

Tuesday Morning, October 21, 2008

Energy Science and Technology Focus Topic

Room: 203 - Session EN+BI+SS+SE-TuM

Catalysis for Energy Sustainability

Moderator: D.E. Ramaker, George Washington University

8:00am **EN+BI+SS+SE-TuM1 Size, Shape, and Support Effects in Oxidative Coupling Reactions**, *C.L. Marshall, W. Sethapun, S. Mucherie*, Argonne National Laboratory, *H.S. Kim*, Northwestern University, *J.A. Libera, J.W. Elam*, Argonne National Laboratory, *P.C. Stair*, Northwestern University **INVITED**

In this paper we describe the characterization and catalytic performances in the reaction of ODH of propane over new nanostructured membrane catalysts composed of vanadium species supported on different metal oxides (Al₂O₃, Nb₂O₅, TiO₂), which have been fabricated using the combination of anodic aluminum oxide (AAO) and atomic layer deposition (ALD).¹ The aim of this study is to determine the role played by the nanostructured materials and the nature of the support oxide on the reactivity of these AAO membrane catalysts in terms of activity and selectivity to propylene.

8:40am **EN+BI+SS+SE-TuM3 Application of Single-Wall Carbon Nanohorns**, *M. Yudasaka*, Advanced Industrial Science and Technology (AIST), Japan **INVITED**

The discovery of spherical aggregates of single-wall carbon nanohorns (SWNHs) was reported in 1999. The aggregates were called dahlia-like, bud-like, and seed-like SWNHs based on their forms. Since the dahlia-type aggregate (D-NHag) was obtained with the highest purity (about 90%) among the three types, SWNH applications have been studied mainly using the D-NHag. The individual SWNH has a structure similar to SWNTs, namely, a tube-like structure made of a graphene sheet, but with larger diameters (2-5 nm), shorter length (40-50 nm), and horn-shaped tips with a cone angle of about 19°. Studies of various applications of D-NHag revealed that they are a unique medium for adsorption, support, and storage of materials. This uniqueness mainly comes from mountain-valley structure of the D-NHag surfaces and wide inner-hollow spaces. The mountain-valley surface morphology was suitable for supporting material clusters with small sizes. The reason for this may be because migration on the SWNHag surface was suppressed, so coalescence of the clusters was avoided. In fact, the sizes of Pt-particles supported on D-NHag were small, about 1 nm. When the Pt/SWNHag was used as fuel-cell electrodes, the battery characteristics were significantly improved. The inside spaces of SWNHs were made accessible by making holes at the tips and defects of sidewalls. It was easy to incorporate various materials (C₆₀, metals, inorganic and organic molecules including drugs, etc.) inside SWNHs in the liquid-phase at room temperature, where the incorporating quantities were controllable. The materials were moderately bound inside SWNHs, which enabled the rate-controlled release of the incorporated materials. It was also easy to individually disperse D-NHag in various solvents. They were well dispersed even in aqueous solutions, which will make possible biological applications of D-NHag. We previously reported that dexamethasone, a drug, was loaded in/on SWNHs in aqueous solutions and released in cell culture medium, exhibiting its drug effect in several ways. SWNH is quasi-SWNT, but, its usefulness is different from that of SWNT. We believe that D-NHag will be suitable for a catalyst support and material-delivery medium. Acknowledgement: I am grateful to all the collaborators, especially Professor Iijima, and JST for supporting this research through ICORP and SORST schemes.

¹S. Iijima, et al., Chem. Phys. Lett. 309 (1999) 165.

9:20am **EN+BI+SS+SE-TuM5 Reducing Carbon Dioxide to Methane under Visible Light Illumination by Non-stoichiometric Mixed Phase Titania Thin Films**, *L. Chen, M.E. Graham, P.A. DeSario, K.A. Gray*, Northwestern University

