Surface Science
Room 210B - Session SS1-ThM
Metal Oxide and Clusters III: Supported Cluster Formation and Reactivity

Moderator: G.S. Hwang, The University of Texas at Austin

8:20am **SS1-ThM1 Decomposition of Dimethyl Methylphosphonate on TiO@sub2@(110)-Supported Ni Clusters of Different Sizes***, **D.A. Chen**, S. Ma,* University of South Carolina*; J. Zhou,* Oak Ridge National Laboratory

The thermal decomposition of dimethyl methylphosphonate (DMMP) on Ni clusters deposited on TiO@sub2@(110) has been studied in ultrahigh vacuum by TPD and XPS. Ni cluster sizes were characterized by STM; the small Ni clusters (5.0±0.8 nm diameter, 0.9±0.2 nm height) were deposited at room temperature while the large clusters (8.8±1.4 nm diameter, 2.3±0.5 nm height) were prepared by room temperature deposition followed by annealing to 850 K. TPD experiments show that CO and H@sub2@ were the major gaseous products evolved from the decomposition of DMMP, and molecular DMMP and methane desorption were also observed. The product yields for CO and H@sub2@ were higher for reaction on the small Ni clusters. Furthermore, XPS experiments demonstrate that the small Ni surfaces decompose a greater fraction of DMMP at room temperature. The loss of activity for the large annealed clusters is not caused by a reduction in surface area, which does not change substantially before and after annealing. Since CO adsorption studies suggest that the loss of activity cannot be completely due to a decrease in surface defects upon annealing, we propose that a TiO@subx@ moiety is responsible for blocking active sites on the annealed Ni surfaces. Low ion scattering studies show that the Ni clusters are not completely encapsulated after heating to 850 K, but these experiments are also consistent with partial encapsulation. Although DMMP decomposes on TiO@sub2@ to produce gaseous methyl radicals, methane and H@sub2@, the activity of the substrate surface itself appears to be quenched in the presence of the Ni clusters. However, the TiO@sub2@ support plays a significant role in providing a source of oxygen for the recombination of atomic carbon on Ni to form CO, which desorbs above 800 K.

8:40am **SS1-ThM2 Nucleation and Growth of 1B Metals on Rutile TiO2(110): Role of Oxygen Vacancies***, **D. Pillay**, G.S. Hwang,* The University of Texas at Austin

Oxide supported metal nanoparticles exhibit distinctly different chemical and physical properties from their bulk counter parts. The unique properties are greatly determined by their size and shape. Tailoring the structural properties with atomic scale precision will therefore offer great opportunities to open up a range of novel chemical, biological, and electronic applications. Due to the complexity of oxide-metal interactions, many fundamental aspects of metal particle nucleation and growth on an oxide are not well understood. We have investigated the nucleation and growth of 1B metals (Cu, Ag, Au) on a rutile TiO2(110) surface using density functional theory slab calculations. Our results clearly demonstrate that Au shows a distinctly different growth behavior from Ag and Cu. In this talk, we will present i) diffusion, nucleation, and early stage of growth of 1B metals on reduced TiO2(110) and ii) role of oxygen vacancies in the metal particle growth. Also, we will discuss the underlying reasons for sintering enhancement upon O2 exposure.

9:00am **SS1-ThM3 Cluster Size and Support Effects on Activity in Supported Gold and Iridium Catalysts***, S. Lee, C. Fan, T. Wu, W. Kaden, **S.L. Anderson**,* University of Utah **INVITED**

Size-selected model catalysts are prepared by deposition of mass-selected gold and iridium cluster ions on single crystal TiO@sub 2@ and thin film Al@sub2@O@sub 3@. Physical properties and adsorbate binding to the resulting samples is probed by a combination of XPS and ion-scattering (ISS). Chemical activity is probed by a combination of temperature-programmed desorption and constant temperature pulse dosing mass spectrometry. CO oxidation on Au@sub n@/TiO@sub 2@ is found to be very strongly dependent on deposited cluster size, with activity turning on at Au@sub 3@, and varying with size for larger clusters. The activity appears to be correlated with changes in the binding of CO from atop gold to peripheral sites associated with the clusters. Comparison of samples prepared by deposition over a wide temperature range suggests that substantial sintering occurs only at temperatures well above room temperaure. Reactions of hydrazine and ammonia on Ir@sub n@/Al@sub2@O@sub 3@, and sintering behavior in this system will also be discussed.

