Surface Science

Room: 608 - Session SS1-MoM

Catalysis on Clusters and Nanoparticles

Moderator: M. Mavrikakis, University of Wisconsin - Madison

8:00am SS1-MoM1 Platinum Nanoparticle Shape and Stabilizing Agent Effects on Catalysis, *K.M. Bratlie, H. Lee, P. Yang, K. Komvopoulos, G.A. Somorjai*, University of California, Berkeley
Our goal is to understand the behavior of real catalyst systems on a molecular level. To accomplish this task, a model system of capped platinum nanoparticles on a silica substrate is used. The nanoparticles exhibit a narrow size distribution and well defined shape. We were able to monitor two different shapes: cubes, comprised of {100} facets, and cuboctahedra, made of {111} and {100} facets. We were also able to investigate the influence of the capping agent on the catalytic activity of the particles. Kinetic studies of benzene hydrogenation on platinum nanoparticles over a range of temperatures (310 - 400 K) were used to relate nanoparticles to single crystals. In this manner, we uncovered implications for reaction mechanisms nanoparticle surfaces identical to analogous single crystal faces.

8:20am SS1-MoM2 Catalytic Properties of Pt Nanoparticles on HOPG, *J. Nakamura, K. Izumi, Y. Iwasaki, T. Kondo*, University of Tsukuba, Japan
Reduction in Pt usage is one of the key requirements for the commercialization of polymer electrolyte fuel cells (PEFCs) for use in everyday life, because of its high price and limited availability, and the difficulty of finding suitable substitutes. We have reported that use of carbon nanotube (CNT) as an electrode material results in high performance with low loading of Pt. That is, the electric power of 12 wt% Pt/CNT was found to be higher than that of 29wt% Pt/carbon black. Moreover, we have observed that RuPt/CNT catalysts show higher tolerance for CO poisoning compared to RuPt/carbon black(CB) catalysts. We have thus found superior performance of CNT as a support material. The CNT used is thicker tubes with diameter of 50-80 nm compared to single wall CNT (0.7-1.5 nm). The diameter of catalyst particles ranges from 2 to 8 nm. The use of thick CNTs in PEFC is very promising because the price is going down recently. Why does CNT show good performance as a support material? There are several physical and chemical reasons. Here, we emphasize the chemical aspect of the interface between catalysts and carbon electrode. That is, difference between CNT and generally used carbon black (CB) is the surface of carbon, at which catalyst particles are attached and electron flows. The surface of thick CNT can be regarded as basal plane of graphite, while the surface of CB is composed of edges of graphene sheets. We thus use a model system of metal catalysts/HOPG (Highly oriented pyrolytic graphite). STM observation shows that Pt particles are attached like two dimension islands on HOPG instead of spherical particles. XPS measurements show that Pt 4f core level is shifted to higher energy compared to bulk Pt. The 2-d Pt particles on HOPG show very high catalytic activity for H2-D2 exchange reaction at high pressures (24 Torr). However, the catalytic activity is reduced by a factor of 30-50 upon heating above 320 K in the presence of hydrogen although no decrease in the amount of Pt is observed by the heating. This is consistent with lower peak temperature shift in TPD of H2 from Pt on HOPG. The change in the catalytic properties of 2-d Pt particles can be ascribed to electronic modification due to a lattice strain of 2-d Pt islands on HOPG. This explains the support effect of carbon supported fuel cell catalysts, that is, Pt/CNT described above.

8:40am SS1-MoM3 Environmental Effects on Morphology of Oxide Supported Gold Nanoparticles, *S. Shaikhutdinov*, Fritz-Haber Institute, Germany
Metal particles deposited on thin oxide films have been shown to be suitable model systems for studying structure-reactivity relationships of metal catalysts. In this paper, the morphology of Au particles deposited on thin FeO(111) and CeO2(111) films at elevated (up to 10 mbar) pressures of H2, CO, O2 and CO+O2 has been examined using in situ STM at room temperature. The Au particles are found to be fairly stable in oxygen and hydrogen environments. However, in CO+O2 (and CO) atmospheres, the destabilization of Au particles located at the step edges occurs leading to the formation of mobile Au species, which migrate across the oxide surface.

General problems encountered with high-pressure STM studies will be also discussed, in particular trace impurities of the gas feedstock may play a big role in system behaviour and data interpretation.

