

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-WeM

Advances in Materials and Analysis in Heterogeneous Catalysis II

Moderators: Sanjaya Sennayake, Brookhaven National Laboratory, Jason Weaver, University of Florida

8:20am **HC+AS+SS-WeM-2 Development and Characterization of Highly Stable ALD Coated Catalysts for Dehydrogenation of Light Alkanes, Jonathan Travis, J. Burger, A. Dameron, Forge Nano**

Catalysts are critical materials for enabling many modern industrial chemical processes, such as the dehydrogenation of light alkanes to produce "on purpose" alkenes. Catalyst deactivation costs the chemical industry billions of dollars. One of the major mechanisms of deactivation is metal sintering during high temperature regeneration. Atomic Layer Deposition (ALD) overcoating has previously been demonstrated to stabilize catalyst materials against sintering and deactivation, as well as improve selectivity in certain cases. In this study the properties and performance of 0.1% Pt/Al₂O₃ catalysts are investigated as a function of surface modification via ALD Al₂O₃ coatings. The catalysts are characterized in Forge Nano's in-house catalyst characterization laboratory. Physical characterization is performed using various techniques including moisture analysis, BET Surface Area, Porosimetry, TGA, CO Chemisorption, ICP-MS, and Temperature Programmed Reduction, Desorption, and Oxidation. Performance is characterized using propane dehydrogenation under a variety of conditions. This talk will present the effects of Forge Nano's ALD Al₂O₃ coating on the properties and performance of the 0.1% Pt/Al₂O₃ catalysts.

8:40am **HC+AS+SS-WeM-3 Combining Theory with Ambient Pressure XPS to Reveal Chemistry at Interfaces Under *In Situ* and *Operando* Conditions, Ethan Crumlin, Lawrence Berkeley National Laboratory** INVITED

Interfaces play an essential role in nearly all aspects of life and are critical for electrochemistry. Electrochemical systems ranging from high-temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of essential interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and converted. This talk will focus on using ambient pressure XPS (APXPS) to directly probe the solid/gas and solid/liquid electrochemical interface. APXPS is a photon-in/electron-out process that can provide both atomic concentration and chemical-specific information at pressures greater than 20 Torr. Using synchrotron X-rays at Lawrence Berkeley National Laboratory, the Advanced Light Source has several beamlines dedicated to APXPS endstations that are outfitted with various *in situ/operando* features such as heating to temperatures > 500 °C, pressures greater than 20 Torr to support solid/liquid experiments and electrical leads to support applying electrical potentials support the ability to collect XPS data of actual electrochemical devices while it's operating in near ambient pressures. This talk will share our efforts to combine theory and APXPS to understand the chemistry at solid/gas and solid/liquid interfaces under *in situ* and *operando* conditions. At the solid/gas interface, we will share our work to understand how carbon dioxide interacts with copper and silver surfaces using APXPS and theory to generate observables that we could experimentally verify. Separately I will introduce our strategy to introduce a chemical reaction network to generate spectra of water interacting with a silver surface that directly resembled our APXPS measurements. At the solid/liquid interface, the combination of theory and APXPS revealed how stable magnesium electrodes and stable diglyme electrolytes could be unstable when in contact with each other. In addition, it facilitated the prediction of the sensitivity for probing interfacial chemical species at a solid/liquid interface. To further advance these directions and synergy for combining theory and experiments, I will show our recent progress in creating an interfacial Digital Twin that we hope will rapidly accelerate our understanding of interfacial chemistry.

9:20am **HC+AS+SS-WeM-5 The Electrochemical Interface as a Reactive Environment to Resynthesize Electrode Surface Chemistry Using the Dissolution-Redeposition Dynamics, Feng Lin, Virginia Tech** INVITED

The solid-liquid electrochemical interface offers a two-dimensional environment for geometrically confined interfacial reactions to tailor electrode surface chemistry under operating conditions. Herein, we

demonstrate that the dissolution and redeposition kinetics of transition metal cations, a ubiquitous phenomenon at the electrochemical interface, can be manipulated to regulate the chemical composition and crystal structure of the electrode surface as well as the overall electrochemical performance. Foreign cations, either added as electrolyte additives or dissolved from surface coatings, can rapidly participate in the electrode dissolution-redeposition process, and facilitate the establishment of the dissolution-redeposition equilibrium. We will present scientific case studies in electrocatalysis. Our work expands the control over the electrochemical reactions at the solid-liquid interface and provides new insights into interfacial studies in electrochemistry, and surface science.

11:00am **HC+AS+SS-WeM-10 Ambient Pressure Spectroscopy of Catalytic Porous Nanofilms, C. Eads, MAX IV Laboratory, Sweden; T. Hu, S. Tenney, Ashley Head, Brookhaven National Laboratory** INVITED

Porous materials offer an opportunity for catalysis in confined spaces. By spatially confining chemistry, reaction dynamics and selectivity can change in unknown ways. Two examples will be discussed, including Pt nanoparticles embedded in a thin film of the metal-organic framework UiO-66(NH₂) and a two-dimensional silicate on Pd(111). Ambient pressure X-ray photoelectron spectroscopy (APXPS) has been used to characterize the electronic structure of the Pt-embedded metal-organic framework. CO oxidation and CO₂ reduction have been followed with IR spectroscopy and mass spectrometry. In a second system, the space between a two-dimensional silicate and a Pd(111) surface promotes more CO oxidation than a bare Pd surface. IR spectroscopy shows that the silicate film changes the surface adsorbates, resulting in increased CO₂ formation, as confirmed with mass spectrometry. These results will help enable the rational design of materials to spatially confine reactions in a desired way.

