Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 103A - Session HC+SS-WeM
Bridging Gaps in Heterogeneously-catalyzed Reactions

Moderator: Ashleigh Baber, James Madison University

8:00am **HC+SS-WeM1 Vinyl Acetate Formation Pathways and Selectivity on Model Metal Catalyst Surfaces***, **Theodore Thuening**,* University of Wisconsin-Milwaukee

Surface reaction pathways are explored on model single crystal catalyst surfaces using a combination of surface science experiments in ultrahigh vacuum, in-situ monitoring of the surface intermediates during reaction, and by using density functional theory (DFT) calculations. This approach enables detailed reaction pathways to be obtained and is illustrated using palladium catalyzed synthesis of vinyl acetate monomer (VAM). It is shown that vinyl acetate is formed on a Pd(111) and Pd(100) model catalysts via the so-called Samanos pathway, where reaction is initiated by coupling between ethylene and surface acetate species to form an acetoxyethyl intermediate that decomposes by β-hydride elimination to form VAM. The way in which adsorbate coverage affects both reactivity and selectivity is discussed.

8:20am **HC+SS-WeM2 In situ Monitoring of Acetylene Hydrogenation over a Pd/Cu(111) Single Atom Alloy Surface with Polarization Dependent Infrared Spectroscopy***, **Christopher M. Kruppe**, J.D. Krooswyk, M. Trenary,* University of Illinois at Chicago

Low coverages of catalytically active metals deposited onto less active metal surfaces can form single atom alloys (SAAs), which often display unique catalytic properties. Such alloys are particularly attractive for selective hydrogenation reactions. It is therefore of interest to probe the surface structure and chemistry of such alloys in the presence of gas phase reactants. We have used polarization dependent reflection absorption infrared spectroscopy (PD-RAIRS) to monitor the in situ hydrogenation of acetylene to ethylene over a Pd/Cu(111) SAA surface. The coverage and morphology of the deposited Pd is elucidated with Auger spectroscopy (AES), temperature programmed desorption (TPD) of H_2, and PD-RAIRS of CO. After exposing clean Cu(111) and Cu(111) with various Pd coverages to 10 L CO at 100 K, the RAIR spectra show that the surface is largely unchanged by the presence of less than 0.5 ML of Pd. In the presence of 1×10^{-2} Torr of CO at 300 K, significant CO coverages are only achieved when Pd is present on the surface. The Pd coverage determined from the areas of the CO peaks in the PD-RAIR spectra is approximately equal to the Pd coverage calculated from peak-to-peak ratios in the Auger spectra. Surface species and gas phase products of C_2H_2 hydrogenation are monitored between 180 K and 500 K on clean Cu(111) and Pd/Cu(111). With a total pressure of 1 Torr and a C_2H_2:H_2 ratio of 1:100, annealing a SAA-Pd/Cu(111) surface to 360 K results in complete conversion of all gas phase C_2H_2 to gas phase ethylene (C_2H_4), without producing any gas phase ethane (C_2H_6). The results demonstrate the utility of PD-RAIRS for monitoring the selective hydrogenation of acetylene to ethylene.

8:40am **HC+SS-WeM3 Novel in Situ Techniques for Studies of Model Catalysts***, **Edvin Lundgren**,* Lund University, Sweden **INVITED**

Motivated mainly by catalysis, gas-surface interaction between single crystal surfaces and molecules has been studied for decades. Most of these studies have been performed in well-controlled environments, and has been instrumental for the present day understanding of catalysis. We have in recent years explored the possibilities to perform experiments at conditions closer to those of a technical catalyst, in particular at increased pressures. In this contribution, results from catalytic CO oxidation over Pd single crystal surfaces using High Pressure X-ray Photo emission Spectroscopy (HPXPS), Planar Laser Induced Fluorescence (PLIF), and High Energy Surface X-Ray Diffraction (HESXRD) will be presented.

Armed with structural knowledge from ultra-high vacuum experiments, the presence of adsorbed molecules and gas-phase induced structures can be identified, and related to changes in the reactivity and/or to reaction induced gas-flow limitations. The strength and weaknesses of the experimental techniques will be discussed.

