

Monday Afternoon, October 31, 2005

Surface Science

Room 202 - Session SS1-MoA

Catalysis for the Hydrogen Economy

Moderator: G.B. Fisher, Delphi Research Labs

2:00pm SS1-MoA1 In-situ CV and XPS Evaluation of Tungsten Carbides as Alternative Electrocatalysts, M.B. Zellner, J.G. Chen, University of Delaware

The purpose of this research is to examine the feasibility of using tungsten carbides (WC) and platinum modified tungsten carbides (Pt/WC) as direct methanol fuel cell (DMFC) and hydrogen fuel cell electrocatalysts. The motivation to study tungsten carbides stems from the fact that current fuel cells require the use of Pt or Pt/Ru anodes, which are expensive and easily poisoned by CO. The successful development of tungsten carbide electrodes as Pt/Ru substitutes can therefore positively influence the commercialization of DMFC and hydrogen fuel cell systems. Previously, reactions of CH₃OH, H₂O, H₂ and CO over single crystal and physical vapor deposited (PVD) thin film WC and Pt/WC surfaces have been studied with temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). The results show that the carbide surfaces possess characteristics critical to application as fuel cell anodes. In particular, these surfaces are highly active toward the decomposition of CH₃OH and H₂O, and are able to desorb CO at relatively low temperatures. Recently, Pt-modified WC films along with PVD thin films of WC and W₂C have been tested for stability in an acidic environment and activity of methanol oxidation using an in-situ cyclic voltammetry (CV)/ X-ray Photoelectron Spectroscopy (XPS) test station. The tests show stability of WC to ~0.8 V wrt. NHE and a synergistic effect at monolayer Pt coverage, resulting in enhanced stability to ~1 V. Additionally, WC and Pt/WC surfaces show methanol O-H and C-H oxidation states, with the Pt/WC surface displaying greater methanol oxidation activity compared to WC or pure Pt foil.

2:20pm SS1-MoA2 Development of a High Temperature Electrochemical Reactor with Differential Electrochemical Mass Spectrometry for Kinetic Rate Analysis of Methanol Oxidation, L.M. Roen, E.M. Stuve, University of Washington

Direct methanol fuel cells have nearly the same potential as hydrogen fuel cells, ~1.2 V, though practical implementation has been limited by the kinetics of methanol oxidation. A full Langmuir-Hinshelwood model was previously developed¹ in order to ascertain the kinetic rates of each elementary step of methanol oxidation on platinum. The strongest criticism of this model was its neglect of partial oxidation products. In addition to the empirical approach, we are collaborating with a theoretical group using Density Functional Theory to predict the kinetics rates from first principles. Experimentally, we need 4 independent measurements at different temperatures to find the kinetic rates and activation energies. The experimental system was designed to meet several requirements: (1) clean electrolyte environment, (2) no loss of potential control between measurements, (3) heating control from room temperature to 95°C, (4) quantitative detection of CO₂, and, (5) minimal time delay for detection of volatile species. We have successfully constructed an electrochemical microreactor with on-chip heating attached to a differential electrochemical mass spectrometer (DEMS) to meet these requirements. Expected results of the measurements are kinetic rate constants, activation energies, and Tafel slopes for five elementary steps in the methanol oxidation process; direct oxidation to CO₂, series oxidation of CO to CO₂, accumulation of the CO intermediate, incomplete oxidation of methanol, and adsorption of methanol; over temperature, potential, and concentration ranges of 22 - 100°C, 0.2 - 0.6 V_{rhe}, and 0.01 - 5 M respectively. ¹S. Sriramulu, T.D. Jarvi, E.M. Stuve, Reaction mechanism and dynamics of methanol electrooxidation on platinum(111), J. Electroanal. Chem. 467 (1999) 132-142.

2:40pm SS1-MoA3 Hydrogen Production and Conversion, I. Chorkendorff, Center for Individual Nanoparticle Functionality CINF, Denmark INVITED

On many levels there are strong efforts being made to find alternative ways of distributing energy in the future. Hydrogen is considered to be one of the more potential energy carriers. Since there is still a long way to go before we can produce hydrogen in sufficient amounts - and at competitive prices - directly from renewable energy sources, we will still have to rely on fossil fuels for many years to come. The fact that hydrogen, if combined

