

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room A213 - Session HC+2D+SS-ThM

Nanoscale Surface Structure in Heterogeneously-Catalyzed Reactions

Moderators: Rebecca Fushimi, Idaho National Laboratory, Eric High, Tufts University

8:20am **HC+2D+SS-ThM2 Low-temperature Investigation of Propylene on TiO₂/Au(111)**, *M. Gillum, M. DePonte, J. Wilke, E. Maxwell, V. Lam, D. Schlosser, Ashleigh Baber*, James Madison University

The partial oxidation of propylene creates industrially important feedstocks that are used in a multitude of chemical fields ranging from textiles to cosmetics to air sanitation. One avenue of research on propylene oxidation is being conducted using metal/oxide model catalysts, as they have shown an affinity for high selectivity oxidation reactions. To gain a comprehensive understanding of olefin intermolecular and surface interactions, temperature programmed desorption (TPD) studies were conducted using Au(111)-based model catalysts with different surface preparations. Using TPD, we were able to identify the specific adsorption sites of propylene on a TiO₂/Au(111) model catalyst, differentiating between the TiO₂ nanoparticles, the Au-TiO₂ interface, and the gold surface. Desorption kinetics propylene were studied on pristine and titania-modified Au(111) surfaces. Desorption products were monitored using quadrupole mass spectrometry and the surface morphology was analyzed using ex-situ atomic force microscopy. The presence of titania was confirmed via X-ray photoelectron spectroscopy. By understanding the characteristic behaviors with combined experimental techniques, active sites and reaction pathways for partial olefin oxidation over Au-based catalysts may be identified.

8:40am **HC+2D+SS-ThM3 Structure and Reactivity of Supported Oxide and Metal Nanoparticles**, *Geoff Thornton*, University College London, UK
INVITED

Heterogeneous catalysts typically consist of metal nanoparticles on an oxide support. Model experiments involving nanoparticle growth on single crystalline oxide have been successfully employed to understand aspects of the nucleation, structure and reactivity. This contributes to catalysis design programs. Many subtleties continue to emerge, some of which will be discussed in this talk. For instance, low temperature STM experiments have allowed direct imaging of CO overlayers formed on the Pd nanoparticles themselves supported on TiO₂. The results show that the nanoparticles grow like a carpet over substrate step-edges, giving rise to a curved top facet that changes the adsorption behavior. Au nanoparticles supported by TiO₂ have been the subject of much work since the discovery by Haruta that Au is a low temperature oxidation catalyst. Despite this earlier work there has been no definitive evidence for the binding site or the direction of charge transfer associated with gold atoms and nanoparticles on the model substrate TiO₂(110). We show with STM that single Au atoms are in indeed bound to oxygen vacancies on the substrate, with dimers similarly anchored. Associated DFT calculations suggest electron transfer from bridging O vacancies to Au. XPEEM in conjunction with STM have also been used to probe the electronic character of Au nanoparticles as a function of particle size and coverage. Pt and related metals on CeO₂/ZrO₂ are used for CO oxidation in autocats. The accepted mechanism is that the oxide supplies oxygen to the metal to react with CO, with the oxide being directly reoxidized. In XPEEM studies of a model inverse catalyst we show that the reoxidation can also involve the metal.

9:40am **HC+2D+SS-ThM6 Structural and Chemical Effects of Cesium on the Cu(111) and Cu₂O/Cu(111) Surface**, *Rebecca Hamlyn*¹, Stony Brook University; *M. Mahapatra*, Brookhaven National Laboratory; *I. Orozco*, Stony Brook University; *M.G. White*, *S. Senanayake*, *J.A. Rodriguez*, Brookhaven National Laboratory

Surface additives, particularly those of alkali metals, are commonly used for promotion of catalytic processes. These processes include carbon oxide reactions such as the water-gas shift and methanol synthesis over Cu-based catalysts. Both reactions are known to be promoted by Cs doping. Partially oxidized Cu is also understood to have a critical role in the activity of the aforementioned processes, as strictly metallic copper will not survive under

redox conditions. In an effort to better understand how small additions of alkalis such as Cs act as promoters, we have carried out model studies of cesium over a metallic and oxidized copper surface using scanning tunneling microscopy and x-ray photoelectron spectroscopy. We find that the oxide structure assists in anchoring Cs over the weaker electrostatic interactions with the bare copper surface, allowing for room temperature imaging. Furthermore, with higher coverages or elevated temperature, cesium induces formation of a new ordered structure. This work provides a molecular-scale understanding of the cesiated surface, and serves as a basis for insight toward its mechanism of action in conversion of relevant gases (H₂O, CO, CO₂).