9:20am **HC+SS-WeM5 Metastable Cluster Formation and Polymorphism of Hydrogen-bonding Molecules on Gold are a Consequence of the Pulse-deposition of a Solution into Vacuum***, **Ryan Brown**, S.A. Kandel,* University of Notre Dame

A primary motivation in studying the assembly of molecules at an interface is to determine the underlying principles which drive the spontaneous formation of supramolecular structures under specific environmental conditions, with the ultimate goal being an understanding which allows control over such processes. Recently we have postulated the importance of solution-phase cluster formation during the pulse-deposition, in vacuum, of small organic and organometallic molecules which contain strong hydrogen bonding components, namely carboxylic acid functional groups, in addition to weak hydrogen bonding donors. Specifically, we have studied the cluster formation of 1,1'-ferrocenedicarboxylic acid, Fc(COOH)$_2$, which has been pulse deposited on Au(111)-on-mica substrates. We employed low temperature scanning tunneling microscopy (LT-STM) to observe which molecular clusters persist at the interface following pulse-deposition from solution. We subsequently performed annealing experiments to determine which of these species represent stable conformations, and which are metastable species formed in the solution droplet during deposition. LT-STM images of Fc(COOH)$_2$ show a coexistence between dimer, chiral hexamer, and square tetramer clusters. Since the bulk crystal structures for Fc(COOH)$_2$ are all comprised entirely of molecular dimers, the most stable 2D supramolecular structure likely is some array of dimers, whereas the other species present are metastable. We attribute the initial strong presence of metastable species to the formation of clusters in solution, followed by their precipitation as predicted by Ostwald's rule, then their adsorption on to the substrate in a kinetically-trapped conformation. Electrospray ionization mass spectrometry (ESI-MS) of Fc(COOH)$_2$ solutions supports the presence of hexamer clusters in solvent droplets, which confirms the possibility that the chiral hexamers observed after deposition precipitate from the solution droplet. Sequential mild annealing stepsof this surface results in the formation of linear rows of square tetramers, chiral dimer domains, and eventually tilted dimer arrays. The prevalence of each of these species is related to the surface's thermal history, and this is characteristic of a system evolving under kinetic control. We propose that injection of solution into a vacuum environment can be exploited to produce supramolecular 2D-structures not observed in the bulk crystal, and that the frequency of nature of the metastable species present should be dependent on variables such as the solution concentration, solvent, and droplet size.

9:40am **HC+SS-WeM6 Understanding the Activity of Pt-Re Bimetallic Clusters on Titania and Pt-Re Alloy Surfaces in the Water Gas Shift Reaction***, **Donna Chen**, A.S. Duke, K. Xie, A.J. Brandt, T.D. Maddumapatabandi,* University of South Carolina

The chemical activities of bimetallic Pt-Re clusters supported on TiO_2(110) and single-crystal Pt-Re alloy surfaces are investigated as model systems for understanding Pt-Re catalysts in the water gas shift (WGS) reaction. The activities of these Pt-Re bimetallic surfaces are studied in a microreactor coupled to an ultrahigh vacuum chamber so that the surfaces can be characterized by X-ray photoelectron spectroscopy (XPS) before and after reaction. Bimetallic clusters consisting of a Re core covered by a Pt shell have turnover frequencies that are almost twice as high as that of the pure Pt clusters at 160 **°**C. Furthermore, the Re in the active bimetallic clusters remains in its metallic state because Re is not readily oxidized when it remains subsurface; there is no evidence that ReO_x is active in promoting the WGS reaction. Pure Re clusters are not active for the WGS reaction, and bimetallic clusters with significant Re at the surface are less active than pure Pt clusters. Surface Re is oxidized under reaction conditions and sublimes as Re_2O_7. Post-reaction infrared spectroscopy studies show that CO and hydroxyls are detected on the surface.

11:00am **HC+SS-WeM10 Fundamental Studies of the Water-gas Shift and CO_2 Hydrogenation on Metal/oxide Catalysts: From Model Systems to Powders***, **Jose Rodriguez**,* Brookhaven National Laboratory **INVITED**