with carbon dioxide sequestration, can be made from fossil fuel without contributing to the green house effect may be a route of soft transition. Today hydrogen is essentially produced by the so-called steam reforming process of natural gas. In a number of studies we have investigated the fundamental aspects of methane and CO conversion on Ni and Ru surfaces - especially with respect to the effect of structure. From studies of Nitrogen dissociation on Ru we have learned that the so-called B5 sites are simply dominating the reactivity. It is therefore also of interest to investigate how these types of defect sites may influence other reactions - for example those related to the hydrogen production, such as the steam reforming process and its reverse reaction: the methanization reaction. Non-conventional production and conversion of hydrogen are also interesting, particularly because the extensive use of fuel cells will require developing new electrode materials that can replace the expensive and scarce Platinum. We will discuss different routes for development of new electrode materials, involving both screening of alloy materials under well defined conditions combining high pressure cells with conventional UHV equipment, but also biomimetic approaches. The latter involves materials inspired by the active co-factors of nitrogenase and hydrogenase enzymes for electrochemical hydrogen production.¹ B. Hinnemann, P. G. Moses, J. Bonde, I. Chorkendorff & J. K. Nørskov, Accepted JACS (2005).

3:20pm SS1-MoA5 The Electronic Structure Effect in Heterogenous Catalysis, A. Nilsson, Stanford University; L.G.M. Pettersson, Stockholm University, Sweden; B. Hammer, University of Aarhus, Denmark; T. Bligaard, C.H. Christensen, J. Nørskov, Technical University of Denmark

Transition metals are used extensively as catalysts and the variation in the catalytic activity for a given reaction is determined largely by the differences in the strength of the adsorbate-surface interaction from one metal to the next. In the following presentation we will demonstrate how we can understand trends in adsorbate-surface interactions based on a particularly simple picture that was originally developed to describe the difference in reactivity for hydrogen dissociation on metal surfaces, the d-band center model.¹ We will show that it applies quite generally and in particular we will show that it can be validated through an experimental determination of the electronic structure of both occupied and unoccupied adsorbate states in an atom specific way using x-ray emission spectroscopy (XES) and x-ray absorption spectroscopy (XAS) together with density functional theory calculations (DFT).² It has been shown that the catalytic activity of different transition metals as catalysts for ammonia synthesis is given by the strength of the nitrogen-surface bond.³ We will show that XES, XAS and DFT studies of atomic nitrogen can probe details of the metal d induced adsorbate electronic structure that can be linked to the chemisorption bond strength. ¹B. Hammer and J. K. Nørskov, Nature 376, 238 (1995). ²A. Nilsson and L. G. M. Pettersson, Surf. Sci. Repts. 55, 49 (2004). ³A. Logadottir, T. H. Rod, J. K. Nørskov, B. Hammer, S. Dahl and C. J. H. Jacobsen, J. Catal. 224, 206 (2001).

3:40pm SS1-MoA6 Microcanonical Transition State Theory: Closing the "Nonequilibrium Gap" Between Surface Science, Catalysis, and Electronic Structure Theory, I. Harrison, University of Virginia

Progress towards achieving a unified kinetic picture of surface reactions has been uneven when nonequilibrium surface science and thermal equilibrium catalysis experiments have been compared and contrasted with electronic structure theory (EST) calculations of transition state characteristics. A simple microcanonical unimolecular rate theory (MURT) model of gas-surface reactivity has been able to largely close this "nonequilibrium gap" for several activated dissociative chemisorption reactions [e.g., CH₄ on Ni(100), Pt(111), and Ir(111); SiH₄ on Si(100); H₂ on Cu(111)]. The MURT's ability to quantitatively predict and directly compare the results of disparate equilibrium and nonequilibrium experiments to one another and to the calculations of EST will be shown to open up some useful new opportunities to rigorously test and refine our understanding of reactive transition states and kinetics at surfaces.

4:00pm SS1-MoA7 First Principles Study of Factors Controlling the Rate of Ammonia Decomposition on Ni and Pd Surfaces, S. Stolbov, T.S. Rahman, Kansas State University

Using the plane wave pseudopotential method within the density functional theory with the generalized gradient approximation for exchange and correlation potential, we have calculated adsorption energies (E_{ad}), diffusion barriers and the first dissociation barriers (E₁) for NH₃ on Ni(111), Pd(111), Ni(211), and Pd(211). While the top site is found

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to be preferred for NH₃ adsorption on both Ni(111) and Pd(111), the calculated diffusion barrier is substantially higher for Pd(111) than for Ni(111). We also find that during the first dissociation step (NH₃ => NH₂ +H) on both surfaces NH₂ moves from the top site to the nearest hollow site, while on the stepped surface (211) it moves from the initial top site at the step edge to the bridge site in the same step chain. H is found to occupy the hollow sites for all four surfaces. For the reaction on Ni(111), E₁ is found to be 0.23 eV higher than E_{ad}, while at the step of Ni(211), E₁ and E_{ad} are almost equal. This suggests that the molecule would rather desorb than dissociate on Ni(111), and dissociate on the stepped surface. On the other hand in the case of Pd surfaces, we find that the dissociation barrier is much higher than E_{ad}, even for the stepped surface. This may explain why ammonia decomposition rate on Pd is much lower than that on Ni.

