Surface Science
Room 328 - Session SS3-MoA
Structure and Reactivity of Metal Clusters

Moderator: C.T. Campbell, University of Washington

2:00pm **SS3-MoA1 Catalysis by Supported Metal Nanoclusters***, **D.W. Goodman**,* Texas A&M University **INVITED**

Model catalysts consisting of metal clusters of varying sizes have been prepared on single crystal TiO2 and ultra-thin films of TiO2, Al2O3, and SiO2. The morphology, electronic structure, and catalytic properties of these metal clusters have been investigated with emphasis on the unique properties of those clusters <5.0 nm in size. An array of surface techniques including scanning tunneling microscopy (STM) and polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) have been used to study the metal cluster morphology, electronic properties, and chemistry. These studies illustrate the novel physical and chemical properties of nanosized metal clusters, and suggest that their catalytic properties may be tailored for specific chemical transformations.

2:40pm **SS3-MoA3 Gold Nano-Clusters on Rutile TiO@sub 2@(110) - A Combined UHV and High Pressure STM Study***, E. Walström, R. Schaub, E.K. Vestergaard, A. Ronnau, **F. Besenbacher**,* Interdisciplinary Nanoscience Center, Denmark

Through an interplay between scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, we show that bridging oxygen vacancies are the active nucleation sites for Au clusters grown on the rutile TiO@sub 2@(110) surface under UHV conditions. We show both experimentally and theoretically that a single oxygen vacancy can bind 3 Au atoms on average. A new growth model for the Au/TiO@sub 2@(110) system involving vacancy-cluster complex diffusion is presented. The fate of the Au nano-particles in various gas environments is studied in detail through a new high-pressure STM capable of atomic resolution at atmospheric pressures. Sintering and morphological changes are followed in-situ when the Au/TiO@sub 2@(110) system is exposed to reducing (H@sub 2@,CO) and oxidizing (O@sub 2@) conditions.

3:00pm **SS3-MoA4 Dimethyl Methylphosphonate Decomposition on Supported Ni Nanoparticles Deposited on a TiO@sub 2@(110) Surface***, **J. Zhou**, Y.C. Kang, K. Varazo, D.A. Chen,* University of South Carolina

Sizes and structures of oxide-supported metal nanoparticles are very important in determining their catalytic reactivity. In our study, the thermal decomposition of dimethyl methylphosphonate (DMMP) on supported nickel nanoparticles has been investigated as a model system to understand the relationship between the particle size and reactivity. All the experiments were performed under UHV conditions by scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). Our STM studies show that various sizes of Ni particles with uniform particle size distributions can be prepared on TiO@sub 2@(110) surface by varying the diffusion (D) to deposition flux (F). The most uniform size distribution of Ni nanoparticles can be obtained with the lowest D/F ratio. XPS and TPD studies indicate that mainly molecular DMMP adsorbs on the supported Ni nanoparticles at room temperature. Between room temperature and 800 K, the adsorbed DMMP decomposes to produce H@sub 2@ and CO as primary gaseous products and CH@sub 4@ and HCHO as minor products. After heating to 800 K, all carbon desorbs from the surface while atomic phosphorous still remains. DMMP decomposition on various sizes of Ni nanoparticles as well as on the bulk Ni surface will be compared. Furthermore, studies of DMMP reaction will be also carried out on the supported Pt nanoparticles.

3:20pm **SS3-MoA5 Dynamics and Chemical Reactivity of Au on TiO@sub2@ (110) Rutile***, **D. Pillay**, Y. Wang, G.S. Hwang,* University of Texas at Austin

Au has long been known to be chemically inert in its bulk form, as compared to other transition metals, such that it has received little attention as a catalyst. However, Au nanoclusters dispersed on oxide (particularly TiO@sub2@) shows an extraordinarily high activity for low-temperature catalytic combustion, partial oxidation of hydrocarbons, hydrogenation of unsaturated hydrocarbons, and reduction of nitrogen oxides. But, due to weak metal-oxide interfacial bonding interactions, Au nanoclusters become unstable toward sintering even at moderate temperatures. This may in turn undermine their catalytic activity and selectivity. Hence, along with their chemical reactivity, a detailed understanding of dynamical behaviors of Au atoms is necessary for an accurate description of underlying reaction mechanisms and performance of the oxide supported nanometal catalytic systems under realistic processing conditions. In this talk, we will present our first principles [DFT with plane waves and pseudopotentials] study of Au adsorption and diffusion on regular and defective (with oxygen vacancies) TiO@sub2@ (110) rutile. We will also present the diffusion of oxygen vacancies (Fs center) and their interactions with Au atoms. Based on our calculation results, we will discuss underlying reasons for the enhancement of Au cluster sintering upon exposure to a high-pressure oxygen environment.

