell and batch-type reactor was designed and constructed. The sample can be transferred without exposure to air from another UHV chamber where the sample preparation (ion sputtering, annealing and metal deposition) and its surface characterization (LEED, XPS) are carried out. The sample in the compact chamber can be heated at high temperatures (< 700 °C in the presence of reactant gases (typically 10~100 Pa), which makes the operando PTRF-XAFS measurements possible. Thus 3D structure-activity relationship of the active metal species on an oxide surface in heterogeneous catalysis can be obtained. We will show the details of the operando PTRF-XAFS technique and its application to CO oxidation on a Pt/Al_2O_3(0001) surface.

(References)

[1] S. Takakusagi et al., *Chem. Rec.* **18** (2018) 1*, J. Phys. Chem. C***120** (2016) 15785, *Top. Catal.* **56**(2013*)* 1477, *Phys. Chem. Chem. Phys.* **15**(2013*)* 14080.

3:00pm HC+OX+SS-WeA3 Understanding and Tuning Catalytic Materials Using Nanocrystal Precursors, *Matteo Cargnello,* Stanford University
INVITED

Catalytic processes are central to the goal of a sustainable future. A promising approach in developing catalytic materials is represented by the design of catalytic sites based on the knowledge of reaction mechanisms and structure-property relationships and aided by computation, and in the precise synthesis of these sites at the atomic and molecular level. The materials-pressure gap, however, still hinders the full realization of this strategy. Nanocrystal precursors, with tunable active sites and compositions, can help bridge this gap. The goal of this talk is to show how

this approach can provide not only fundamental understanding of catalytic reactions, but also~ represents a way to precisely engineer catalytic sites and metal-support interactions to produce efficient catalysts that are active, stable and selective for several important catalytic transformations. Examples of the use of these building blocks as supported systems or in combination with hybrid organic materials will be shown, both to understand trends in methane and CO2 activation, and in the preparation of optimized catalytic systems combining multiple active phases. In all these examples, important efforts to obtain useful structure-property relationships will be highlighted, with this knowledge used to prepare more efficient catalysts for sustainable production of fuels and chemicals.

4:20pm HC+OX+SS-WeA7 CO₂ Hydrogenation on Supported Zirconium Oxide Clusters, *Yilin Ma[1],* Stony Brook University*; M.G. White,* Brookhaven National Laboratory

In this work, zirconium atoms and zirconium oxide clusters are deposited onto metal/metal oxide surfaces as model "inverse" catalysts for the study of CO_2 hydrogenation. The control over the stoichiometry of clusters and the oxidation state of the metal centers enables the study of atomic level details such as identification of active sites, interfacial electron transfer and the role of sulfur vacancies. Recent AP-XPS, AP-IR and STM results of supported zirconium oxide on Cu_2O/Cu(111) surface will be presented. Reactivity studies over Zr/Cu_2O/Cu(111) show that the formation of CO_2^-(ad)and $HCOO^-$ can be seen on regions with the presence of Zr on Cu_2O surface during the reaction condition(CO_2/H_2=1, total pressure=0.5torr), however CO_2 only binds weakly on bare Cu_2O/Cu(111) surface. Moreover, the change of zirconium oxidation state indicates the adsorption of CO_2 happens on metal or metal-support interface, where the zirconium gets oxidized when exposing to CO_2. Some DFT studies of above systems will also be shown, including the electronic structures of clusters, binding sites of CO_2 molecules, etc.

4:40pm HC+OX+SS-WeA8 Tuning Surface Hydrophobicity to Enhance Reaction Rate of the Lewis Acid Zeolite Nano Sn Beta for Alcohol Ring Opening of Epoxides, *Nicholas Brunelli, A.P. Spanos, A. Parulkar, N. Deshpande,* The Ohio State University

Ring opening epoxides produces compounds that are valuable in the production of fine chemicals and pharmaceuticals. Recent work[1]has demonstrated that the bulky reactants typically involved in fine chemical synthesis benefit from reducing the length scale of the materials to produce nano-zeolites (nano-Sn-Beta), which requires using a custom-synthesized structure directing agent in hydroxide conditions. While the nanozeolites can achieve higher overall conversion than Sn-Beta synthesized using fluoride conditions, the initial reaction rate is higher for Sn-Beta that tends to be hydrophobic compared to nano-Sn-Beta that is demonstrated to be hydrophilic. These results suggest that the alcohol ring opening reaction is sensitive to the reaction environment. The surface of nano-Sn-Beta can be treated to reduce the amount of defects and correspondingly increase the hydrophobicity. Interestingly, the treatment of nano-Sn-Beta materials more than doubles the observed reaction rate. Overall, this demonstrates a valuable method to tune the reaction environment that could be widely applicable to many chemical reactions.

References

(1) Parulkar, A.; Spanos, A. P.; Deshpande, N.; Brunelli, N. A. Synthesis and catalytic testing of Lewis acidic nano zeolite Beta for epoxide ring opening with alcohols. *Applied Catalysis A: General,* **2019**, *577,* 28–34.

5:00pm HC+OX+SS-WeA9 Understanding Metal-Metal and Metal-Support Interactions in Bimetallic Catalysts, *Donna Chen,* Univeristy of South Carolina*; S. Farzandh, D.M. Shakya, A.J. Brandt, T.D. Maddumapatabandi,* University of South Carolina
INVITED

Bimetallic catalysts are known to exhibit superior properties compared to their individual pure metal components, but in many cases the nature of these improved properties is not well understood. The main goal of this work is to understand how oxidation states, metal-support interactions, and metal-metal interactions in supported bimetallic clusters can be used to control catalytic activity. Specific catalytic reactions investigated are the water gas shift reaction (WGS)on Pt-Re and selective hydrogenation of unsaturated aldehydes on Pt-Sn. Model catalyst surfaces are prepared via vapor-deposition of metal clusters on single-crystal oxide and carbon supports. These surfaces are fully characterized by a variety ultrahigh vacuum (UHV) surface science techniques and their activities are studied in a microreactor (P~ 1 atm) coupled to the UHV chamber. Scanning tunneling

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[1] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

microscopy investigations indicate that exclusively bimetallic clusters can be prepared by sequential deposition of metals. For the WGS reaction, the active site is determined to be Pt with subsurface Re, while Re oxide does not play a role. Density functional theory studies show that the presence of subsurface Re decreases the adsorption energy of CO on Pt, thus preventing Pt active sites from being poisoned by CO. WGS activity increases with increasing perimeter for Pt/TiO_2 clusters, and the turnover frequency is also lower in the absence of the TiO_2 support. For hydrogenation on furfural, the Pt-Sn alloy surface exhibits high selectivity to furfuryl alcohol compared to pure Pt, whereas furan and tetrahydrofuran are the main products on Pt.

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