4:20pm SS1-MoA8 Water Chemistry on Cu(110): from Ultra High Vacuum to Ambient Conditions, K. Andersson, Stanford University / Stockholm University, Sweden; *H. Bluhm, G. Ketteler*, Lawrence Berkeley National Laboratory; *H. Ogasawara, T. Schiros*, Stanford Synchrotron Radiation Laboratory; *D.F. Ogletree, M. Salmeron*, Lawrence Berkeley National Laboratory; *A. Nilsson*, Stanford Synchrotron Radiation Laboratory

Probing the coverage and chemical speciation of molecules at surfaces are of fundamental interest in the fields of heterogeneous catalysis and molecular environmental science. We present in-situ studies of water adsorption on Cu(110) at pressures up to 1 Torr in the temperature range 270 - 470 K using synchrotron-based photoelectron spectroscopy. Partial coverages of atomic O, OH, and H@sub 2@O are reported under various conditions. We compare our results to those obtained under ultra high vacuum conditions where we have found a water dissociation onset at about 160 K with an activation barrier of 0.53-0.56 eV.¹ ¹K. Andersson, A. Gómez, C. Glover, D. Nordlund, H. Öström, T. Schiros, O. Takahashi, H. Ogasawara, L.G.M. Pettersson, A. Nilsson, Surf. Sci. Lett., in press (2005).

4:40pm SS1-MoA9 Hydrogen Interactions with Quasicrystalline Aln-; Pd- & n-; Mn Surfaces, C.J. Jenks, T.A. Lograsso, Ames Laboratory, Iowa State University; *J. Whaley, R. Bastasz*, Sandia National Laboratories

The interaction of molecular and atomic deuterium with the fivefold surface of icosahedral (i-) Aln-Pdn-Mn using angular-resolved low-energy ion scattering under ultrahigh vacuum conditions will be discussed. i-Aln-Pdn-Mn is known to form a clean laterally-bulk-terminated surface after sputtering and annealing in excess of 800 K. Despite no two layers within a this material being identical, certain types of planes are favored, namely those that are Al-rich (> 77 atomic percent). The density of Al atoms on the clean surface of fivefold i-Aln-Pdn-Mn is about that of Al(111) and thus we compare our results to studies of molecular and atomic hydrogen on Al(111). We are able to confirm, using ion scattering of 2 keV neon ions and direct recoil measurements, previous thermal desorption studies that indicated that molecular deuterium does not dissociate on this surface. Molecular deuterium, likewise, does not dissociate on Al(111). Atomic hydrogen, however, we find readily adsorbs on both surfaces. On fivefold i-Aln-Pdn-Mn we find that atomic deuterium adsorbs on top of the surface and that it strongly attenuates the signals for Al, Pd and Mn along particular azimuthal directions. Based on this information we will discuss the deuterium adsorption geometry on i-Aln-Pdn-Mn and compare the results to those for Al(111). This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences under Contracts no. W-405-Eng-82 and DE-AC04-94AL85000.

5:00pm SS1-MoA10 Detection of Nitric Oxide using Gold Nanoparticle Catalysts on WO@sub3@ Chemiresistive Sensors, A.L. Martin, University of Maine; *J. Wang*, Bangor High School; *G. Bernhardt*, University of Maine; *M. Sander*, Inst. Materials Res. Eng., Singapore; *R.J. Lad, F.G. Amar, B.G. Frederick*, University of Maine

Detection of nitric oxide at parts-per-billion levels is important for environmental and medical applications. We have shown that NO can be detected on tungsten trioxide chemiresistive sensors if gold or silver nanoparticles are present. The sensitivity, dynamic range, and response time depend upon the metal coverage and particle size distribution. In the limit that NO to NO@sub2@ conversion and spillover/diffusion is fast compared to NO@sub2@ reaction, the mean field solution is consistent with the initial, linear dependence of sensor response on NO partial pressure. Changes in the gold nanoparticle particle size distribution were measured with high resolution SEM. We have modeled the adsorption and conversion of NO to NO@sub2@ on the metal catalyst, followed by spillover, diffusion and reaction of NO@sub2@ with oxygen vacancies on the WO@sub3@(001) surface using kinetic Monte Carlo simulations. The

spatial inhomogeneity results in a non-linear sensitivity curve, which is consistent with sensor response after aggregation.

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