

Tuesday Afternoon, October 30, 2012

Surface Science

Room: 21 - Session SS+NS-TuA

Reactivity of Size and Shape Selected Nanoparticles

Moderator: C.T. Campbell, University of Washington

2:00pm SS+NS-TuA1 2012 AVS Gaede-Langmuir Award Lecture: Surface Photochemistry on Compact Crystals and on Metal Nanoparticles, D. Menzel*, Fritz-Haber Institut, and Techn. Univ. Muenchen, Germany **INVITED**

Adsorbing a molecule on a substrate changes its photochemistry. I shall briefly review characteristics of surface photochemistry, established mechanisms, and effects such as whether the substrate acts mainly as source or sink of electronic excitations of adsorbates, how long the latter survive, and how effects which influence their localization and delocalization influence the success rate of excitations. For laser excitation, linear and nonlinear response to excitations can occur.

Use of nanoparticles (MNPs) instead of bulk metals further changes surface photochemistry, mainly by changing the substrate optical excitations (e.g. the Mie plasmon of MNPs), and excitation lifetimes and efficiency (by confinement). This will be illustrated by data obtained in the past years in Berlin on NO dimers adsorbed on Ag NPs with varied size (2 to 10 nm) supported on thin alumina films on NiAl single crystals, laser-excited with 2 to 5 eV, with *in situ* comparison with Ag(111). The main channel is photodesorption of NO; conversion to N₂O + O, and to NO(ad) stabilized by O also occur. Adsorption energies were characterized by TPD, cross sections (PCS) by photo-depletion, and desorbate energy distributions (translation, rotation, vibration) by TOF and REMPI analysis. Linear and nonlinear fluence dependencies of desorption signals have been found with *ns* and *fs* laser pulses, respectively. The main changes in NO photodesorption are found in the PCS which are strongly enhanced by plasmon excitation and more weakly by excitation confinement, and show clear size dependences interpreted by counteracting influences. The branching into the minor photoreaction channels is also changed at Ag NPs compared to Ag(111) which is due to varying PCS enhancement factors. The photochemical mechanism, however, as evidenced by state-resolved analysis of the desorbing NO molecules, remains the same – formation of transient negative ions by hot electrons in the substrate – for most of the investigated range (with an exception for high energy and small particles). With *fs* laser pulses further drastic PCS increases are found even at low fluences at the NPs but not at Ag(111). This nonlinear effect is explained by re-excitation of hot electrons confined in the NPs within a single laser pulse. But even here the individual dynamics stay the same. This action of NPs on the success probability of excitations with essentially unchanged dynamics appears to be the typical behavior for photochemistry on MNPs. Only in an unusual case (Xe/Ag NPs) we have seen a direct influence of plasmon excitation on desorption.

These findings may help in the understanding of photocatalysis on MNPs.

2:40pm SS+NS-TuA3 Photocatalytic Deposition of Au onto Ordered Linear Arrays of TiO₂ Nanoparticles, J. Taing, A. Margarella, Y. Liu, J.C. Hemminger, University of California Irvine

TiO₂ nanoparticles were decorated onto the step edges of highly oriented pyrolytic graphite (HOPG) via physical vapor deposition. Gold shells and nanoparticles were then grown on the TiO₂ nanoparticles using a photoelectrochemical cell whereupon a photocatalytic reduction mechanism is verified by photocurrent measurements. Samples of TiO₂ nanoparticles on HOPG, acting as a photoelectrode, were placed in a half-cell and immersed in either an electrolyte solution of 1.0 M NaCl or 1.0 M NaNO₃. Bare HOPG, acting as a counter electrode, was placed in a second half-cell and immersed in the same electrolyte solution. The two half-cells were connected by a salt bridge and the electrodes by a picoammeter. Upon irradiation of the TiO₂ nanoparticles by 365 nm UV light from a 200 W Hg lamp, photogenerated electrons produced a photocurrent. Subsequent to introducing 1 mL of 15 μM HAuCl₄ into the cell containing the TiO₂ nanoparticles, the photocurrent decreased as a result of the reduction of Au³⁺ to Au on TiO₂. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray dispersive spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS) were used to characterize the morphology, crystal structure, and chemical identity of the nanoparticles. Images of TiO₂ nanoparticles encapsulated in Au are included in the supplement.