3:40pm **SS3-MoA6 Oxygen-Induced Morphological Changes in Cu and Ni Islands on TiO@sub2@(110)***, **D.A. Chen**, J. Zhou,* University of South Carolina*; Y.C. Kang,* Pukyong National University, South Korea

Metal particles supported on oxide surfaces serve as excellent model systems for developing a better understanding of commercial heterogeneous catalysts. Scanning tunneling microscopy (STM) studies of Cu islands grown on a rutile TiO@sub2@(110)-(1x1) surface demonstrate that these islands disappear from the STM images after exposure to oxygen gas. Based on X-ray photoelectron spectroscopy (XPS) experiments, the disappearance of the Cu islands cannot be explained by the loss of Cu from the surface or by a dramatic change in the electronic properties of the islands. The adsorption of oxygen appears to weaken the Cu-Cu bond, allowing two-dimensional (2D) Cu islands to form on the surface at the expense of the existing three-dimensional (3D) islands. The formation of 2D islands is thermodynamically favorable for Cu based on the lower surface free energy of oxidized compared to that of both Cu and TiO@sub2@. Oxygen-induced disappearance of Ni islands has also been observed, but the rate of disappearance is much slower even though Ni is more easily oxidized than Cu. This effect can also be explained in terms of thermodynamics; oxidation of Ni islands does not reduce the surface free energy of the islands below that of TiO@sub2@, and therefore there is less driving force for the Ni islands to become 2D. As expected, oxidation of Cu islands at 500 K increases the rate of disappearance of the 3D islands. However, oxidation of the Ni islands at 500 K causes significant changes in the surface morphology due to the oxidation of the TiO@sub2@ surface itself. The new titania layers preferentially regrow around the Ni islands, resulting in a much rougher surface.

4:00pm **SS3-MoA7 Chemical Reactions on Free Iridium and Platinum Clusters***, **M. Andersson**, T. Jarvdalen, P. Nystrom, A. Rosen,* Chalmers University of Technology and Goteborg University, Sweden

In a cluster beam experiment metal clusters are produced with a pulsed laser vaporization source, kept at room temperature or liquid nitrogen temperature. The beam of neutral clusters passes two low-pressure collision cells and clusters and reaction products are detected with laser ionization and time-of-flight mass spectrometry. Thus, the reaction probability in a cluster-molecule collision can be determined.@footnote 1@ We have measured the CO and O@sub 2@ adsorption on iridium clusters, 5-32 atoms. The overall size-dependence in reaction probability is similar for both molecules, with minima at Ir@sub 8@, Ir@sub 12@ and Ir@sub 18@, and a significantly higher reactivity for all clusters with more than 18 atoms. When the cluster source was cooled to liquid-nitrogen temperature, the reaction probability increased. For platinum clusters with more than 6 atoms we measured stable reaction products with both oxygen and hydrogen, with moderate variations with size. Using the two reaction cells we can let the clusters react first with O@sub 2@ and then with H@sub 2@ and observe that reaction of Pt@sub n@(O@sub 2@)@sub m@ with H@sub 2@ results in removal of oxygen atoms from the cluster. This is interpreted as formation of a water molecule, which subsequently desorbs. The efficiency of the catalytic water formation is high on all cluster sizes measured (7-30 atoms), with only a weak dependence on cluster size.@footnote 2@ @FootnoteText@@footnote 1@ M. Andersson, J.L. Persson, A. Rosen, J. Phys. Chem. 100, 12222 (1996).@footnote 2@ M. Andersson, A. Rosen, J. Chem. Phys. 117, 7051 (2002).

4:20pm **SS3-MoA8 STM Study of Copper Growth on ZnO(0001)-Zn and ZnO(0001bar)-O Surfaces***, **O. Dulub**,* Tulane University*; L. Vogel Koplitz,* Loyola University*; M. Batzill, U. Diebold,* Tulane University