9:40am **SS1-ThM5 Fullerene Surfaces as Templates for Cluster Formation: The Interaction with Silicon and Gold***, **P. Reinke**,* University of Virginia*; H. Kroeger,* Universitaet Goettingen, Germany*; M. Buettner, P. Oelhafen,* Universitaet Basel, Switzerland

Clusters made from different elements are envisaged as building blocks for nanoelectronic devices. The properties of small clusters (@<@100 atoms) exhibit a strong size dependence which allows to tune their properties but places considerable demands on the synthesis of size-selected cluster arrays. The present investigation explores a novel path to the synthesis of size-selected clusters exploiting the strong corrugation and wide range of adsorption sites on the C@sub 60@ surface. Si and Au are the first elements investigated and the possibility to form arrays and network structures will be explored in the future. Amorphous Si (a-Si) and Au were deposited on a fullerene surface and the sequential evolution of the surface and the electronic properties of the interface were observed in-situ by photoelectron spectroscopy (PES) in the ultraviolet and x-ray regime. The growth of the Si on the C@sub 60@ surface begins with the formation of clusters, and analysis of the Si2p core level indicates that they are surrounded by carbon atoms and located interstitially between the C@sub 60@ molecules. As the growth continues the clusters coalesce and an a-Si overlayer forms. The interface contains no SiC covalent bonds and the electronic properties of this sharp interface are determined from the PES data. In contrast, the growth of the Au overlayer begins with the formation of islands, followed by a Vollmer-Weber type growth. The analysis of the core level and valence band spectra yields a wealth of information on the cluster size, electronic structure of the clusters and the interface. A model to describe this behavior will be discussed with special attention to the suitability of the system for cluster array and network formation, and with respect to the future use of highly corrugated surfaces of macromolecule solids to aid these self organization processes.

10:20am **SS1-ThM7 The Role of Defects in the Nucleation, Structure, and Stability of Gold Clusters on Titania***, **W.T. Wallace**, M.-S. Chen, B.K. Min, K.K. Gath, D.W. Goodman,* Texas A&M University

The discovery that Au clusters dispersed on certain metal oxides are efficient catalysts for a variety of low-temperature reactions has stimulated extensive study with the goal of developing a new generation of superior, Au-based catalysts. In this study, the interaction of Au with titania, a commonly used industrial support, has been addressed. Titania, as a 3-D cluster, or a titanium cation, introduced as a heterogeneous defect into a silica thin film, acts as a nucleation site for Au clusters, leading to an enhanced cluster density. Furthermore, both types of defects inhibit Au cluster sintering under reaction pressures and temperatures, thereby circumventing a serious limitation of the typical nanostructured Au catalysts. The growth mode of Au deposited onto titania thin films grown on Mo(112) illustrates the crucial role of surface structure on the Au morphology. On titania films grown on Mo(100), Au forms 3-D clusters when annealed, whereas on a highly defective titania surface grown on Mo(112), Au grows layer-by-layer, forming a thin, ordered film that exhibits exceptional catalytic activity toward CO oxidation.

10:40am **SS1-ThM8 Interaction of CO, Au, and O on Ru(0001)**, ***Q. Wu**, J. Hrbek,* Brookhaven National Laboratory

The coadsorption of O, Au, and CO is studied on the Ru(0001) surface using temperature programmed desorption, Auger electron spectroscopy, and low energy electron diffraction. For low oxygen coverage (O(2x1) or @theta@@sub O@ = 0.5 ML), Au is found to compress the surface oxygen, and contributes to two first-order-like desorption peaks of O@sub 2@ (e.g. ~1150K and ~1200K). The double-peak structure of O@sub 2@ desorption is also observed when Au compresses the "O-rich" Ru(0001) surface (O(1x1) or @theta@@sub O@ ~1 ML excluding subsurface oxygen); the desorption of subsurface oxygen occurs at ~1050K. Desorption is a dynamic process: after subsurface O desorption, compressed surface oxygen starts to desorb and gold spreads on the Ru surface. Au desorption (0.5 ML to 5 ML) from the oxygen modified Ru surface (both O(2x1) and O(1x1)) is consistent with the presence of 3D Au islands. The majority of CO coadsorbed on Au/O/Ru(0001) surface desorbs at low temperatures around 200K; a small fraction reacts with the compressed oxygen to form CO@sub 2@ that desorbs at ~300K.

