

Surface Science Division

Room 319 - Session SS2+AS+HC-WeM

Nanoparticle Surfaces

Moderator: Zdenek Dohnalek, Pacific Northwest National Laboratory

9:40am **SS2+AS+HC-WeM-6 Understanding the Growth of Sn and Pt-Sn Clusters on Titania and Carbon Surfaces**, *S. Beniwal*, University of South Carolina; *W. Chai*, University of Texas at Austin; *M. Qiao*, *P. Kasala*, University of South Carolina; *K. Shin*, *G. Henkelman*, University of Texas at Austin; *Donna Chen*, University of South Carolina

Supported Pt-Sn bimetallic clusters have applications in number of catalytic processes, including dehydrogenation of alkanes and selective hydrogenation of unsaturated aldehydes. In these reactions, the presence of Sn is known to promote the desired selectivity of the Pt-based catalyst. However, the chemical activity the supported Pt-Sn catalysts is dependent on the Sn oxidation state and the nature of Sn interaction with the support, as well as dispersion. Sn and Pt-Sn clusters have been vapor-deposited on TiO₂(110) and highly oriented pyrolytic graphite (HOPG) and studied by scanning tunneling microscopy, X-ray photoelectron spectroscopy, and low energy ion scattering. Deposition of Sn on titania results in the formation of small, uniformly sized clusters with SnO_x at the cluster-support interface and reduction of the titania support. Subsequent deposition of Pt produces exclusively bimetallic clusters, and Sn diffuses away from cluster-support, resulting in a decrease in SnO_x and Sn-rich cluster surfaces. Density functional theory (DFT) calculations demonstrate that M-TiO₂ bonding is favored over M-M bonding for M=Sn, unlike for transition metals such as M=Pt, Au, Ni, and Co. Furthermore, the substantial charge transfer from Sn to TiO₂ leads to dipole-dipole repulsion of Sn atoms that prevents agglomeration into the larger clusters that are observed for the mid-late transition metals. DFT studies also confirm that addition of Pt to a Sn cluster results in strong Pt-Sn bond formation and diminished Sn-O interactions. In the case of Sn deposition on HOPG, the clusters are surprisingly small given that Sn does not interact strongly with the support, whereas other metals such as Pt, Re and Pd readily diffuse to form large clusters that aggregate at step edges. DFT investigations show that Sn is unique in that the per atom binding energy of Sn in small clusters (<15 atoms) is as low as 0.14 eV/atom compared to Sn atoms in the bulk; for Pd, Pt, and Re, the binding energy is 0.9-1.9 eV/atom. Therefore, it is thermodynamically favorable for Sn to form small clusters and for other metals to form large clusters.

11:00am **SS2+AS+HC-WeM-10 Single Nanoparticle Surface Chemistry: Structure-Reactivity Relationships, Evolution During Reactions, and an Approach to Ultra-High Temperature Surface Chemistry**, *C. Lau*, *A. Friese*, *D. Rodriguez*, *Scott Anderson*, University of Utah

Nanoparticles (NPs) are inherently heterogeneous, with variations in size, shape, and distributions of reactive sites. This talk will explore the kinetics for oxidative etching of *individual* carbon and silicon NPs, tracking changes in reactivity as the NP structure evolves under reaction conditions.

Examples of O₂ oxidation of typical carbon black and graphene oxide NPs is shown in the figure, which shows the NP mass vs. time at 1200 K under inert (unshaded background) and oxidizing conditions (cyan background). The lower frames show how EE_{O₂}(the etching efficiency in terms of Da of mass lost *per* O₂ collision) varies with the NP mass. Oxidative etching of carbon NPs varies significantly between NPs from different feedstocks, but there are also variations between NPs from the same feedstock, reflecting variations in the distributions of surface sites. Furthermore, the reactivity of individual NPs evolves non-monotonically in time as the NPs etch, with rate fluctuations of up to 5 orders of magnitude. Eventually, all carbon NPs become nearly inert to O₂, signaling that the surface layer(s) have transformed to multiwall fullerene-like structures.

For silicon NPs, we are able to study oxidation over a temperature range from 1200 to 2500 K, spanning the bulk T_{melt} of both silicon and silica. Etching involves several interacting processes that depend differently on temperature and time, thus etching of silicon-based NPs can have quite complex time dependence. For example, at temperatures (e.g. 1200 K) well below the silicon melting point (T_{melt} = 1683 K), the etching mass loss rate is initially low, accelerating as etching progresses, then eventually dropping several orders of magnitude to ~zero as the NP surface grows a passivating silica layer. At temperatures closer to the melting point (e.g. 1500 K), the oxidative mass loss rate starts high and remains high as the NP loses 15 – 30% of its initial mass, then abruptly drops to near zero as the surface

passivates. For temperatures above T_{melt}, the etch rate begins to decrease immediately upon O₂ exposure, but it never drops to zero, i.e., the NP surface never passivates.