The study of Cu particles on ZnO surfaces is of great interest due to the wide application of this system in the low-temperature synthesis of methanol, the water-gas shift reaction, and the production of hydrogen by steam reforming. The mechanism that enhances the catalytic activity of Cu is still poorly understood. Therefore, a detailed study of this system on the atomic level is desirable. Scanning Tunneling Microscopy (STM) has been used to study the room temperature growth of Cu on the polar (0001)-Zn and (0001bar)-O surfaces of zinc oxide. The (0001)-Zn surface prepared by sputtering and annealing at 500-750°C, shows flat terraces with a high density of triangular pits and islands. STM shows that Cu grows on the (0001)-Zn surface as three-dimensional clusters at coverages between 0.05 and 0.25 monolayers (ML)); two-dimensional (2D) islands are only observed at very low coverages (0.001-0.05 ML). The average size of the 3D clusters increases with coverage and their density increases slowly. The size and morphology of Cu clusters depends on the terrace size of the substrate. The triangular pits and islands on the terraces do not act as preferred nucleation sites for Cu, but, surface roughness and sputter damage change the growth mode to more 2D-like. The Cu clusters are well-separated and exhibit a well-defined hexagonal shape. Equilibrium crystal shape analysis of the largest clusters yields an apparent work of adhesion of 3.4 ± 0.1 J/m@super 2@, which is size dependent and decreases with the size of the cluster. The morphology of the clean (0001bar)-O surface is distinctly different from that of the (0001)-Zn surface. The terraces are smooth and have no small islands. Formation of two-dimensional Cu clusters at coverages of less than 0.1 ML was observed on the (0001bar)-O surface.

4:40pm **SS3-MoA9 Charge Exchange between Alkali Ions and Nanocrystal Metal Surfaces*, G. Liu*,** *J. Yarmoff,* University of California, Riverside

Au nanocrystals grown on TiO@sub 2@(110) possess unique catalytic properties, which depend on the cluster size.@footnote 1@ Presumably, the catalytic properties are the result of the electronic configuration of the nanocrystals. Earlier, we showed that the probability for neutralization of low energy alkali ions scattered from metal surfaces is determined by the local electrostatic potential (LEP) a few Å's above the scattering site.@footnote 2@ In the present work, we are using the charge exchange between alkali ions and metallic nanocrystals as a probe of their electronic structure. 2 keV @super 23@Na@super +@ ions were scattered from Au nanocrystals grown on TiO@sub 2@(110), and the neutral fractions of the Na particles singly scattered from Au were measured with time-of-flight. As the average size of the Au nanoclusters increases, the neutral fraction decreases until a uniform Au film is formed. The neutral fraction of Na scattered from bulk Au is very small (~2%) due to the large work function of Au. For small Au clusters, however, the neutral fractions can be as high as 30% or more. The high neutral fraction of the small Au clusters suggests that the alkali ions are coupling to electronic states that are specific to the nanocrystals. The work function change, measured as a function of cluster size, shows a smooth change from the clean TiO@sub 2@(110) surface to that of bulk gold. In order to understand the influence of the work function on the neutral fraction, Cs was deposited onto Au/TiO@sub 2@(110) surface to controllably decrease the work function. In addition, the dependence of the neutral fraction on the ion exit angle and energy was studied. @FootnoteText@ @footnote 1@X. Lai, T. P. St. Clair, M. Valden, and D. W. Goodman, Prog. Surf. Sci. 59 (1998) 25.@footnote 2@C. B. Weare and J. A. Yarmoff, Surf. Sci. 348 (1996) 359.

5:00pm **SS3-MoA10 Electronic Detection of Oscillatory Reactions on Supported Platinum Particles*, M.C. Wheeler,*** University of Maine*; R.E. Cavicchi, S. Semancik,* National Institute of Standards and Technology

A MEMS device, capable of surface temperature control and electrical resistance measurements, has been used to detect and explore the oscillatory reaction of CO oxidation on oxide-supported platinum particles. The behavior has been monitored for a range of conditions, but as an example, when the supported platinum is heated to 165°C in a 340 ppm CO/air mixture at atmospheric pressure, periodic switching between a low-resistance (excess CO) state and a high-resistance (excess oxygen) state is observed. During these cycles, the resistance ranges from 7.1 k@ohm@ to 17. k@ohm@ and back to 7.1 k@ohm@ over a period of 200 s. The resistance switching that we have studied on small (on the order of 30 nm) platinum particles is likened to the temporal oscillations of the reaction on platinum films@footnote 1@ and single crystal samples,@footnote 2@ which were monitored by infrared and photoemission electron microscopy respectively. We have shown that the frequency of the resistance oscillations can be manipulated by varying the CO partial pressure in order to influence the rate of CO uptake. Also, synchronization observed between oscillations for physically separate devices in multi-element arrays is evidence that the oscillations are due to a globally-coupled, mass-transfer and reaction rate effect. Indeed, effects such as doubling of the oscillation frequency on neighboring devices are similar to the rate behavior observed by Yamamoto et al. In addition to the global synchronization, transient oscillations are observed prior to switching that suggests microscale-coupling occurs between the individual platinum particles on the support. @FootnoteText@@footnote 1@ Yamamoto, Surko, and Maple, J. Chem. Phys. 103, 8209 (1995).@footnote 2@ G. Ertl, Science 254, 1750 (1991).

Author Index

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