## Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
## Room 103A - Session HC+NS+SS-WeA
## Nanoscale Surface Structures in Heterogeneously Catalyzed Reactions

**Moderator:** Arthur Utz, Tufts University

2:20pm **HC+NS+SS-WeA1 Ceria Nanoclusters on Graphene/Ru(0001): A New Model Catalyst System***, Z. Novotny,* Pacific Northwest National Laboratory*; F.P. Netzer,* Karl-Franzens University, Austria*; **Zdenek Dohnalek**,* Pacific Northwest National Laboratory **INVITED**

Cerium oxide is an important catalytic material known for its ability to store and release oxygen, and as such, it has been used in a range of applications, both as an active catalyst and as a catalyst support. Using scanning tunneling microscopy and Auger electron spectroscopy, we investigated the growth of ceria nanoclusters and their oxygen storage/release properties on single-layer graphene (Gr) on Ru(0001) with a view towards fabricating a stable system for model catalysis studies. The ceria nanoclusters are of the $CeO_2$(111)-type and are anchored at the intrinsic defects of the Gr surface and display a remarkable stability against reduction in ultrahigh vacuum up to 900 K, but some sintering of clusters is observed for temperatures > 450 K. The evolution of the cluster size distribution suggests that the sintering proceeds via a Smoluchowski ripening mechanism, i.e. diffusion and aggregation of entire clusters. To follow the cluster redox properties we examined their oxygen storage and release in an oxygen atmosphere ($<10^{-6}$ Torr) at elevated temperature (550 – 700 K). Under oxidizing conditions, oxygen intercalation under the Gr layer is observed. Time dependent studies demonstrate that the intercalation starts in the vicinity of the $CeO_x$ clusters and extends until a completely intercalated layer is observed. Atomically resolved images further show that oxygen forms a p(2×1) structure underneath the Gr monolayer. Temperature dependent studies yield an apparent kinetic barrier for the intercalation of 1.2 eV. At higher temperatures, the intercalation is followed by a slower etching of the intercalated Gr (apparent barrier of 1.6 eV). Vacuum annealing of the intercalated Gr leads to the formation of carbon monoxide and causing etching of the Gr film thus revealing that the spillover of oxygen is not reversible. These studies demonstrate that the easily reducible $CeO_x$ clusters act as intercalation gateways capable of efficiently delivering oxygen underneath the Gr layer.

3:00pm **HC+NS+SS-WeA3 Lowering the Barrier to C-H Activation using Pt/Cu Single Atom Alloys***, **Matthew Marcinkowski**, M. El Soda, F.R. Lucci, E.C.H. Sykes,* Tufts University

Due to the increased in shale gas production in recent years the availability of light alkanes such as ethane and propane has increased significantly. Although these chemicals are typically considered inert, the ability to cleave C-H bonds in alkanes would allow for production of alkenes, which are important precursors to polymers. In this work, we use a surface science approach to model C-H activation on a Cu(111) surface using methyl iodide. Methyl iodide is known to decompose to produce methyl groups and iodine atoms on Cu(111) below 200 K. The methyl groups are then stable on the surface up until 450 K, at which temperature they decompose to form a number of products including methane, ethylene, ethane, and propylene. The rate limiting step to forming these products is the activation of one of the C-H bonds in the methyl group to produce surface bound hydrogen and methylene. Pt(111) is also able to activate the C-I bond in methyl iodide, but methyl groups on this surface only produce methane, hydrogen, and surface bound methylene groups at 290 K. While the barrier to C-H activation is lowered on Pt compared to Cu, the Pt surface is unable to perform carbon coupling reactions. Inspired by these previous results, we fabricated surfaces consisting of 1% Pt in the Cu(111) surface. At this concentration, Pt exists as single, isolated atoms substituted into the Cu(111) lattice. These *single atom alloys* exhibit synergistic chemistry and yield the desirable properties of each of the two pure metal surfaces. They are able to produce carbon coupling products like pure Cu, but are able to activate the C-H bond necessary to begin these reactions at 340; 110 K cooler than on Cu(111). Increasing the concentration of Pt further decreases the temperature necessary to activate C-H bonds, but also decreases the amount of carbon coupling products formed as the surface becomes more similar to Pt(111). Single atom alloys therefore provide an ideal model catalyst for the decomposition of methyl iodide, allowing for more facile activation of the C-H bond than pure Cu while also producing the desired coupling products, which Pt(111) is unable to do.