11:40am **HC+AS+SS-WeM-12 Catalytic Oxidation of Methane on IrO₂(110) Films, Jovenal Jamir, R. Martin, University of Florida; M. Kim, Yeungnam University, Republic of Korea; C. Lee, V. Mehar, University of Florida; A. Asthagiri, The Ohio State University; J. Weaver, University of Florida**

In recent years, IrO₂(110) films have gained increasing interest for their ability to strongly adsorb light alkanes and cleave C-H bonds below room temperature. Our group has shown, via ultrahigh vacuum (UHV) temperature programmed reaction spectroscopy (TPRS) experiments, that initial methane activation occurs at temperatures as low as 100 K and leads to the desorption of CO, CO₂ and H₂O above 400 K. The large temperature range over which partially oxidized methane-derived species exist, along with the facile nature of C-H bond cleavage motivates further study of methane oxidation under catalytically relevant conditions. In this talk I will discuss recent kinetic studies performed in a batch reactor to investigate the catalytic oxidation of CH₄ on IrO₂(110) films at gas pressures near 1 Torr as well as results of ambient pressure x-ray photoelectron spectroscopy (AP-XPS) measurements and molecular simulations. We find that IrO₂(110) is highly active for the catalytic combustion of CH₄ at moderate temperatures (500-650 K), with comparable activities to PdO catalysts. Our results further show that catalytic CH₄ oxidation is mildly activated on IrO₂(110) and that the catalytic rates depend slightly inversely on the O₂ partial pressure, suggesting that the dissociative chemisorption of O₂ is more efficient than CH₄ activation and acts to block CH₄ adsorption sites. AP-XPS measurements reveal that high coverages of OH groups and CH₃O₂ species form on IrO₂(110) during CH₄ oxidation and that O-rich IrO₂(110) surfaces are maintained even under highly CH₄-rich conditions (up to 95% CH₄), consistent with efficient O₂ adsorption and site competition with CH₄. Finally, I will discuss how we have combined our AP-XPS results with catalytic rate measurements to develop first principles, microkinetic models for methane oxidation over IrO₂(110). Of particular significance is that earlier models did not consider surface CH₃O₂ species. Our AP-XPS results thus inspired efforts to identify additional reactions and determine the roles that various adsorbed species play during catalytic CH₄ oxidation on IrO₂(110). Our findings highlight how *operando* surface spectroscopy can provide key guidance for understanding catalytic reaction mechanisms and developing accurate kinetic models.

Wednesday Morning, November 9, 2022

12:00pm **HC+AS+SS-WeM-13 HC Graduate Student Finalist Talk: *Operando* Observation of Metal Encapsulation Causing Strong Metal-Support Interaction at the Pt-Co₃O₄ Interface, *Daeho Kim***, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea; *D. Park*, Korea Advanced Institute of Science and Technology, Republic of Korea; *H. Song*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea; *B. Jeong*, Korea Basic Science Institute (KBSI), Republic of Korea; *Y. Jung*, Korea Advanced Institute of Science and Technology, Republic of Korea; *J. Park*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Noble metal nanoparticles (NPs) supported on metal oxide (e.g., Co₃O₄, NiO, TiO₂, CeO₂, and Fe₂O₃) have been commonly utilized as a heterogeneous catalyst for improving catalytic performance and modifying the reaction pathway of various catalytic reactions, such as CO oxidation, CO₂ hydrogenation, and Fischer-Tropsch synthesis. The unique interaction at the interface of the metal NP and oxide, which is known as the strong metal-support interaction (SMSI), gives synergistic enhancement to the catalytic activity. Hence, a fundamental understanding of SMSI with bridging pressure and material gaps using operando surface characterization is necessary for developing high-performance heterogeneous catalysts.

Herein, we show the direct evidence of SMSI at the interface of Pt NP and Co₃O₄, utilizing operando surface analysis. The Pt-Co₃O₄ interfaces were prepared as powder catalysts using colloidal Pt NPs embedded on the mesoporous Co₃O₄. The two-dimensional model system is also constructed on Co₃O₄-coated Si wafer via a Langmuir-Blodgett trough to bridge the material gap. The surface of prepared Pt-Co₃O₄ is comprehensively characterized under dynamic conditions: a reducing environment (H₂ or CO) and a catalytic reaction environment (CO + O₂). Combining computational calculation and the operando surface characterizations using ambient pressure X-ray photoelectron spectroscopy, environmental transmission electron microscopy, and diffuse reflectance infrared Fourier-transform spectroscopy, we suggest that the interface between Pt NPs and the thin oxide overlayer is a key state of the SMSI enhancing the catalytic activity.

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