

Surface Science

Room 2002 - Session SS1-TuM

Reactivity of Metal Clusters

Moderator: A.J. Gellman, Carnegie Mellon University

8:00am SS1-TuM1 Thermal Stability of Metallic Nano-Clusters and Film Patterning on Solid Surfaces Studied Via Weakly Bound Buffer Layer, M. Asscher, Hebrew University, Israel

Growth of metallic nano-clusters and control over their size are critically important for catalysis. Development of film patterning at the nanometer scale has significant impact on future lithography. In this work we combine a method to deposit metallic nano-clusters using weakly bound buffer layer as an intermediate substance to control the clusters size with laser patterning that modulates their surface density. Using optical probes, the size selected diffusion of gold nano-clusters on metallic and oxygen modified surfaces has been studied. Information on clusters mobility is critical for understanding and control the thermal stability of clusters toward the development of sintering resistant catalysts. The same technique was further developed at thicker film thickness to pattern the layer at the sub-micron to nanometer scale employing a single laser pulse. This technique is discussed as a novel approach for lithography.

8:20am SS1-TuM2 CO and NO Reactions over Rh Nanoparticles Supported on Ceria Thin Films@footnote 1@, S.D. Senanayake, D.R. Mullins, Oak Ridge National Laboratory

The reduction of noxious automotive emissions such as CO and NO@sub X@ with the use of solid catalysts is of great importance at present due to ever tightening regulatory standards for gas emissions. Novel catalysts consisting of metal particles supported on various oxide surfaces are often employed. The oxidation reaction of CO to CO@sub 2@ and the sequential reduction of NO to N@sub 2@ are frequently found to be strongly dependent on the composition and oxidation state of the oxide support. In this work we investigated reactions over one such catalytic system, Rh/CeO@sub X@, with the use of temperature programmed desorption (TPD), soft x-ray photoelectron spectroscopy (SXPS) and near edge x-ray absorption fine structure (NEXAFS) spectroscopy. The CeO@sub 2@ and CeO@sub X@ surfaces are grown in situ by evaporation of Ce in a low-pressure O@sub 2@ ambient (1x10@sup -7@ Torr) on a Ru(0001) single crystal. Rh nanoparticles are subsequently deposited onto this surface. Isotopic labeling of the substrate (Ce@sup 18@O@sub X@) and reactants (@sup 13@CO and @sup 15@NO) were used to elucidate reaction mechanisms. Surface intermediates are identified using SXPS and NEXAFS performed at Beamline U12a at the NSLS. In addition we also present preliminary results of this same reaction under dynamic reaction conditions. The pressure gap is a very difficult obstacle to overcome in the study of real time reaction dynamics under UHV conditions. We have addressed this problem by using an effusive molecular beam of CO and NO produced by a directed-doser attached to the UHV system. We have compared the reaction on a Rh(111) single crystal surface with that on Rh nanoparticles supported on ceria. @FootnoteText@ @footnote 1@Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

8:40am SS1-TuM3 Size Dependent Composition and Catalytic Reactivity of Platinum Clusters from First Principles, W.F. Schneider, University of Notre Dame

INVITED

Three central questions have emerged in nanoscale heterogeneous catalysis: First, how does the structure and catalytic function of transition metal catalysts evolve as particles decrease in size from the micro to the nanoscale? Second, how do these particles interact and communicate with supports, and what are the effects on structure and reactivity? Third, how does the particle/support system respond to realistic and dynamic reaction environments? In this work we use first-principles density functional theory methods to consider these three questions in the context of oxidation catalysis on 1-10 atom Pt clusters. Using DFT-parameterized thermodynamic models, we explore the structure and composition of the clusters as a function of oxidation conditions, illustrating the pronounced tendency to become partially to completely oxidized under most practically relevant conditions.@footnote 1@ This tendency is shown to persist but to be modified in clusters supported on an undefected MgO surface. To probe the consequences of environment and support on reactivity, we contrast

the reactivity of the clusters toward strong (CO) and weak (NO) reductants. The results illustrate that both particle size and reactive environment can have a significant influence on the reactivity of metal clusters and start to clarify the origins of these effects. @FootnoteText@ @footnote 1@ Y. Xu, W. A. Shelton, and W. F. Schneider, "Effect of Particle Size on the Oxidizability of Platinum Clusters," J. Phys. Chem. A, 2006, in press.