3:20pm **HC+NS+SS-WeA4 Formation, Migration and Reactivity of Au-CO Complexes on Gold-Surfaces***, **Jun Wang**,* Oak Ridge National Laboratory*; M. McEntee, W. Tang, M. Neurock,* University of Virginia*; A.P. Baddorf, P. Maksymovych,* Oak Ridge National Laboratory*; J.T. Yates, Jr.,* University of Virginia

We report experimental as well as theoretical evidence that suggests formation of Au-CO complexes upon the exposure of CO to active sites (step edges and threading dislocations) on a Au(111) surface. Room-temperature scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy, transmission infrared spectroscopy, and density functional theory calculations point were combined to investigate morphological changes of the Au(111) surface with an intentionally created array of etch-pits. Room-temperature STM of the Au(111) surface at CO pressures in the range from $10^{-8}$ to $10^{-4}$ Torr (dosage up to $10^6$ langmuir) indicates Au atom extraction from dislocation sites of the herringbone reconstruction, mobile Au–CO complex formation and diffusion, and Au adatom cluster formation on both elbows and step edges on the Au surface. The formation and mobility of the Au–CO complex result from the reduced Au–Au bonding at elbows and step edges leading to stronger Au–CO bonding and to the formation of a more positively charged CO ($CO^{\delta+}$) on Au. Our studies indicate that the mobile Au–CO complex is involved in the Au nanoparticle formation and reactivity, and that the positive charge on CO increases due to the stronger adsorption of CO at Au sites with lower coordination numbers.

ACKNOWLEDGEMENTS: Part of this research was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility .

Reference: J. Wang, M. McEntee, W. Tang, M. Neurock, A. P. Baddorf, P. Maksymovych, and J. T. Yates, Jr., *J. Am. Chem. Soc.* 138, 1518 (2016)

4:20pm **HC+NS+SS-WeA7 Sulfur-Metal Complexes on Surfaces of Copper, Silver, and Gold***, **Patricia A. Thiel**,* Iowa State University*; H. Walen,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan*; D.-J. Liu,* Ames Laboratory, Ames, IA*; J. Oh,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan*; H.J. Yang,* University College London, UK*; Y. Kim,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan **INVITED**

The nature of sulfur interaction with surfaces of coinage metals (M=Cu, Ag, Au) is relevant to aspects of heterogeneous catalysis, corrosion, and self-assembled monolayers. We have discovered a number of unexpected complexes—independent, molecule-like MxSy species—that form on low-index M surfaces. In a sense, these complexes are iidway between the well-known phenomena of chemisorption and adsorbate-induced reconstruction. Our primary experimental tool is scanning tunneling microscopy (STM) used in ultrahigh vacuum. We tailor our experimental conditions to isolate the complexes, by working at ultra-low sulfur coverage to avoid competition from surface reconstructions. Furthermore, we prepare the surface at 300 K, but image at 5 K, in order to immobilize these small species. Density fucntional theory (DFT) is used to interpret the experimental results. For instance, application of DFT is essential to identify the complexes that form on Cu(111), Ag(111), and Au(100), and this identification is made both on the basis of their physical characteristics in real vs. stiimulated STM images (size, orientation, shape) as well as their calculated stability. On other surfaces, including Au(111), Cu(10o0), and Au(110), MxSy complexes do not form under comparable conditions. This broad database and extensive analysis provides insights into factors that favor complexation in this class of systems.

5:00pm **HC+NS+SS-WeA9 Titania/Gold Inverse Model Catalysts for Acetaldehyde Formation from Ethanol***, **Ashleigh Baber**, D.T. Boyle, W. Andahazy, V. Lam, D. Schlosser, N. Tosti, J. Wilke,* James Madison University

The fundamental investigation of the catalytic chemistry of ethanol at interfaces is important for many fields including the automotive industry due to the use of ethanol as a fuel. The redox chemistry of small alcohols, including methanol and propanol, has been studied on Au(111) supported $TiO_2$ nanoparticles, yet the active site for the chemistry has not yet been elucidated. Here, the systematic study of ethanol has been investigated on Au(111) and $TiO_2$/Au(111) via temperature programmed desorption in an effort to gain insight on the interfacial role of the reactivity for ethanol, as a function of titania coverage. Ex situ atomic force microscopy was used to image the gold–supported titania particles, and X-ray photoelectron spectroscopy was used to confirm the presence of titania on the surface.

