

Surface Science

Room 203 - Session SS2-WeA

Reactions on Nanoclusters

Moderator: I. Chorkendorff, Technical University of Denmark

2:00pm SS2-WeA1 Physical and Chemical Properties of Model Catalysts Prepared by Size-Selected Cluster Deposition, T. Wu, S. Lee, C. Fan, W. Kaden, S.L. Anderson, University of Utah

In surface chemistry, one of the most important goals is to understand the relationship between surface structure and catalyst reactivity, especially at an atomic level. An interesting aspect of this field is the effect of particle size in supported catalysts, i.e., how cluster size affects the physical properties of the surface, as well as the activity for specific reactions. In our lab, model gold, iridium, and palladium catalysts were prepared by deposition of size-selected metal clusters on well defined oxide surfaces, and characterized by a combination of X-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), temperature-programmed desorption, and pulse-dosing mass spectrometry. Activity is strongly size-dependent. For example, in reaction of hydrazine on Ir/alumina model catalysts, both activity, and the distribution of products change dramatically with cluster size. Strong dependence on size is also seen for CO oxidation.

2:20pm SS2-WeA2 Probing the Chemical Reactivity of Oxide-Supported Pd Nanoparticles with STM, J. Zhou, A.P. Baddorf, S.V. Kalinin, S.H. Overbury, D.R. Mullins, Oak Ridge National Laboratory

Oxide-supported metal nanoparticles play a central role in current heterogeneous catalysis. They may exhibit unique catalytic properties that can be tuned by particle size and structure as well as by choice of oxide substrate. However, there is still a need to understand the origins of catalytic activity of metal/metal-oxide interfaces at the atomic scale. We report scanning tunneling microscopy (STM) studies of supported Pd nanoparticles evaporated on a rutile TiO₂(110) single crystal surface in ultrahigh vacuum as a model catalytic system. A range of particle sizes with narrow size distributions was prepared by varying Pd coverage, substrate growth and post-annealing temperatures. Electronic properties of the particles and adjacent substrate were determined with I-V and dI/dV spectroscopies. The surface chemistry of supported Pd particles was explored for reactive gases such as O₂, CO and benzene between 20 and 300 K. Images of specific particles are compared before and after in situ exposures. Research was sponsored by the Laboratory Directed Research and Development Program of ORNL, managed by UT-Battelle, LLC for the U. S. DOE under Contract DE-AC05-00OR22725.

2:40pm SS2-WeA3 Structure and Reactivity of Metal Clusters, H.J. Freund, Fritz-Haber-Institute of the Max-Planck-Society, Germany

INVITED

Model catalyst systems have been prepared by growth of metal nano-aggregates on thin well-ordered oxide films of alumina and silica. These systems lend themselves to structural and morphological characterization via scanning probe microscopies and transmission electron microscopy and bridge to a certain extent the materials gap between metal single crystal studies and the investigation of real catalyst samples. It is possible to infer direct structure-reactivity relations when simple reactions of small molecules are studied. We have applied a variety of surface sensitive techniques, both under ultrahigh vacuum as well as under ambient conditions to relate observations from surface science to those in catalysis under realistic gas pressure conditions. Examples are presented.

3:20pm SS2-WeA5 The Active Structure of Supported Au Catalysts, M.S. Chen, Z. Yan, Y. Cai, W.T. Wallace, X.F. Lai, D.W. Goodman, Texas A&M University

The high catalytic activity of gold clusters on oxides has been attributed to structural effects, including particle thickness and shape, metal oxidation state, as well as support effects. The best catalytic performance of supported Au particles was found for clusters with sizes of 2-3 nm. For Au clusters supported on TiO₂(110), the unique properties have been associated with Au structures two atomic layers in thickness based on STM and kinetic measurements (M. Valden, X. Lai, D. W. Goodman, Science 281, 1647 (1998)), and confirmed by our recent results. Specifically, we have synthesized well-ordered Au monolayers [(1x1)] and bilayers [(1x3)] that completely wet (cover) the oxide support [a titanium oxide monolayer film grown on the Mo(112) surface] (M. S. Chen, D. W. Goodman, Science 306 (2004) 252.). Kinetic measurements for CO catalytic oxidation show that

the Au bilayer structure is significantly more active (by more than an order of magnitude) than the monolayer structure, and is approximately 45 times higher than that reported for the most active high-surface-area Au/TiO₂ catalysts. These specific rates clearly indicate that bilayer Au is the active structure for CO oxidation. These results eliminate particle shape and direct support effects as significant contributions to the special catalytic properties of nano-sized Au clusters.

3:40pm SS2-WeA6 Neutralization of Low Energy Li Ions Scattered from Au Nanoclusters, G.F. Liu, University of California, Riverside; Z. Sroubek, Czech Academy of Sciences; J.A. Yarmoff, University of California, Riverside

Charge exchange during the scattering of low energy (0.5-10 keV) alkali ions provides a sensitive measure of the confined quantum states of nanomaterials. In earlier work, we showed that the neutralization of Na⁺ scattered from Au nanoclusters correlates with the presence and position of the confined states.¹ In this work, we scatter Li ions from Au nanoclusters grown on TiO₂(110). The neutralization probability of the Li singly scattered from the Au nanoclusters is measured with time-of-flight spectroscopy. Au nanocrystals grown on TiO₂(110) possess unique catalytic properties, which depend on the cluster size. The size of the clusters is determined by the amount of Au deposited and the surface temperature, and increases with the amount deposited. The neutral fraction was found to have a maximum at ~0.2 ML Au coverage, which is consistent with the maximum seen for the catalytic activity.² This provides clear evidence that the ion scattering is probing the same states that are responsible for unique properties of these materials. When additional Au is deposited, the neutral fraction first drops to a minimum (at ~10 ML Au), and then increases to the bulk Au value. This shows that ion scattering is able to monitor the formation of the conduction band as a transition is made from isolated clusters to a continuous film. In addition, the dependence of the neutral fraction on the ion exit angle and energy was investigated. In order to better correlate the dependence of the cluster sizes on the neutral fraction, future experiments will involve Li and Na ions scattered from size-uniform nanoclusters grown by chemical synthesis. ¹G. F. Liu, Z. Sroubek, and J. A. Yarmoff, Phys. Rev. Lett. 92, 216801 (2004). ²M. Valden, X. Lai, and D.W. Goodman, Science 281, 1647 (1998).

