

Surface Science

Room: 208 - Session SS2+NC-ThM

Catalysis on Nanoclusters

Moderator: J. Hrbek, Brookhaven National Laboratory

8:00am **SS2+NC-ThM1 Hybrid Nano-Oxide System for Oxidation of Methanol at Lower Temperatures**, A.S. Karakoti, A. Vincent, T. Spalding, University of Central Florida, D. Patel, NJ Institute of Technology, S. Seal, University of Central Florida

Paradigm shift in the global energy policy towards cleaner and alternate fuels, arising out of uncontrolled greenhouse emissions and rapid depletion of fossil based fuels, paved the way for various challenging areas of research. Among the various alternatives, direct oxidation of alcohols to hydrogen offer one promising alternative to primary fuels. Hydrogen produced from the alcohols can be used as a primary fuel source for DMFCs. Preliminary work on conversion of methanol to hydrogen and other byproducts, in presence of noble metals such as platinum and gold as catalysts, has shown promising results. However, the use of noble metal catalysts makes the conversion an expensive deal. Nanomaterials such as titanium oxide (titania), zirconium oxide (zirconia), cerium oxide (ceria) have been tried as active catalyst supports in varying range of particle sizes and molar ratios of noble metals with limited success. To overcome the hurdles in the existing systems, we have focused on the hybrid ceria-titania nanostructures synthesized using sol gel and co-precipitation methods for optimizing the efficiency of the catalyst in methanol oxidation. The percent conversion of methanol to various species was studied using an in-house built catalytic reactor coupled to a mass spectrophotometer for analysis of gaseous reaction products. The selectivity and efficiency of the hybrid nano-oxide system as a catalyst support was studied as a function of mixture concentration, percent loading of the noble metal catalyst and the phase structure. Experimental results were normalized with respect to the surface area of the supporting catalysts. The adsorption characteristics of methanol and byproducts on the catalyst surface were evaluated using Diffuse Reflectance Infra-red Fourier Transform Spectroscopy (DRIFTS). Powder samples were characterized using X-ray Diffraction (XRD) and Transmission Electron Microscope (TEM) for determining the phase, particle size and shape of the particles in mixed systems. X-ray Photoelectron spectroscopy (XPS) was used to verify the oxidation state of the metal catalyst as well as mixed ceria-titania supports as a function of molar concentration of the constituents. Preliminary results have shown that the onset temperature for methanol decomposition was as low as 150°C and both the onset as well as complete conversion temperature varies as a function of molar ratio of ceria to titania.

8:20am **SS2+NC-ThM2 Decomposition of Methanol on High Surface Area Titanium Carbide Films**, D.W. Flaherty, N.T. Hahn, C.B. Mullins, University of Texas at Austin

We are investigating the surface chemistry of small alcohols on novel, high surface area, titanium carbide films using a combination of temperature programmed desorption, molecular beam reactive scattering, and infrared absorption spectroscopy. High-surface area catalytically active films can be synthesized by glancing angle deposition of a metal onto a cold surface in a low ambient pressure of gas. The subsequent surface reaction of the two components results in the growth of nano-porous films with controllable stoichiometry and morphology. We have employed this technique, referred to as reactive ballistic deposition (RBD), to deposit nano-structured, high surface area films of metal carbides. It is well known that transition metal carbides have catalytic properties similar in some respects to platinum group metals, with the added benefits of comparatively low cost, high thermal stability, and mechanical durability. Building on our knowledge from the previous investigation of high surface area TiO₂ films, we are developing high surface area, porous, transition metal carbide films for the purpose of studying their physical properties and chemical reactivity. Our current work has focused on the deposition and physical characterization of titanium carbide (TiC) films deposited using the RBD technique. Auger electron spectroscopy is used to investigate the stoichiometric dependence of the films on growth conditions. The specific surface area and distribution of binding site energies of the films are measured as functions of growth temperature, deposition angle, and annealing conditions using temperature programmed desorption (TPD) of chlorodifluoro-methane. Results from TPD studies suggest that TiC films grown using the RBD technique have specific surface areas of at least 100 m²/g and are thermally stable to nearly 1000 K. The combination of high surface area and thermal stability suggest that these films could be effectively utilized for heterogeneous catalysis.

