Monday Afternoon, November 15, 2004

Surface Science
Room 210B - Session SS1-MoA
Simulation and Theory of Adsorption

Moderator: S.B. Sinnott, University of Florida

2:00pm **SS1-MoA1 Theoretical Insights into Chemistry and Catalysis at the Aqueous Metal Interface***, **M. Neurock**,* University of Virginia **INVITED**

The metal-solution interface is important in controlling a number of relevant processes including catalysis, electrocatalysis, and corrosion chemistry. Relatively little, however, is known about the structure and dynamics of the metal solution interface and its impact on elementary physicochemical surface processes, including adsorption, diffusion, and reaction. Density functional theory and ab initio molecular dynamic methods have been used to analyze the effects of aqueous media on the mechanism and the kinetics of different surface processes. The presence of protic solutions on well-defined metal substrates leads to a wealth of interesting surface behavior. Hydrogen bonding can modify the structure of adsorbed intermediates, alter the strength of the adsorbate surface-bond, stabilize charged intermediates, enhance surface kinetics and even provide new mechanistic pathways in which the solution directly participates. We describe the direct, as well as the indirect, effects of solution on different surface processes including the heterolytic dissolution of organic and inorganic intermediates, molecular and dissociative adsorption and desorption of organic intermediates over well-defined metal surfaces, surface reactivity, and diffusion. There are many cases where the solution can directly participate in these mechanisms by directly participating in proton transfer processes. These effects can be quite different in electrochemical systems since the chemical potential can have an important influence on the structure and reactivity at the metal solution interface. We examine here the energetics and pathways for methanol oxidation well-defined Pt(111) substrates over a range of different applied potentials for application to the direct methanol fuel cell.

2:40pm **SS1-MoA3 Atomistic Modeling of CO Oxidation on Pd(100): Ordering of the Reactant Adlayer, Bistability of Steady States, and TPR***, **D.-J. Liu**, J.W. Evans,* Iowa State University

We develop a realistic atomistic lattice-gas model for CO-oxidation on Pd(100) under UHV conditions which describes equilibrium c(2@sq@2 x @sq@2)R45° ordering of CO(ads) on bridge sites, and both non-equilibrium c(2 x 2) and equilibrium p(2 x 2) ordering of O(ads) on four-fold hollow sites. The latter requires suitable treatment of the dissociative adsorption kinetics of O@sub 2@(gas) via an 8-site rule (reflecting strong repulsions between neighboring O) together with transient mobility. CO-CO and O-O adspecies interactions are tuned to match experimental LEED, TPD, and heat of adsorption data for the separate adspecies. Description of the interaction and reaction between CO(ads) and O(ads) is guided by DFT results and by comparison with TPR data. With this model, we map out the bifurcation diagram for the reactive steady states identifying the bistability regime and critical (cusp) point. We also relate various features of the experimental TPR spectra to details of the adspecies interactions in this system. We also discuss extension of the model to the regime of higher pressures, where oxide formation produces a clear signature in the TPD spectra for oxygen, and impacts the reaction kinetics.

3:00pm **SS1-MoA4 CO Coupling Reaction on UO@sub2@(111)Single Crystal Surface: An Experimental and Theoretical Study***, H. Idriss, **S.D. Senanayake**, A.S.L. Soon,* The University of Auckland, New Zealand

The unique electronic properties of UO@sub2@ makes it an ideal prototype material for investigation of new chemical pathways. Carbon monoxide molecules were found to selectively couple to C2 compounds over O-defected surfaces of UO@sub2@(111) single crystal. The most plausible reaction can be described by: 4CO + H@sub2@ -> C@sub2@H@sub2@ + 2CO@sub2@. This unique reaction is studied using temperature programmed desorption (TPD), X-ray Photoelectron Spectroscopy (XPS) and valence band, targeting surface intermediates and oxidation states of uranium and oxygen ions. Evidence of CO dissociation upon adsorption is seen by the disappearance of XPS lines due to U metal, the increase of those related to U@super4+@ and the formation of surface carbides. Preliminary steady state catalytic experiments on polycrystalline H@sub2@-reduced UO@sub2@ have further confirmed the selective pathway to acetylene and ethylene. Relativistic density functional theory (DFT) calculations have been performed using the Amsterdam Density Functional Theory for molecules and with BAND code for embedded clusters and periodic slab studies. Binding energies and conformations of CO adsorption on the surface are probed to offer a deeper understanding of surface energetics. The structures of interests were fully optimised with the inclusion of scalar relativistic effects, which were treated with the Zeroth-Order Regular Approximation (ZORA) formalism.