* Gaede Langmuir Award Winner

3:00pm SS+NS-TuA4 Catalytic Activity of Gold-supported TiO₂ Nanocrystals Towards Simple Alcohols, D.V. Potapenko, Z. Li, Y. Lou, R.M. Osgood, Columbia University

Titanium oxide is a versatile photocatalytic material and it has been the subject of much research throughout the last two decades. Nanostructuring is one approach for tailoring the properties of a catalyst. Previously we have developed a method of preparation of structurally homogenous TiO₂ nanocrystals on Au(111) substrate through oxidation of Ti-Au surface alloy. In this work we explore catalytic properties of the nanocrystals through a series of temperature programmed desorption (TPD) studies with simple alcohols: ethanol and 2-propanol. Similarly to the single crystal TiO₂ rutile(110) surface, TiO₂ nanocrystals on Au(111) catalyze dehydrogenation of ethanol and 2-propanol into ethylene and propene. Dehydrogenation was observed in a wide range of temperatures from 400 to 550 K, which is lower than the temperature of the corresponding reaction on rutile(110). More interestingly, we have observed formation of acetone from 2-propanol on our TiO₂/Au(111) surface at around 450 K; this reaction was not observed on rutile(110). The reactivity patterns of TiO₂/Au(111) show strong dependence on geometry and structure of the nanocrystals.

4:00pm SS+NS-TuA7 Structure, Chemical State, and Reactivity Investigations of Size- and Shape-Selected Nanocatalysts under Operando Conditions, B. Roldan Cuenya, University of Central Florida **INVITED**

The rational design of the next-generation of catalysts requires detailed knowledge of the correlation between structure, chemical composition, and reactivity. Even though Pt and Pd are among the most industrially relevant and widely investigated nanocatalysts, their complex interaction with common reactants such as oxygen still provides many challenges to the scientific community. In this work, the relation between the structure and reactivity of nanocatalysts “at work” was obtained via X-ray absorption fine-structure spectroscopy, X-ray photoelectron spectroscopy, and mass spectrometry. Homogeneous size- and shape-selected metal nanoparticles (NPs) have been synthesized by means of diblock copolymer encapsulation.

The influence of the nanoparticle *shape* on the reactivity of Pt nanocatalysts on γ-Al₂O₃ will be described. Nanoparticles with similar size distributions (~0.8-1 nm) but with different shapes were found to display distinct reactivities for the oxidation of 2-propanol. A correlation between the number of undercoordinated atoms at the NP surface and the onset reaction temperature was observed. Furthermore, platinum oxides were found to be the active species for the partial oxidation of 2-propanol, while the complete oxidation was catalyzed by oxygen-covered metallic Pt NPs.

The evolution of the structure and oxidation state of ZrO₂-supported Pd nanocatalysts during the *in situ* reduction of NO with H₂ will also be discussed. Prior to the onset of the reaction, NO-induced redispersion of the Pd NPs over the ZrO₂ support was observed, and Pd^{δ+} species detected. This process parallels the high production of N₂O observed at the onset of the reaction (>120°C), while at higher temperatures (≥ 150°C) the selectivity shifts toward N₂. Interestingly, concomitant with the onset of N₂ production, the Pd atoms re-aggregate into large metallic Pd NPs, which were found to constitute the active phase for the H₂-reduction of NO. The evolution of the oxidation state of Pd and Pt NPs during the oxidation of NO and the role of the NP size will also be presented.

Our findings highlight the decisive role of the nanoparticle structure and chemical state in catalytic reactions and the importance of *in situ* reactivity studies to unravel the microscopic processes governing catalytic reactivity.

4:40pm SS+NS-TuA9 Particle Size, Support and Alloying Effects in Electrocatalysis: Relationships with Heterogeneous Catalysis, B.E. Hayden, University of Southampton, UK **INVITED**

High-Throughput Physical Vapour Deposition (HT-PVD) based on Molecular Beam Epitaxy methods¹ has been used to synthesize libraries of catalysts which have subsequently been screened for their electrochemical activity and stability. A screening method is briefly described² which has been applied to measurements on model supported metal nano-particle HT-PVD catalyst libraries.