8:40am **SS2+NC-ThM3 Catalysis by Atomic-Size Centers**, H. Metiu, University of California, Santa Barbara **INVITED**

We perform density functional calculations to explore the properties of two new classes of catalysts, both consisting of atomic-size active centers. In one class the cation at the surface of an oxide is replaced with another cation which we call a dopant. By an appropriate choice of the dopant-oxide pair we can weaken the bond of the oxygen atoms at the surface of the oxide and make the system a better oxidant and a better oxidation catalyst. Other choices of dopant-oxide pairs will cause the dopant to adsorb oxygen and weaken the O-O bond to activate oxygen for oxidation reactions. A second class of catalysts with atomic-size active center consists of small oxide clusters supported on a different oxide (for example, a VO₃ cluster supported on TiO₂). Some of the oxygen atoms in the cluster end up bridging two different cations (for example, V-O-Ti) and if the two cations are well chosen, the bridging oxygen becomes active in oxidation reactions. We study the mechanism of methanol oxidation to formaldehyde by VO₃ supported on TiO₂ and plan to screen a large set of oxide clusters on an oxide for hydrocarbon activation.

9:20am **SS2+NC-ThM5 The Oxidative Dehydrogenation of Methanol by Vanadia Particles Supported on Ceria Thin Films**, H.L. Abbott, A. Uhl, M. Baron, D.J. Stacchiola, S.K. Shaikhutdinov, H.-J. Freund, Fritz Haber Institute of the Max Planck Society, Germany

Vanadia particles and monolayer or submonolayer coverage vanadia films supported on metal oxide surfaces have shown high activity for the selective oxidation of alcohols. In particular, methanol oxidative dehydrogenation to formaldehyde occurs readily on ceria-supported vanadia. Although support and coverage effects are known to be important for this reaction, questions remain about the relationship between the structure and the reactivity. Here, a well-defined model system, consisting of vanadia nanoparticles deposited on thin ceria films, has been employed. X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), infrared reflection absorption spectroscopy (IRAS), and temperature programmed reaction (TPR) were used to characterize the VO_x/CeO₂ model system. XPS measurements indicated that the oxidation state of the vanadium atoms increases with decreasing coverage. Under low coverage conditions, STM images revealed the presence of isolated vanadia species. Vanadyl stretching vibrations detected by IRAS vary between 1000 and 1050 cm⁻¹, depending on the coverage and the annealing temperature. Two TPR peaks, corresponding to the selective oxidation of CH₃OH on VO_x, were observed, including a new low temperature peak at ~350 K that is believed to correlate with isolated species.

9:40am **SS2+NC-ThM6 Photochemistry of (NO)₂ Layers on Alumina-Supported Ag Nanoparticles: Size and Excitation Influences**, D. Mulugeta, K.H. Kim, K. Watanabe, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, D. Menzel, Fritz-Haber-Institut der Max-Planck-Gesellschaft and Technical University Muenchen, Germany, H.-J. Freund, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

The unique electronic and optical properties of metal nanoparticles (MNPs) are caused by their small size compared to typical interaction lengths with photons and electrons, the confinement of excitations in them, and their specific excitations, in particular the Mie plasmon which causes strong field enhancement.¹ Modifications of photochemical reactions occurring on them are expected. We have investigated the photochemical reactions in (NO)₂ layers on AgNPs deposited on alumina films, using ns laser pulses off and on the plasmon resonance, and for varied NP size. Photoexcitation of (NO)₂ leads to photodesorption of NO as well as photochemical conversion to N₂O and to chemisorbed NO. Results include total removal and conversion efficiencies, desorbed species and their cross sections, and mean translational energies of photodesorbed NO. Excitation in the plasmon resonance strongly enhances yields and cross sections, compared to off-resonance excitation and to Ag(111) surfaces. The similar (nonthermal) translational energies of desorbed NO in all cases indicate a common mechanism believed to proceed via temporarily trapped hot electrons forming transient negative ions (TNI) which leads to desorption and reaction. Recent results obtained for variable sizes of the AgNP (2 - 10 nm) have shown that characteristics of both thermal and photochemical reactions depend on size. To explain these results, the influences of the size dependences of a number of excitation and decay processes, based on knowledge of the photophysics of the AgNPs, will be discussed. Time permitting, the changes introduced by the use of fs laser pulses will also be presented. These examples show some important consequences of the small dimensions of NMPs, size-dependent confinement effects, and influences of plasmon excitations.