9:00am SS1-MoM4 The Growth and Characterization of Bimetallic Nanoclusters on Oxide Surfaces: Au-Pt on TiO2(110), *J.B. Park, D.A. Chen*, University of South Carolina
Gold (Au) nanoclusters deposited on TiO2 supports have been shown to be excellent catalysts for various oxidation reactions such as propylene epoxidation and CO oxidation. The size of the nanoclusters is known to be the most critical factor for their unique catalytic activity. However, Au nanoclusters sinter rapidly at elevated temperature, losing their catalytic activity. In this study, we have investigated how the rate of sintering can be controlled by adding Pt to Au nanoclusters since pure Pt nanoclusters are less sintered than pure Au due to stronger metal-metal bonds. As a model system, Pt and Au nanoclusters were deposited on a single crystal TiO2(110) substrate and investigated by STM, XPS, LEIS, and TPD in UHV. When Au is deposited on Pt clusters, Pt nanoclusters act as seeds for Au nucleation. However, for Pt deposition on Au, the Au clusters do not nucleate the growth of bimetallic Au-Pt clusters. The extent of cluster sintering at 1000K decreases with increasing Pt composition within the clusters. Intermixing of Au and Pt occurs readily at room temperature; for bimetallic Au-Pt clusters prepared by depositing Au on Pt, the surface contains a significant fraction of Pt atoms, despite immiscibility of Au and Pt and lower surface free energy of Au.

9:20am SS1-MoM5 The Fabrication and Reactivity of Anchored Metal Nanoparticles on TiO2(110), *M. Bowker*, Cardiff University, UK**INVITED**
We have investigated the interaction of Pd particles with the TiO2(110) surface in some detail using high temperature STM, XPS and a molecular beam reactor. Upon formation of nanoparticles at low anneal temperatures (<600K), a high adsorption probability of CO is found, much higher than expected from the fraction of the surface covered by Pd. This is due to the influence of a precursor state; this is a weakly-held form of CO on the support, which has a short lifetime at 300K (~ 1 micros), but which can nevertheless find nearby Pd nanoparticles (at which it gets trapped) by surface diffusion, which is extremely efficient. Nonetheless the CO is actually held more weakly on the nanoparticles than on bulk Pd, due, we believe, to modifications of the Pd by the presence of Ti in the surface of the particle. Upon heating to only 700K, the CO is further destabilised on the Pd, such that the sticking probability and uptake become very low; this is NOT due to sintering which is minimal at this temperature. Investigation by XPS shows that Ti has migrated onto the surface of the Pd as the surface was heated. From the chemical shifts this Ti is probably present as surface TiO, with Ti in the 2+ oxidation state. STM shows that, at least for surfaces annealed above 700K, beautiful ordered structures of the surface layer are formed, with large unit cells. The two main structures are a pinwheel and a zig-zag. In this talk I will try to assign the detailed structures of these layers which is proposed to be intermetallic-like, with the two structures being very specific intermetallics with Pd:Ti ratios of 1:1 and 2:1 respectively. This material causes the loss of activity seen for CO adsorption and for catalysis.

10:20am SS1-MoM8 Enhanced Bonding of Gold Nanoparticles on Oxidized TiO2(110), *S. Wendt, J. Matthiesen, D. Matthey, J.G. Wang, R. Schaub, E. Lægsgaard, B. Hammer, F. Besenbacher*, University of Aarhus, Denmark
Finding of distinctive catalytic properties of dispersed gold nanoparticles on oxide supports has stimulated extensive research activities, and a general consensus now exists on several aspects of this system. The size of the gold particles significantly affects the catalytic activity, and the gold clusters must be smaller than 5 nm for high catalytic activity.[1,2] The choice of the oxide support influences the catalytic activity, so there is a strong 'support effect' in addition to the 'size effect'.[1] However, the relation of the adhesion properties of nanosized gold with catalytic activity is still unresolved. We studied the nucleation of gold clusters on TiO2(110) surfaces in three different oxidation states by high-resolution scanning tunneling microscopy (STM). The three TiO2(110) supports chosen were (i) reduced having bridging oxygen vacancies, (ii) hydrated having bridging hydroxyl groups, and (iii) oxidized having oxygen ad-atoms.[3] At room temperature gold clusters nucleate homogeneously on the terraces of the reduced and oxidized supports, while on the hydrated TiO2(110) surface clusters form preferentially at the step edges. From interplay with density functional theory (DFT) calculations, we identified two different gold - TiO2(110) adhesion mechanisms for the reduced and oxidized supports. The adhesion of gold clusters is strongest on the oxidized support, and the implications of this finding for catalytic applications are discussed.[4]

[1]Meyer, R., Lemire, C., Shaikhutdinov, Sh.K., Freund, H.-J., Gold Bulletin 37 (2004) 72-124.