Considerable effort has been made to find alternative supports for platinum based catalysts in order to improve the particle stability and improve the three-phase boundary in fuel cell applications. HT-PVD model catalyst methodology has been applied to the study of support and particle size effects in electrocatalysis.³ Experiments have demonstrated the potential for using a support such as titania to induce CO oxidation electro-catalytic activity in gold particles,⁴ with an optimum particle size observed at ca. 3nm (Figure). No induced activity is observed for carbon supports. The

similarities with the low temperature oxidations exhibited by supported Au in heterogeneous catalytic are highlighted. Extending this methodology to supported platinum based catalysts, the effect of particle size is demonstrated in the reduction of oxygen for the model carbon supported platinum catalysts, highlighting the limitations of catalyst dispersion. Supporting platinum on titania can result in a strong poisoning of the oxygen reduction catalysis.⁵

The combination of ab-initio theory and electrocatalyst screening also provides a powerful combination in the search for precious metal alloy and non noble metal alloy catalysts. Examples are given for anode hydrogen oxidation (HOR) catalysts such as Pd based,⁶ and tungsten copper⁷ alloys.

References

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5:20pm **SS+NS-TuA11 The Growth and Structures of Metal Nanoparticles on Ordered ZrO₂(111) Surfaces**, *Y. Han, S.W. Hu, Y.H. Pan, J.B. Hou, H.B. Pan, J.F. Zhu*, University of Science and Technology of China

Metal nanoparticles supported on zirconia have attracted much attention in recent years owing to their variety of technological applications such as heterogeneous catalysis and gas sensor operation. In particular, as catalysts, the interface properties of metal/ZrO₂ referring to the morphology, charge transfer, thermal stability and reactivity play crucial roles in determining their real applications. In this presentation, we report our recent studies on the growth, electronic structures and thermal stabilities of metal nanoparticles (Cu, Ag and Au) on well-defined ZrO₂ thin films by synchrotron radiation photoemission spectroscopy (SRPES) together with scanning tunneling microscopy (STM) and low electron energy diffraction (LEED). The well-defined ZrO₂(111) oxide thin films were epitaxially grown on Pt(111). It was found that the growth behavior of metals on ZrO₂(111) strongly depends on the morphologies of oxide surfaces and the interfacial interactions between the metal deposits and the ZrO₂(111) films. The binding energies of all three metal core-level peaks shift monotonically toward higher binding energy with decreasing the metal particle sizes. The contributions of initial and final state effects to the core level binding energy shifts are differentiated using the Auger parameters. At very low coverages, most likely Au forms Au⁺, while Ag remains the metallic state and Cu forms Cu⁺ on ZrO₂(111).

5:40pm **SS+NS-TuA12 Structure and Electronic Properties of Ni Nanoparticles Supported on Reducible CeO₂(111) Thin Films**, *Y.H. Zhou*, Xiamen University, Republic of China, *J. Zhou*, University of Wyoming

Ceria-supported Ni nanoparticles have been of great interest as ethanol and methane reforming catalysts for hydrogen production in fuel cell applications. Recent studies have indicated that the catalytic reactivity of these ceria-supported Ni nanoparticles can be influenced by the redox properties of ceria as well as the synergistic effect between the two. To elucidate the nature of their activity, we studied Ni particles deposited on fully oxidized CeO₂(111) and reduced CeO_{1.88}(111) thin films using scanning tunneling microscopy and x-ray photoelectron spectroscopy at the fundamental level. Ceria thin films were grown in situ on Ru(0001) under ultrahigh vacuum conditions. Ni was vapor-deposited onto ceria thin films. At 300 K, metallic Ni is the only species present on the reduced ceria. However, a small amount of Ni is oxidized to Ni²⁺ on CeO₂. Oxidation of Ni on CeO₂ can be facilitated by annealing as well as by depositing Ni at 500 K. Scanning tunneling microscopy studies show that Ni forms two-dimensional particles on ceria at room temperature, which suggests a strong Ni-ceria interaction. The particles can agglomerate into large three-dimensional structures with further heating. The structure and electronic

properties of Ni metal particles on ceria were further compared to those of bimetallic Ni-Au and Ni-Rh particles.

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