9:20am SS1-TuM5 Formic Acid Decomposition on Pd Nanoparticles Deposited on TiO@sub 2@(110), J. Zhou, S. Dag, V. Meunier, S.V. Kalinin, D.R. Mullins, S.H. Overbury, A.P. Baddorf, Oak Ridge National Laboratory Adsorption and dissociation of formic acid molecules on clean TiO@sub 2@(110) and on TiO@sub 2@(110) with deposited Pd nanoparticles were investigated using scanning tunneling microscopy (STM), temperature programmed desorption (TPD) and first-principles calculations. Our TPD data indicate that formic acid can decompose on bare titania and produce CO, CO@sub 2@, H@sub 2@ and H@sub 2@O upon heating after adsorption at 110 K. H@sub 2@ was detected in multiple peaks between 200 K and 600 K, while CO and CO@sub 2@ desorbed with a single peak around 550 K and H@sub 2@O evolved at 270 K. After deposition of Pd to titania, formic acid dissociation was greatly enhanced. Furthermore, multiple CO, CO@sub 2@ and H@sub 2@ desorption peaks were observed. At 300 K, individual species were seen bonded to the atomic Ti rows in the STM image, due to the formate formation after adsorption. Bonding of formate on reduced 1x2 strands was also observed in our study. Formate was further identified near and on Pd particles by STM at 300 K. Upon heating to 375 K, formate reacted to form a new species observed bridging the Ti rows. An atomic scale understanding of the experimental STM images is provided from detailed first-principles calculations. 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.

9:40am SS1-TuM6 Pd Cluster Growth on the SnO2 (101) Surface, Kh. Katsiev, U. Diebold, M. Batzill, Tulane University

Tin oxide is widely used as 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 using STM, XPS, ARUPS and LEED. The SnO2(101)-(1x1) surface was prepared in stoichiometric (Sn(IV)) and in full- reduced (Sn(II)) form. Palladium was vapor-deposited on both surfaces at room temperature. On the stoichiometric surface round 3-D clusters with an average size of ~1 nm nucleate at surface defects. On the reduced surface, 1-D nanostructures form on the terraces; these are imaged in STM as straight, parallel structures, all with the same characteristic width of one substrate unit cell and height of one ML. The length of the Pd clusters is limited by the size of the substrate's terraces. XPS shows metallic Pd with a 0.45 eV shift in the Pd 3d core level peak position to lower binding energy during the initial stages of the growth. ARUPS measurements show that the position of the Pd-4d valence band "follows" the position of the Sn-5s derived surface state for the reduced SnO2(101) surface. This indicates a strong electronic interaction between the Sn-5s state and the Pd d-band. Clusters nucleated at sputter-created defects are wider and shorter. From LEED it appears that the 1D clusters are commensurate with the substrate in one direction. Formic acid adsorbs on the 1D nanoclusters, but not the SnO2 surface at RT. The clusters are thermally not stable, they coarsen upon annealing to a temperature of 200°. DFT calculations of various test structures suggest that the formation of the 1-dim clusters is dominated by kinetic effects. Pronounced one-dimensional diffusion, combined with strong interaction between Pd and surface Sn appear to be responsible for the formation of the one-dimensional islands.

10:40am SS1-TuM9 New Atomic-Scale Insights Into Promoter and Support Effects on MoS@sub 2@ Nanoclusters from STM Studies of Hydrotreating Model Catalysts, J. Kibsgaard, J.V. Lauritsen, University of Aarhus, Denmark; H. Topsøe, B.S. Clausen, Haldor Topsøe A/S, Denmark; F. Besenbacher, University of Aarhus, Denmark

To meet the stringent requirements for upgrade and clean-up of transport fuels by hydrotreating there is currently an urgent need to understand and improve the MoS@sub 2@-based catalyst applied for this service. The active phase of this catalyst is composed of 2-3nm wide MoS@sub 2@-like nanoclusters, typically promoted by Co or Ni, forming the so-called CoMoS and NiMoS nanostructures. Despite intense research efforts, the morphology of CoMoS and NiMoS and the detailed location and coordination of the promoter atoms have not been resolved. Consequently, the role of the Co and Ni is poorly understood, and existing

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models are not able to account for the difference in the specific selectivity of Co or Ni promoted catalysts with respect to hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrogenation (HYD). In this study, we present atom-resolved scanning tunneling microscopy (STM) of CoMoS and NiMoS nanoclusters supported on Au(111). In the STM images we observe a promoter dependent morphology, which is explained by the different affinities for Co and Ni to replace Mo at the edge sites of MoS@sub 2@ nanoclusters. This finding shows that the location and coordination of the promoter atoms are different in CoMoS and NiMoS, which may explain the different selectivity observed in the industrial catalysts. In order to include the effect of a different support, we also synthesized MoS@sub 2@ nanoclusters on highly oriented pyrolytic graphite (HOPG). HOPG as a substrate is indeed very interesting since carbon-supported hydrotreating catalysts have previously been found to exhibit very high HDS reactivity. STM images reveal that the morphology of the MoS@sub 2@ nanoclusters is very dependent on the exact preparation temperature. Furthermore, images of the top facet of the clusters provide new atomic-scale information on the MoS@sub 2@-HOPG topotaxy, and we find good correspondence between the edge structure and previous studies of MoS@sub 2@ on an Au substrate.