¹K. Watanabe, D. Menzel, N. Nilius, and H.-J. Freund, Chem. Rev. 106 (2006) 4301.

10:40am **SS2+NC-ThM9 Effects of Nanocluster Surface Chemistry on Electrocatalysis**, *B.L. Abrams, P.C.K. Vesborg, S. Dobrin, D. Mowbray, I. Chorkendorff*, Technical University of Denmark

Nanocluster catalysts in the small size regime (<10nm) offer the opportunity for enhanced catalytic reactivity due to increased active site availability. This reactivity is also materials dependent and related to how tightly or weakly the nanocatalyst binds the reactants of interest such as hydrogen for the hydrogen evolution reaction (HER).^{1,2} Corresponding to the decrease in size is an increase in nanocatalyst surface area. The high surface to volume ratio of nanoclusters in this small size regime thus allows for the ability to impact their catalytic properties by altering their surface chemistry. In this work we alter the cluster surface chemistry by varying the type of surfactants present on metal and metal alloy nanoclusters such as Pt, Au, AuPt, AgPt. These nanoclusters are synthesized using a modified inverse micelle³ technique where the presence of surfactant molecules (non-ionic or cationic) is crucial to maintaining the nanocluster monodispersity. Following synthesis in the solution phase, the nanoclusters are evaluated electrochemically as a function of surfactant type and amount. In the case of Pt nanoclusters stabilized by a non-ionic surfactant, the HER activity is comparable to standard polycrystalline Pt. The negligible suppression of HER indicates that the surfactant may not significantly block the active sites necessary for HER. In relation to the activity measurements, we have studied the attachment mechanism of the surfactants to the cluster surface utilizing density functional theory (DFT) calculations. An evaluation of the charge transfer processes and reactions as revealed by electrochemical measurements will be presented for each material as a function of surface chemistry alterations. Preliminary result for other reactions of interest to fuel cells such as the hydrogen oxidation reaction will also be discussed.

¹J.K. Nørskov, et al., "Trends in the Exchange Current for Hydrogen Evolution" *J. Electrochem. Soc.* (152), J23 (2005).

²Greeley, J., et al., "Computational High-Throughput Screening of Electrocatalytic materials for Hydrogen Evolution", *Nature Materials*, 5, 909-913 (2006).

³Wilcoxon, J.P.; Abrams, B.L., "Synthesis, Structure and Properties of Metal Nanoclusters" *Chemical Society Reviews*, 35, 1162-1194 (2006).

11:00am **SS2+NC-ThM10 Size-Dependent Structure of MoS₂ Nanoclusters**, *J. Kibsgaard**, *J.V. Lauritsen*, University of Aarhus, Denmark, *S. Helveg*, *H. Topsøe*, *B.S. Clausen*, Haldor Topsøe A/S, Denmark, *F. Besenbacher*, University of Aarhus, Denmark