The presence of $TiO_2$ nanoparticles on Au(111), ~25 nm in diameter, led to the catalytic conversion of ethanol to acetaldehyde at temperatures greater than 400 K. The interaction of ethanol with Au(111)–supported $TiO_2$ nanoparticles is markedly different than its interaction with the individual counterparts: bulk titania and gold, which both lead to the desorption of molecular ethanol at temperatures lower than 400 K.

5:20pm **HC+NS+SS-WeA10 Shape and Support Interaction of Size Selected Pt Nanoparticles in Presence of $H_2$*, Mahdi Ahmadi,*** *F. Behafarid,* University of Central Florida*; B. Roldan Cuenya,* Ruhr-University Bochum, Germany

Pt nanoparticles (NPs) supported on TiO2 have been widely used as a catalysts in industrial applications.

Strong metal-support interaction (SMSI) is expected to occur for this system under reducing environments

such as vacuum and H2. Since the morphology of NPs depends on their surface energy and their interaction

with the support, investigating the shape of NPs could be an excellent pathway to understand the metal

support interactions. In this study we have investigated the in situ shape evolution of TiO2 supported Pt NP

using grazing incidence small angle X-ray scattering (GISAXS) during annealing in H2 environment. The

size selected Pt NPs with an initial spherical shape were synthesized via inverse micelle encapsulation

method. The sample was step annealed up to 700°C in H2 environment and the onset for NPs faceting was

found to be 600°C. Annealing at a higher temperature (700°C) did not cause any further change in NPs

structure. The presence of a sharp scattering ray at 45° with respect to the surface normal indicates the (110)

facet to be the dominant side facet for Pt NPs and the top and interfacial facets to be Pt(100). These features

point out that the shape of Pt NPs supported on TiO2 under hydrogen environments is pyramidal. The

specific shape of Pt NPs are discussed based on the SMSI phenomenon.

5:40pm **HC+NS+SS-WeA11 Single Atom Alloys as a Strategy for Selective Heterogeneous Hydrogenation and Dehydrogenation Reactions*, Charles Sykes,*** Tufts University **INVITED**

Catalytic hydrogenations are critical steps in many industries including agricultural chemicals, foods and pharmaceuticals. In the petroleum refining, for instance, catalytic hydrogenations are performed to produce light and hydrogen rich products like gasoline. Typical heterogeneous hydrogenation catalysts involve nanoparticles composed of expensive noble metals or alloys based on platinum, palladium, rhodium, and ruthenium. We demonstratedhow single palladium and palladium atoms can convert the otherwise catalytically inert surface of an inexpensive metal into an ultraselective catalyst.(1-3) High-resolution imaging allowed us to characterize the active sites in single atom alloy surfaces, and temperature programmed reaction spectroscopy to probe the chemistry. The mechanism involves facile dissociation of hydrogen at individual palladium atoms followed by spillover onto the copper surface, where ultraselective catalysis occurs by virtue of weak binding. The reaction selectivity is in fact much higher than that measured on palladium alone, illustrating the system's unique synergy.

Our *single atom alloy* approach may in fact prove to be a general strategy for designing novel bi-functional heterogeneous catalysts in which a catalytically active element is atomically dispersed in a more inert matrix. Very recently we demonstrated that this strategy works in the design of real catalysts. Platinum/copper nanoparticles can perform the industrially important butadiene hydrogenation at lower temperature using just 1% platinum.(3) Moreover, some of the best industrial alloy catalysts to date may already be operating via this mechanism, but there is currently no method to directly probe the atomic geometry of a working catalyst. Our scientific approach allows one to parse out the minimal reactive ensembles in an alloy catalyst and provide design rules for selective catalytic nanoparticle. *From another practical application standpoint, the small amounts of precious metal required to produce single atom alloys generates a very attractive alternative to traditional bimetallic catalysts.*

**References:**

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