11:00am **SS1-TuM10 Deposition and Reactivity of Mo@sub x@S@sub y@ (x/y=4/6, 6/8, 7/10) Clusters on Au(111)**, *J.M. Lightstone, M.J. Patterson, J. Lofaro*, Stony Brook University; *P. Liu, M.G. White*, Brookhaven National Laboratory

We have recently constructed a cluster deposition apparatus which employs a magnetron sputtering source for generating gas-phase cation clusters of pure metals and metallic compounds. Our current focus has been the production of early transition metal sulfide clusters for reactivity studies in both the gas-phase and deposited on well defined surfaces. The transition metal sulfides are particularly interesting due to their catalytic properties@footnote 1@ and their ability to form fullerene-like nanostructures that reflect the S-M-S layered structure of the bulk material.@footnote 2@ The work reported here examines preliminary electron spectroscopy and temperature programmed desorption results from size-selected Mo@sub x@S@sub y@ (x/y=4/6, 6/8 and 7/10) clusters deposited on a Au(111) single crystal. A wide array of molybdenum sulfide clusters, Mo@sub x@S@sub y@@super +@ (x/y= 2/6, 3/7, 4/6, 5/7, 6/8, 7/10, 8/12), were generated using a magnetron sputtering source, including the "magic" number species Mo@sub 4@S@sub 6@@super +@. Several Mo@sub x@S@sub y@@super +@ clusters were mass selected using a quadrupole mass spectrometer and deposited on a Au(111) single crystal under ultra-high vacuum conditions. The presence of deposited clusters was confirmed using Auger Spectroscopy (AES) while Ultraviolet and X-Ray Photoelectron Spectroscopy (UPS, XPS) were used to probe the electronic structure of the cluster covered surface. Temperature Programmed Desorption (TPD) of carbon-13 labeled CO shows cluster-dependent desorption peaks which were used to estimate CO binding energies. The TDP spectra are also found to depend on annealing temperature, which suggest surface modifications or cluster decomposition at higher temperatures. @FootnoteText@ @footnote 1@T. R. Thurston and J. P. Wilcoxon, *J. Phys. Chem. B*, 103 (1997) 11.@footnote 2@R. Tenne and C. N. R. Rao, *Phil. Trans. R. Soc. Lond. A*, 362 (2004) 2099.

11:20am **SS1-TuM11 The Structure of Catalytically Active Gold**, *M.S. Chen, D.W. Goodman*, Texas A&M University

Well-ordered Au mono- and bi-layer films were synthesized on a TiOx/Mo(112). The wetting of Au on the (8x2)-TiOx is clearly evidenced by recent STM studies, and the ordered (1x1) mono- and (1x3) bi-layer structures are atomic resolved. The electronic and chemical properties of these ordered Au films were characterized by IRAS using CO as a probe molecule and UPS. Kinetic measurements for the catalytic oxidation of carbon monoxide show that the Au bi-layer structure is significantly more active (by more than an order of magnitude) than the monolayer, and is about 45 times higher than that reported for the most active higher-surface-area Au/TiO2 catalyst. The common structural features of ordered Au bi-layers and Au bi-layer nanoparticles on TiO2(110) are described, the nature of the active site and structure of supported Au catalysts are discussed, and the exceptionally high catalytic activity of the Au bi-layer structure are related to its unique electronic properties.

11:40am **SS1-TuM12 Novel Gold Catalysts: UHV and Ambient Studies on Nanoporous Gold Surfaces**, *M. Baeumer, T. Nowitzki, B. Juergens, C. Schulz, V. Zielasek*, University Bremen, Germany; *J. Biener, M. Biener, A.V. Hamza*, Lawrence Livermore National Laboratory

While a lot of questions regarding the underlying mechanisms of gold catalysis are still under debate, it is evident that low-coordinated Au atoms play a decisive role for reactions such as the low-temperature oxidation of CO, for instance. In order to elucidate how low-coordinated Au atoms can be stabilized and in which way they interact with CO, we performed UHV model studies pursuing two different approaches. On the one hand, a Au(111) single crystal surface was sputtered by argon and oxygen ions, resulting in rough pit-and-mound structures. Annealing experiments clearly revealed that the oxygen sputtered surface exhibits a higher thermal stability, indicative of the stabilization of under-coordinated Au atoms by adsorbed oxygen. In both cases, two CO TPD desorption peaks are observed between 100 K and 200 K. For the oxygen sputtered surface also CO2 formation is detected concurrently with desorption of CO. On the other hand, Au was deposited on graphite as a weakly interacting support. Interestingly, the same TPD spectrum with 2 peaks is found in this case. Deposition under various conditions (variation of the support temperature, defect-assisted growth) reveals that both states are defect-related. In line with theoretical results, one state may be attributed to step edges, the other to even less coordinated sites. As a similar desorption behaviour was observed for other particle systems and rough single crystal surfaces, this seems to be a general feature. In addition to the UHV studies, we performed catalytic studies with a gold foam prepared by dealloying of a Ag/Au alloy. It exhibits a very similar morphology as compared to the sputtered Au(111) surface. We could demonstrate that this material has an unexpectedly high catalytic activity for CO oxidation at temperatures down to -20 °C. @FootnoteText@ Part of this work was performed under the auspices of the U.S. Dep. of Energy by Univ. of California, Lawrence Livermore National Laboratory under contract No.W-7405-Eng-48.

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