[2]Valden, M., Lai, X., Luo, K., Guo, Q., Goodman, D.W., Science 281 (1998) 1647-1650.

[3]Wendt, S., Schaub, R., Matthiesen, J., Vestergaard, E.K., Wahlström, E., Rasmussen, M.D., Thostrup, P., Molina, L.M., Lægsgaard, E., Stensgaard, I, Hammer, B., Besenbacher, F., Surf. Sci. 598 (2005) 226-245.

[4]Matthey, D., Wang, J. G., Wendt, S., Matthiesen, J., Schaub, R., Lægsgaard, E., Hammer, B., Besenbacher, F., Science 315 (2007) 1692 - 1696.

10:40am SS1-MoM9 Tuning the Properties of Gold Atoms and Clusters on MgO by Film Thickness, *T. Risse*, *M. Sterrer, M. Heyde, N. Nilius,* Fritz-Haber-Institut der MPG, Germany*, G. Pacchioni,* Universita di Milano-Bicocca, Italy*, H.-J. Freund*, Fritz-Haber-Institut der MPG, Germany

The catalytic activity of Au clusters deposited on oxide supports is extensively studied in recent years. There is evidence that the charging of Au particles may play an important role in this respect. In particular, combined theoretical and experimental evidence shows that nucleation of Au clusters at point defects of MgO leads to a charging of the particles and this may be connected with the enhanced catalytic activity in low-temperature CO oxidation. According to theoretical calculations a similar charging is expected for Au deposits on very thin MgO films of a few monolayer.[1,2] In this contribution we present a low-temperature scanning tunneling microscopy investigation on the properties of gold atoms and clusters adsorbed on ultrathin MgO films grown on a Ag(001) single crystal surface. The gold adsorption was studied at 5-10 K using MgO films of different thickness to provide experimental evidence for the theoretically predicted charging of gold atoms and clusters on very thin films. The adsorption of Au on a 3 ML thin MgO film leads to a preferential ordering of Au atoms revealing a repulsive interaction between the Au atoms which is consistent with the expectation for charged atoms. On the contrary Pd atoms which are predicted to be neutral show a statistical nucleation behavior. In addition, it is found that the adsorption sites of Au atoms change when changing the thickness of the MgO film from 8 ML to 3 ML perfectly in line with the theoretical predictions. Whereas Au clusters on bulk MgO or thick films are expected to grow as 3-dimensional islands, their counterparts on thin MgO films are expected to from 2-dimensional islands. Annealing experiments of Au deposited at 5-10 K show that this crossover in dimensionality does exist for Au particles in the thickness range of 3 ML to 8 ML of the MgO films.

[1]G. Pacchioni, L. Giordano, M. Baistrocchi, Phys. Rev. Lett. 94, 226104 (2005).

[2]D. Ricci, A. Bongiorno, G. Pacchioni, and U. Landman, Phys. Rev. Lett. 97,036106 (2006).

11:00am SS1-MoM10 Catalytic Dehydration of Alcohols on TiO$_2$(110) and (WO$_3$)$_3$/TiO$_2$(110) Model Catalysts[1], *Y.K. Kim*, University of Texas at Austin*, B.D. Kay,* Pacific Northwest National Laboratory*, J.M. White,* University of Texas at Austin*, Z. Dohnálek*, Pacific Northwest National Laboratory

The catalytic dehydration of alcohols on rutile TiO$_2$(110) and on monodispersed (WO$_3$)$_3$ clusters on TiO$_2$(110) was studied using reactive scattering and temperature-programmed desorption (TPD). Two distinct dehydration channels, one at low temperature (LT) and the other at high temperature (HT), are observed on TiO$_2$(110). The LT and HT channels are shown to be related to reactions on the Ti^{4+} rows and on the vacancies of bridge-bonded oxygen (BBO) rows, respectively. The dehydration rates are shown to be influenced by the inductive and steric effects introduced by the hydrocarbon chains of the reacting alcohols. For the (WO$_3$)$_3$/TiO$_2$(110) model catalyst, we find a dramatic increase in catalytic activity compared to bare TiO$_2$(110). The quantitative correlation between the coverage of (WO$_3$)$_3$ clusters and the dehydration yield indicates that the W^{6+} Lewis acid sites are involved in the reaction.