In this talk, it will be shown how a series of *in-situ* techniques {X-ray diffraction (XRD), pair-distribution-function analysis (PDF), X-ray absorption spectroscopy (XAS), environmental scanning tunneling microscopy (ESTM), infrared spectroscopy (IR), ambient-pressure X-ray photoelectron spectroscopy (AP-XPS)} can be combined to perform detailed studies of the structural, electronic and chemical properties of metal/oxide catalysts used for the production of hydrogen through the water-gas shift reaction (WGS, $CO + H_2O \rightarrow H_2 + CO_2$) and the hydrogenation of CO_2 to methanol (MS, $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$). Under reaction conditions most WGS and MS catalysts undergo chemical transformations that drastically modify their composition with respect to that obtained during the synthesis process. The active phase of catalysts which combine Cu, Au or Pt with oxides such as ZnO, CeO_2, TiO_2, CeO_x/TiO_2 and Fe_2O_3 essentially involves nanoparticles of the reduced noble metals. The oxide support undergoes partial reduction and is not a simple spectator, facilitating the dissociation of water, or the adsorption of CO_2, and in some cases modifying the chemical properties of the supported metal. Therefore, to optimize the performance of these catalysts one must take into consideration the properties of the metal-oxide interface. IR and AP-XPS have been used to study the reaction mechanism for the WGS and MS on the metal/oxide catalysts. Data of IR spectroscopy indicate that formate species are not necessarily involved in the main reaction path for these reactions on Cu-, Au- and Pt-based catalysts. Thus, a pure redox mechanism or associative mechanisms that involve either carbonate-like (CO_3, HCO_3) or carboxyl (HOCO) species should be considered. In the last two decades, there have been tremendous advances in our ability to study catalytic materials under reaction conditions and we are moving towards the major goal of fully understanding how the active sites for the production of hydrogen through the WGS or the hydrogenation of CO_2 to methanol actually work.

11:40am **HC+SS-WeM12 The Use of EC-STM to Study the Chemical Reactivity and Nanoscale Structure of Metal Surfaces***, A. Phillips, L. Jackson, H. Morgan, G. Jones,* ***Erin Iski****,* University of Tulsa

In the development of surfaces as efficient catalysts, it is critical to understand and control the surface reactivity in a defined manner. Electrochemical Scanning Tunneling Microscopy (EC-STM) is an advantageous technique in that in addition to providing a local probe of the atomic surface structure, EC-STM also functions as a 3-electrode cell in which redox chemistry can be performed to harness the chemical reactivity of the surface. This technique offers a unique window to study catalysis at conditions outside of a UHV environment, specifically at ambient temperatures and in liquids. Also, cyclic voltammograms (CVs) can be generated to provide specific information regarding the nature of the redox events occurring at the surface. Within this framework, it is possible to study how certain surfaces can become activated and/or deactivated as a result of electrochemical manipulation. One specific example of a thermally deactivated surface is a single Ag layer on a Au(111) crystal. The Ag layer is deposited on the Au(111) surface using Underpotential Deposition (UPD), which is an extremely controllable electrochemical technique for the application of a monolayer (or less) of a metal onto a more noble metal. Surprisingly, this atomically-thin Ag layer when formed in the presence of halides remains on the Au surface after heat treatments as high as 1,000 K. Importantly, thermal stabilization can be contrasted and compared with catalytic activity in which chlorine has shown to be a promoter of ethylene epoxidation over Ag(111), demonstrating why this system is intriguing from multiple vantage points. From a general standpoint, EC-STM offers an environmentally unique handle on how the chemical reactivity of a metal surface can be altered and how that surface can then be studied on a fundamental level.

12:00pm **HC+SS-WeM13 Formation and Stability of Surface Oxides on Ag(111)***,* ***Daniel Killelea****, J. Derouin, R.G. Farber, M.E. Turano,* Loyola University Chicago*; E.V. Iski,* The University of Tulsa

A long-standing challenge in the study of heterogeneously catalyzed reactions on silver surfaces has been the determination of what surface phases are of greatest chemical importance. This is due to the coexistence of several different surface phases on oxidized silver surfaces. A further complication is subsurface oxygen (O_{sub}). O_{sub} are O atoms dissolved into the near surface of a metal, and are expected to alter the surface in terms of chemistry and structure, but these effects have yet to be well characterized. We studied oxidized Ag(111) surfaces after exposure to gas-phase O atoms with a combination of surface science techniques to determine the resultant surface structure; we observed that once 0.1 ML of O_{sub} has formed, the surface dramatically, and uniformly, reconstructs to a striped phase at the expense of all other surface phases. Furthermore, O_{sub} formation is hindered at temperatures above 500 K. We also observed a coexistence of several surface oxides at intermediate deposition temperatures, and the predominance of the $p(4\times5\sqrt{3})$ surface reconstruction at elevated temperatures.

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