11:00am **HC+2D+SS-ThM10 Mythbusting: From Single Crystals in UHV to Catalytic Reactors**, *R.J. Madix, Christian Reece*, Harvard University **INVITED**
For decades it has been an objective of surface science studies of chemical reactivity to make a direct connection to heterogeneous catalysis. Over these years the difficulties encountered in connecting these two areas of research gave rise to the dismissal of this possibility by the catalysis community and the invention of such shorthand terms as “pressure gap” and “materials gap” to express this view. Usually overlooked is also the fact that catalytic reactions are conducted at much higher temperatures than the related studies on single crystal surfaces, so a “temperature gap” also exists. In fact, these regimes of reactivity are directly linked by fundamental knowledge of the identity and rate constants for the operative elementary steps comprising the catalytic cycle under catalytic conditions. Further, for many catalytic materials, its state can be defined by the reaction conditions themselves in quasi-thermodynamic terms. Connection between the reactivity observed on the single crystals with that on the catalyst surface is possible by the use of a transient pressure method which is conducted over the actual catalyst material under Knudsen flow conditions. Recently we have demonstrated this historically elusive connection between UHV-based studies and catalytic performance for the catalytic oxygen-assisted synthesis of methyl formate from methanol over a nanoporous gold catalyst. The connection is entirely based on the kinetics and mechanism determined on single crystal gold surfaces. A brief history of this development will be discussed and the specifics of how this bridge was built examined.

11:40am **HC+2D+SS-ThM12 Cooperativity Between Pd and AgO_x Phases on Ag(111)**, *V. Mehar, M. Yu, Jason Weaver*, University of Florida

Metals dispersed on a reactive metal-oxide have potential to effect selective catalysis through cooperative interactions between the co-existing metal and metal-oxide phases. In this talk, I will discuss our recent investigations of the structure and reactivity of oxidized Ag(111) as well as Pd/AgO_x surfaces that are generated by depositing metallic Pd onto a single-layer AgO_x structure in ultrahigh vacuum (UHV). Scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) show that the oxidation of Ag(111) with atomic oxygen mainly produces a single-layer AgO_x phase with a p(4 x 5r3) structure as well as smaller amounts of p(4 x 4) and c(3 x 5r3) structures during the initial stages of oxidation. Surface infrared spectroscopy and temperature programmed reaction spectroscopy (TPRS) demonstrate that the single-layer AgO_x structures are nearly unreactive and bind CO negligibly at temperatures down to ~100 K. In contrast, we find that CO adsorbs and oxidizes efficiently on Pd islands during TPRS, even when the AgO_x phase is the only oxidant source. STM further demonstrates that the metallic Pd islands induce partial reduction of the AgO_x support structure at 300 K. We find that the Pd/AgO_x surfaces continue to exhibit high CO oxidation activity with increasing Pd coverage up to nearly 2 ML (monolayer), suggesting that oxygen transfer from the AgO_x phase occurs at both the interior and perimeter of Pd islands. Our results reveal a cooperative mechanism for CO oxidation on Pd/AgO_x surfaces wherein O-atoms from the AgO_x support phase migrate onto metallic Pd islands and react with adsorbed CO to produce CO₂. These findings illustrate that oxygen transport across metal/metal-oxide interfaces can be highly efficient when the oxygen chemical potential is lower on the initial metal phase (Pd) compared with the metal-oxide (AgO_x) support.

12:00pm **HC+2D+SS-ThM13 Migration Across Metal/Metal Oxide Interfaces: Enhancing the Reactivity of Ag Oxide with H₂ by the Presence of Pd/Pd Oxide**, *Christopher O'Connor*², *M.A. van Spronsen*, *E. Muramoto*, *T. Egle*, *R.J. Madix*, *C.M. Friend*, Harvard University

An important factor in exploiting bifunctionality in dilute alloy catalysts is surface migration across interfaces separating the dissimilar materials.

¹ Heterogeneous Catalysis Graduate Student Presentation Award Finalist
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² Heterogeneous Catalysis Graduate Student Presentation Award Finalist

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Herein, we demonstrate the transfer of hydrogen atoms from islands of Pd oxide onto a surrounding O/Ag(111) surface using ambient pressure X-ray photoelectron spectroscopy (APXPS) and scanning tunneling microscopy (STM). These Pd oxide islands enhance the rate of reduction of Ag oxide by more than four orders of magnitude compared to pure oxidized Ag(111). The increase in the rate of reduction of Ag oxide by H₂ is attributed to H₂ activation on Pd/Pd oxide followed by migration (spillover) to Ag/Ag oxide and rapid reaction thereafter. The oxidation and subsequent reduction processes induce significant structural changes of the catalyst surface. We further establish that the transfer of hydrogen atoms occurs from islands of metallic Pd onto a surrounding Ag(111) surface using high resolution electron energy loss spectroscopy (HREELS) and temperature programmed reaction spectroscopy (TPRS). For the metallic PdAg system, hydrogen spillover is shown to be a kinetically limited process that can be controlled by temperature, pressure of H₂ and surface concentration of Pd. The highest efficiency for the amount of hydrogen spillover per surface Pd occurs for a dilute concentration of Pd in Ag. This study establishes that the migration of intermediates across interfaces can occur for oxidized PdAg alloy surfaces and specifically that hydrogen atom migration has a significant effect on the catalytic activity of this type of binary material.

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