Non-stoichiometric mixed phase titania composites were deposited by reactive DC magnetron sputtering. Previously we¹⁻³ demonstrated that there are solid-solid interfaces with highly reactive interfacial sites created within mixed phase titania thin films, and we observed by EPR measurement that the bulk composition of the films was not fully stoichiometric. The objective of this study is to explore the role of non-stoichiometry in mixed phase titania in terms of photoresponse and photocatalytic performance in reducing CO₂ to methane. The control of oxygen partial pressure during film deposition yielded different levels of non-stoichiometry in films deposited mostly in the transition mode. Trace amounts of nitrogen were introduced during the sputtering process to stabilize the reactive sputtering

process at the turning point of the transition mode and metallic mode and without incorporation in the films. The photocatalytic results showed that there was an optimal non-stoichiometry of titania films in terms of methane yield from CO₂ reduction. Under UV illumination, the best CO₂ conversion percentage was around 22%. In addition, both from reaction tests under visible light and the optical measurements, we determined that non-stoichiometric mixed phase titania films showed a strong light absorption shift into the visible range compared to commercial standard Degussa P25, which has a similar phase composition. SEM and TEM results showed film morphology with a high density of solid-solid interfaces developed in the films. Both EELS and XPS results identified the Ti³⁺ species in addition to Ti⁴⁺. Most of the Ti³⁺ species were located at the interfaces of titania columns, where they might serve as the reactive interfacial sites for visible light harvesting or electron trapping.

¹L. Chen, et al., Photoreduction of CO₂ by TiO₂ Nanocomposites Synthesized through Reactive DC Magnetron Sputter Deposition. Thin Solid Films, 2008. in review.

²L. Chen, et al., Fabricating Highly Active Mixed Phase TiO₂ Photocatalysts by Reactive DC Magnetron Sputter Deposition. Thin Solid Films, 2006. 515(3): p. 1176-1181.

³Hurum, D.C., et al., Probing reaction mechanisms in mixed phase TiO₂ by EPR. Journal of Electron Spectroscopy and Related Phenomena, 2006. 150: p. 155-163.

9:40am **EN+BI+SS+SE-TuM6 Variations in Metal-Ligand Effects on Pt in Pt_nM (M = Ru, Mo, Sn) Electrocatalysts as Exhibited by in situ XANES and EXAFS Measurements in Methanol**, *D.E. Ramaker, F.J. Scott*, George Washington University, *S. Mukerjee*, Northeastern University
Metal-ligand effects on Pt are commonly utilized to decrease the CO poisoning of the anode in methanol as well as to increase the activity for oxygen reduction at the cathode. However, these effects are not clearly understood because of the general lack of information on the particle morphology (M island size, homogeneity, etc.) and CO or OH adsorbate coverages. In this work, in situ X-Ray Absorption Spectroscopy (XAS) measurements, in the near edge and extended regions (XANES and EXAFS) at the Pt L₃ edge, were carried out on three different carbon-supported electrocatalysts (Pt₃Mo, Pt₄Mo, and PtSn) in an electrochemical cell in 1 M HClO₄ along with 0.3 M methanol. The CO, OH, O, and H_{upd} relative adsorbate coverages on Pt are determined as a function of the applied potential via the ΔXANES technique and compared with comparable data reported for three different PtRu electrocatalysts (PtRu Etek, PtRu Watanabe, and Pt₃Ru) reported previously¹. The average particle morphology of each catalyst is determined from EXAFS coordination numbers and a modeling technique.¹ The onset of the n-fold O atom coverage between 0.5 and 0.9 V (RHE) tracks essentially with the particle size. The more reactive Sn and Mo atoms interact more strongly with Pt, and hence the ligand effect for the M and MO_n islands are comparable, in contrast to that for Ru vs. RuO_n. Our results are correlated with the extensive electrochemical results found in the literature on similar Pt_nM catalysts. The results suggest that the strength of the ligand effect increases in the order Ru < Mo, MoO_n < Sn, SnO_n ≤ RuO_n, where the relative Pt-CO bond strength is found to decrease and the Pt-OH bond strength increases with ligand effect. In the Sn and Mo bimetallics, the ligand effect is found to be sufficiently strong to allow CO replacement by H₂ at low currents.

¹F. J. Scott, S. Mukerjee, and D. E. Ramaker, J. Electrochem. Soc. 154, A396-A406 (2007).

10:40am **EN+BI+SS+SE-TuM9 Controlling the Activity of Fuel Cell Electrode Materials by Tuning the Surface Electronic Structure**, *J.K. Norskov*, Technical University of Denmark **INVITED**

The performance of low temperature fuel cells based on proton conducting membranes is severely hampered by an overpotential at the cathode where molecular oxygen combines with protons and electrons to form water. To understand the origin of this problem a method has been developed that allows a theoretical treatment of chemical reactions at the water-solid interface in the presence of an electrical bias on the basis of electronic structure calculations. Extensive density functional calculations have allowed an identification of the origin of the overpotential for the commonly used electrode material, platinum, as well as insight into the way alloying can change the surface electronic structure of platinum to reduce the overpotential. The reverse reaction, electrochemical water splitting, is also discussed, and it is shown that the performance of different classes of inorganic materials as electrocatalyst as well as the catalytic center for biological water splitting in photosystem II can be understood within the same conceptual framework.