4:00pm SS2-WeA7 Growth and Reactivity of Bimetallic Pt-Rh Nanoclusters on Titanium Dioxide, S. Ma, Brookhaven National Laboratory; J.S. Ratliff, J.B. Park, D.A. Chen, University of South Carolina

Bimetallic Pt-Rh nanoclusters have been grown on rutile TiO₂ by vapor deposition under ultrahigh vacuum conditions. Low energy ion scattering (LEIS) experiments show that Pt tends to segregate to the surface of the nanoclusters, regardless of whether Rh is deposited on top of Pt or Pt is deposited on top of Rh. Pt diffusion into the clusters occurs readily at room temperature and is only slightly slower when the deposition temperature is decreased to 220 K. Scanning tunneling microscopy (STM) experiments indicate that for 2 monolayers of Pt deposited on 2 monolayers of Rh, the resulting clusters have an average height of 0.9 nm and diameter of 5 nm. Although heating to 850 K significantly increases the Pt-Rh cluster size (1.3 nm height, 7 nm diameter), LEIS experiments indicate that the clusters become completely encapsulated with TiO₂ at temperatures above 700 K. In situ STM experiments demonstrate that during the deposition of Pt on Rh clusters, existing clusters grow bigger, new Pt clusters are nucleated, and many growing Pt-Rh clusters merge with neighbors to form larger clusters. The reaction of NO on pure Pt or Rh clusters results in production of N₂ as well as desorption of NO. However, NO chemistry on bimetallic Pt-Rh clusters is qualitatively different since a new product, N₂O, is also observed. The reduction of NO with CO to produce N₂ and CO₂ does not occur on pure Pt or Rh clusters but is observed on the bimetallic Pt-Rh clusters.

4:20pm SS2-WeA8 Reactive-Layer-Assisted Deposition (RLAD) of TiO₂ Nanoparticles on Au(111) Studied by STM and XPS, Z. Song, Columbia University; J. Hrbek, Brookhaven National Laboratory; R.M. Osgood, Columbia University

TiO₂ nanoparticles have been prepared by reactive-layer-assisted deposition (RLAD), in which Ti atoms are initially deposited on a multilayer of H₂O (or NO₂) grown on a Au(111) substrate at temperature <100 K. The chemical, structural and electronic properties of these oxide nanoparticles were studied by XPS, STM and STS. Specifically, ~1nm diameter TiO₂ particles formed with an H₂O reactive layer were obtained after raising the substrate temperature to

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300K. Use of NO₂ reactive layers yields TiO₂ nanoparticles (~1nm at 300K) with NO₃ radicals decorating their surfaces at temperatures below 500K. Further annealing induces the desorption of N-containing species and leaves behind flat TiO₂ rutile and anatase particles (~5nm after being annealed to 700K) with various facets. STS studies showed different electronic structures for different TiO₂ particle sizes. This UHV compatible method for preparing well-defined TiO₂ nanoparticles can be used in molecular-level studies of reaction mechanisms of photocatalytic processes on TiO₂ nanoparticle surfaces.

5:00pm **SS2-WeA10 Bimodal Pd Cluster Growth on the Reduced SnO₂ (101) Surface**, *Kh. Katsiev, M. Batzill, U. Diebold*, Tulane University

Tin oxide is a solid state gas sensor for detection of combustible and toxic gases. Its sensitivity and selectivity can be enhanced by catalytically active dopants, such as Pd. We have studied the growth of Pd on the SnO₂ (101) surface in the sub-monolayer regime in order to gain new insights into the gas sensing mechanism. The SnO₂ substrate exhibits a 1x1 bulk termination, with the surface tin atoms in a reduced Sn²⁺ charge state. This reduction of the surface Sn atoms results in the formation of a Sn-5s derived surface state. Upon deposition of Pd onto SnO₂ (101), bimodal cluster growth was observed. For very low coverages, two-dimensional, round clusters decorate (0-10) -oriented step-edges, a behavior typical for many metal-on-oxide systems. In addition, we observe quasi one-dimensional Pd clusters growing on terraces. In both cases Pd wets the reduced tin oxide surface. The one-dimensional clusters are imaged in scanning tunneling microscopy as straight, parallel nanostructures oriented along the (-101) direction, all with the same characteristic width of 1 nm and a height of 1ML. XPS shows metallic Pd. A 0.45 eV shift in the Pd 3d core level peak position to lower binding energy occurs during the initial stages of the growth. This might be an indication of charge transfer from the Pd clusters to the substrate. Coverage-dependent UPS show that at fractional monolayer coverages, a Pd peak appears at the same position in the band gap as the Sn-5s surface state of reduced SnO₂(101), indicating a possible hybridization of Sn-5s with the Pd d-band. This is the first observation of formation of one-dimensional, metallic nanowires on a wide-band gap material.

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