11:00am **SS1-ThM9 Adsorption and Desorption of Propylene and Ethylene on Au/TiO@SUB 2@*, Y. Yang***, *M.M. Sushchikh, E.W. McFarland,* University of California, Santa Barbara

TiO@sub 2@ supported Au nanoclusters are of interest both as olefin epoxidation catalysts as well as a more general high activity partial oxidation platform. Four different TiO@sub 2@ (110) surfaces were prepared; ideal, fully oxidized, and defected by 0.1% , 1% and 10% surface area sputtering. Identical exposures (270 K (1%) and 300 K (10%)) while the TiO@sub 2@ related peak remains at 150 K. We propose that Au deposited on a sputtered surface is immobilized at defect sites and that with increased sputtering time there is a decrease in the cluster size. The propylene metal interaction is increased in energy as the cluster size decreases. Similar behavior is observed with ethylene desorption.

11:20am **SS1-ThM10 Chemistry of Sulfur Compounds on Au(111)-Supported Mo Nanoparticles.*, D.V. Potapenko,*** Brookhaven National Laboratory*; J.M. Horn, M.G. White,* BNL and SUNY at Stony Brook

We are using the reconstructed (21 x @sr@3)-Au(111) surface as a template and inert support for depositing Mo nanoparticles for subsequent reactivity studies of desulfurization and the formation of Mo sulfide nanoparticles. Bulk molybdenum sulfide is the basis for commercial hydrodesulfurization (HDS) catalysts and this work is focused on exploring the modification of activity for nanostructured Mo and molybdenum sulfide on various supports. Nanoparticles of Mo were prepared on the Au(111) substrate by two methods: physical vapor deposition of Mo and chemical vapor deposition through the Mo(CO)@sub 6@ precursor. STM studies have shown that Mo nanoparticles are thermodynamically unstable on the Au(111) surface and that gold encapsulates Mo at temperatures > 300 K. It follows from TPD/AES experiments that bare Mo nanoparticles are very reactive: they cause complete dissociation of all the S-containing compounds tried and H@sub 2@ was the only major desorption product observed. Au-encapsulated Mo nanoparticles, on the other hand, are much less reactive. They do not chemically interact with thiophene (C@sub 4@H@sub 4@S). Surprisingly, Au-encapsulated Mo nanoparticles react with both H@sub 2@S and CH@sub 3@SH. The latter compound in this case dissociates only partially, causing S deposition and desorption of CH@sub 4@. We believe that interaction of X-SH compounds with Au-encapsulated Mo nanoparticles proceeds through intermediacy of surface gold thiolates.

11:40am **SS1-ThM11 Metal Oxide Nanowires: How Nano-Electronics Can Contribute to Catalysis*, A.A. Kolmakov***, *Y. Lilach, M. Moskovits,* University of California, Santa Barbara

We tested the performance of individual metal oxide single crystal nanowires and nanobelts as catalysts and gas sensors operating in high vacuum and under "real world" reaction conditions. We showed that when nanowire radius is comparable with its Debye length, the adsorption/desorption of donor/acceptor molecules on the surface of the nanowire alters the bulk electron density inside the nanowire what can be sensitively monitored via changes in the conductivity of the nanowire. When nanowire is configured as a field effect transistor the availability of free electrons in the bulk for redox surface reactions can be controlled by the gate thus reactivity (sensitivity) and selectivity of the nanowire surface can be tuned electronically. In vivo conductometric measurements on individual nanowire during its surface doping with catalytic particles manifest the drastic enhance of the reactivity/selectivity of this catalyst (sensor) due to selective adsorption and spillover effect.

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