11:20am **EN+BI+SS+SE-TuM11 Resolving the Electronic Properties of Catalytically Important Pd/Au Alloys at the Sub-Nanometer Level**, *A.E. Baber, H.L. Tierney, E.C.H. Sykes*, Tufts University

Palladium/gold (Pd/Au) bimetallic alloys have been used to catalyze important processes such as the synthesis of vinyl acetate and hydrogen peroxide as well as some oxidative reactions (methanol, formic acid, CO).

Low temperature, ultra-high vacuum scanning tunneling microscopy (LT-UHV STM) is used not only to image bimetallic alloys, but also to spectroscopically probe the local electronic changes in both Pd and Au atoms when the two are alloyed. We have used STM to evaluate the surface composition of a real bimetallic alloy system and have found that the unique herringbone reconstruction of Au{111} provides entry sites for the incorporation of Pd atoms. We were able to differentiate between surface, subsurface and overlayer Pd atoms and study the temperature dependence of the preferred Pd destination. As the deposition temperature increases, the location of Pd changes from mostly overlayer to surface to subsurface. Scanning tunneling spectroscopy was used to examine the local density of states (LDOS) of individual Pd and Au atoms in both surface and subsurface sites in order to investigate the changes in the LDOS of a reactive metal alloyed in a more noble metal. It was found that in both surface and subsurface sites, Pd atoms displayed a LDOS very similar to the surrounding gold atoms, except for a small region at the band edge of the Au surface state in which the electron density was depleted. Pd atoms act as scattering sites for the surface electrons but do not fully quench the surface state. This is the first example of a simultaneous atomic-scale geometric and electronic characterization of a real PdAu catalytic system.

11:40am **EN+BI+SS+SE-TuM12 Water-Gas-Shift Reaction on Metal-Oxide Catalysts**, *P. Liu, S. Ma, J.A. Rodriguez, J. Hrbek*, Brookhaven National Laboratory

The water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) is a critical process in providing pure hydrogen for fuel cells and other applications. However, current industrial catalysts (Fe-Cr or Zn-Al-Cu oxides) are pyrophoric and require complex activation steps before usage. A fascinating puzzle has recently emerged: Au/CeO₂ and Au/TiO₂ nanomaterials show high activity for WGS catalysis. This is remarkable since in bulk form Au, ceria and titania are not known as WGS catalysts. The nature of the active phase(s) in these metal-oxide nanocatalysts is unclear at the present time, which impedes the design and optimization of WGS catalysts. We have carried out coordinated experimental and theoretical studies to address this problem. The experiments show that the model catalysts, Au/CeO₂(111) or TiO₂(110) and inverse CeO₂ or TiO₂/Au(111), display activities comparable to good WGS catalysts (i.e., Cu(100) and Cu(111)). Theoretical calculations based on density functional theory (DFT) are also carried out to understand the active sites in the oxide-gold catalysts, by probing reaction scenarios on Au, titania, and Au-TiO₂ (Au/TiO₂ and TiO₂/Au(111)) catalyst model structure. In accordance with experiments, our calculations show a very high barrier for the dissociation of water on Au and the formation of very stable formate species on titania that prevents the production of H₂ and CO₂. The model Au-TiO₂ catalyst overcomes these bottlenecks: the moderate chemical activity of gold is coupled to the more reactive oxide. The dissociation of water takes place on the oxide easily, a reaction that extended surfaces and nanoparticles of Au cannot perform. CO adsorbs on gold sites located nearby (bifunctional catalyst). Then all the subsequent steps occur at the oxide-metal interface at a reasonable speed. Our results imply that the high activities of Au/CeO₂ and Au/TiO₂ nanocatalysts in the WGS reaction depend heavily on the direct participation of oxide-metal interface. The diversity of nanoparticle structures and the interplay with the support highlight the importance of identifying critical structural motifs to model catalyst function. This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

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