One of the features of this method is that the upper temperature possible is limited only by the sublimation rate of the particle's material. Thus for Si, it is straightforward to examine temperatures well above T_{melt}. For ultra-high temperature ceramic materials, it is possible to study surface chemistry at temperatures to well above 3000 K. Oxidation of HfC (T_{melt}≈ 4200 K), will be used to illustrate this capability.

11:20am **SS2+AS+HC-WeM-11 Oxidation of Size-Selected Ag Clusters on Graphene: Bulk Motifs and Electronic Anomalies at sub-Nanoscale**, *F. Loi*, University of Trieste, Italy; *M. Pozzo*, University College London, UK; *Luca Bignardi*, *L. Sbuclz*, University of Trieste, Italy; *P. Lacovig*, *E. Tosi*, *S. Lizzit*, Elettra Sincrotrone Trieste, Italy; *A. Kartouzian*, *U. Heiz*, Technical University Munich, Germany; *R. Laricprete*, Institute for complex systems - CNR, Italy; *D. Alfè*, University College London, UK; *A. Baraldi*, University of Trieste, Italy

The evolution of the aggregation of condensed matter from single atoms to three-dimensional structures represents an crucial topic in nanoscience since it contains essential information to achieve tailor-made growth of nanostructured materials. Such issue is particularly important in the case of the formation of nano-oxides, which have strong potentialities in heterogeneous catalysis reactions. In this respect, we investigated the oxidation of an Ag nanocluster composed of 11 atoms supported on epitaxial graphene on Ru(0001), combining synchrotron-based core-level photoelectron spectroscopy and *ab initio* DFT calculations. Our analysis indicated that a single Ag₁₁ cluster can bond with up to 12 O atoms. Moreover, we evidenced that the Ag-O bonds in the nanoclusters include contribution from the Ag 4d states, with a remarkable difference with the case of Ag single crystal surfaces, for which only Ag 5s states are involved. The oxidized Ag₁₁O₁₂ nanocluster is indeed more similar to a bulk oxide rather than to an oxidized surface, as it reaches a final hybrid structure formed of d¹⁰ Ag(I) and d⁸ Ag(III) ions which strongly resembles that of AgO bulk oxide. Furthermore, we found that the Ag 3d core level in the Ag₁₁ nanoclusters is dominated by initial state effects and has a unique behavior when increasing the oxygen density. This anomaly seems to be related to the dimensionality of the nanocluster and provides an excellent example of the differences that sub-nanometer atomic aggregates of a material show with respect to the bulk and surface counterparts.

11:40am **SS2+AS+HC-WeM-12 Precision Engineering of Metal Nanoparticle Surfaces for Fundamental Studies of Catalytic Reactivity**, *Michelle Personick*, Wesleyan University **INVITED**

Understanding fundamental structure-activity relationships in catalysis is key to enabling the directed design of improved catalytic materials, but the surfaces of working catalysts are complex. The use of precisely defined nanomaterials provides a powerful tool for facilitating insights into active site structure and reaction mechanisms. Such materials also enable testing and validation of insights from fundamental experimental and computational surface science under catalytic operating conditions. However, synthesizing nanomaterials with the precise surface structures and compositions necessary to test specific hypotheses is a significant challenge, and creative new approaches to materials synthesis are required—particularly for bimetallic materials. This talk will highlight the use of large (~75 nm), well-defined metal nanoparticles as model surfaces to test predictions from computational surface science. In addition, it will describe materials-generalizable synthetic tools developed by our research group for controlling metal nanoparticle shape, surface structure, defect structure, and composition, with an emphasis on dilute bimetallic nanoparticles. Halide-assisted metal ion reduction enables the controlled co-reduction of metals with dissimilar reactivity (Au/Pd, Pd/Cu, Au/Ag), while differentially tuning the relative rates of reduction for each metal to define the shape and surface composition of the material. Plasmon-assisted metal ion reduction takes advantage of the light-responsive properties of materials like Ag to enable (1) the directed deposition of catalytically active but poorly plasmonic metals such as Pt, and (2) the reconfiguration of monometallic Ag materials to modify defect structure while retaining the same surface structure and adsorbates. Together with other techniques developed in our research group, these tools provide a platform for the precision engineering of catalytic metal nanomaterials.

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