Within the area of nanomaterials it is well known that "small is different", which implies that nanostructures may have new functional properties. Properties like conductivity, color, reactivity, magnetism, and melting point may thus be entirely different for the nanomaterial compared to the same properties for materials with macroscopic dimensions. The dimension of a material is therefore an important parameter to consider in the development of new nanomaterials. Not least in catalysis where the active materials today is confined to a limited number of metals, tuning the size of the catalytic particles may help in the development of new and better catalysts. The MoS₂-based desulfurization catalyst constitutes one of the most important environmental catalysts as it removes sulfur from fossil fuels. Without this removal, the sulfur would cause massive acid rain problems such as forest decline. The recent focus on environmental problems and a stricter legislation concerning the sulfur content in fossil fuels have generated great interest in understanding and improving the desulfurization catalyst. We have used atom-resolved Scanning Tunneling Microscopy (STM) to follow the structural progression of triangular MoS₂ nanoclusters as a function of their size, and analyse how the equilibrium structures are altered when the cluster size is reduced. A comprehensive analysis of the size distribution reveals that certain "magic" clusters are favored. The analysis reveals that a rearrangement of the sulfur atoms terminating the cluster edges influences the stability and that the requirement to optimize the sulfur excess relative to molybdenum drives a striking reconstruction of the cluster edge.

11:20am **SS2+NC-ThM11 Size-Selected Deposition of Transition Metal Sulfides**, *M.J. Patterson*, Stony Brook University, *M.G. White*, Brookhaven National Laboratory, Stony Brook University

Supported MoS₂ nanoparticles are known for their ability to catalyze a wide array of heterogeneous reactions and work done in our laboratory is geared towards understanding the role of size, structure, composition and support interactions of the particles in these reactions. This problem has not yet been resolved due to the inhomogeneity of commercial catalysts. We therefore focus on preparing homogeneous samples in ultra high vacuum that can serve as model systems for catalytic reactions such as hydrodesulfurization. A recently constructed cluster beam apparatus in our laboratory uses magnetron sputtering in order to make a variety of transition metal cluster compounds. We are currently investigating the size dependent and substrate dependent properties of these systems in particular Mo_xS_y⁺

clusters (x=2-8, y= 6-12) on single crystal surfaces (i.e. Au(111), Al₂O₃/NiAl(110)). Characterization of the clusters are carried out using surface sensitive techniques such as Auger, photoemission spectroscopy, and thermal desorption. Preliminary work on the reactivity of these clusters with small sulfur containing molecules will also be discussed.

11:40am **SS2+NC-ThM12 Ligand-Spacer Controlled Size Selectivity of Gold Nanoclusters and the Effect of the Ligand on Cluster Geometry and Electronic Structure**, *G. Shafai*, *S. Hong*, University of Central Florida, *M.F. Bertino*, Virginia Commonwealth University, *T.S. Rahman*, University of Central Florida

We have carried¹ out calculations based on the density functional theory in the projector augmented wave scheme (PAW) and the pseudopotential approach, to examine the effect of the size of the diphosphine ligand spacers on the stability of Au clusters containing 8 and 11 atoms, through evaluations of the cluster total energy and proper correction of spurious interactions between charged supercells. We find that Au11+3 is indeed preferred by ligand L3 rather than L5, while Au8+5 is preferred by L5 rather than L3, in agreement with experimental data.² The size selectivity induced by the ligand is found to be a purely electronic effect via coupling of the d-band of Au and p-band of the ligand. We have also examined the effect of the ligand on the geometric and electronic structure of Au clusters. For Au13, for example, we find bare cluster to form a flat flake, in agreement with previous theoretical calculations. On the other hand, Au13 cluster covered with ligands of phosphine (PH3) forms a stable spherical structure (icosahedron), in agreement with experimental findings,² which is 0.08 eV lower in energy as compared to the flat-flake complex. If the phosphine is replaced by H, the spherical structure is no longer stable, but it still maintains a 3 dimensional form, signifying the effect of the ligand in stabilization of the structure. We observe a narrow d-band for gold atoms in the flat-flake complex, while in the icosahedron structure the d-band is wider. We also find a stronger overlap between the p orbitals of the P atom with d orbitals of gold atoms in the icosahedron complex.

¹ Work supported in part by NSF Grant CHE-0741423.

² M. Bertino et al. *Jour. Phys. Chem. B Lett.* 110, 21416 (2006).

* Morton S. Traum Award Finalist

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