11:20am SS1-MoM11 Hot Electron Flow and Chemical Reactivity on Colloid Nanoparticles on Metal-Semiconductor Catalytic Nanodiodes, *J.Y. Park*, *J.R. Renzas, B. Hsu, Y. Zhang, H. Lee., P. Yang, G.A. Somorjai*, Lawrence Berkeley National Laboratory and University of California, Berkeley

Atomic or molecular processes in metals can generate flows of hot electrons with kinetic energy of 1-3 eV, and mean free path of about 10 nm. The electron flow is detected as a chemicurrent if the excess electron kinetic energy generated by the exothermic reaction is larger than the effective Schottky barrier formed at the metal-semiconductor interface. Detection of hot electron flows could allow us to understand the role of electronic energy dissipation and charge transport through the metal-semiconductor interface in exothermic metal catalyzed reactions. We fabricated nanoparticle-nanodiode hybrid systems composed of metal (Pt and Rh) nanoparticles (size 3-13 nm), an Au thin film (2 nm thick), and TiO$_2$. The interface between Au and TiO$_2$ forms a Schottky barrier with an energy barrier of 1.0 eV. Hot electrons are generated on the surface of the metal nanoparticles,

scatter into the Au thin film, and go over the energy barrier between Au and TiO$_2$. The overall thickness of the metal assembly (nanoparticles and Au thin film) is comparable to the electron mean free path, resulting in the ballistic transport of hot electrons through the metal and into the semiconductor. The chemicurrent and chemical reactivity we measured using nanoparticles with sizes of 3-14 nm, and with various capping agents (citrate (trisodium citrate), PVP (polyvinylpyrrolidone), Ctab (tetradecyltrimethylammonium bromide), hexadecylamine, and hexadecylthiol) during catalytic CO oxidation (at pressures of 100 Torr of O$_2$ and 40 Torr of CO at 373 ~513 K). We found that chemicurrent and chemical reactivity depend significantly on the choice of capping layer. While nanoparticles with the citrate capping agent exhibit the highest chemical reactivity and chemicurrent, hexadecylamine, and hexadecylthiol capped nanoparticles shows low reactivity and chemicurrent. We will discuss the size dependence of nanoparticles on the chemicurrent yield. The influence of charging of capping layers on the hot electron transport during the catalytic reaction will be also discussed.

11:40am SS1-MoM12 TiO$_2$ with Buried Ag Nanoclusters for Photocatalysis[1], *F. Wang, A.K. Sekharan, B.M. Watson, O. Kizilkaya, P.T. Sprunger*, *R.L. Kurtz*, Louisiana State University

Many metals readily form nanoclusters on TiO$_2$ and these clusters can have unusual optical and catalytic properties. The lifetime of these clusters can be limited when exposed to an electrochemical environment, so it can be desirable to bury these metallic clusters in a protective oxide layer. Although the clusters do not participate directly in chemical reactions, optical excitations allow them to provide hot electron-hole pairs to the near surface region to stimulate surface chemistry. We will present a multiple-technique surface study of overcoating Ag nanoclusters on TiO$_2$(110) with titania using STM, EELS and synchrotron-based resonant photoemission. STM measurements show that Ag readily forms 5-10 nm clusters on TiO$_2$(110) and EELS measurements show that the bare clusters on TiO$_2$(110) exhibit a sharp plasmon resonance at 3.7 eV. As the cluster density increases, the underlying substrate bandgap is reduced while the bandgap excitation cross-section increases. These Ag clusters are then buried by coating with a thin layer of Ti that is subsequently oxidized. Within the dielectric medium of the oxide, the plasmon resonance is broadened and red-shifted as shown by EELS. Synchrotron-based resonant photoemission has been used to study the electronic structure of the clusters, both bare and with and the titania overcoat. The valence electronic structure and the origin, whether Ti or Ag-induced, of the bandgap defect states within the titania are identified by tuning over photoemission resonances. The role of these bandgap states in determining the surface optical properties and photochemistry will be discussed.

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