3:20pm **SS1-MoA5 Towards an Understanding of the Silver Catalysed Ethylene Epoxidation Process***, **A. Michaelides**,* University of Cambridge, United Kingdom*; K. Reuter, M. Scheffler,* Fritz-Haber-Institut der Max-Planck Gesellschaft, Germany

A number of recent studies indicate that, under moderate pressures of oxygen, some transition metal catalysts are covered in thin oxide overlayers. For oxidation catalysis, it has been suggested that such "surface-oxide" layers are catalytically active, and that this role is not performed by the pure metal surfaces as was traditionally assumed. This contemporary picture can be traced back to Ag catalysis, where it has been believed for 30 years that exposure of oxygen to Ag{111} leads to the formation of an ultra-thin surface-oxide. Extensive experimental and theoretical work has been carried out for oxygen on Ag, motivated mainly by the desire to understand silver's unique ability as a partial oxidation catalyst for ethylene [see, for eg., refs. 1-4]. However, density functional theory results, presented here, augmented with thermodynamic calculations, indicate that previous conclusions are significantly incomplete and that the structure of this original surface-oxide must be reconsidered. Indeed novel oxide overlayers are identified, and, predicted to be stable under the oxygen pressures at which the industrial ethylene epoxidation reaction is carried out. Moreover, we find that under these conditions finite variations in the stoichiometry of the surface oxides can occur with practically no change in free energy. It is suggested that this is one of the essential hallmarks of an effective red-ox catalyst. The first phase diagrams of Ag in contact with gaseous environments of both oxygen and ethylene are also be presented, as are reaction mechanisms for the formation of ethylene-epoxide. @FootnoteText@ @footnote 1@C.T. Campbell, J. Catal. 94, 436 (1985). @footnote 2@C.I. Carlisle, M.-L. Bocquet, J. Cerda, D.A. King, P. Sautet, Phys. Rev. Lett. 84, 3899 (2000). @footnote 3@A. Michaelides, M.-L. Bocquet, P. Sautet, A. Alavi, D.A. King. Chem. Phys. Lett. 367, 344 (2002). @footnote 4@W.X. Li, C. Stampfl, M. Scheffler, Phys. Rev. B 68, 165412 (2003).

3:40pm **SS1-MoA6 Determination of Adsorption Site for Isocyanides and Aminocarbynes on Pt(111) from Theoretical and Experimental Vibrational Spectra***, **E. Herceg**, B. Chatterjee, M. Trenary,* University of Illinois at Chicago

Density funcional theory (DFT) calculations have been used to study the bonding, geometry, and influence of basis set size on the vibrational properties of methyl-isocyanide (CH@sub 3@NC) and aminocarbyne species (CNH@sub 2@ and CNHCH@sub 3@) bonded to different Pt clusters. Calculated spectra were compared with the RAIRS data obtained for the corresponding species adsorbed on the Pt(111) surface. We used Pt, Pt@sub 7@H@sub 6@, Pt@sub 2@, Pt@sub 9@H@sub 14@, and Pt@sub 4@ clusters in order to provide models for adsorption at on-top, two-fold bridge, and three-fold hollow sites. Comparison between experimental and calculated spectra showed that CH@sub 3@NC is bonded to the surface at on-top site for low coverages and at both on-top and bridge sites for high coverages. For aminocarbynes bonded to Pt@sub 2@ and Pt@sub 9@H@sub 14@ (models of the twofold bridge site) calculations successfully reproduce experimental spectra. No significant improvement was achieved by using the Pt@sub 9@H@sub 14@ cluster compared with the Pt@sub 2@ model. On the other hand better agreement between experimental and simulated spectra of CH@sub 3@NC and CNH@sub 2@ can be achieved by increasing the size of the basis sets used for both the adsorbate and Pt cluster atoms.

4:00pm **SS1-MoA7 Ab Initio Molecular Dynamics Study of Methanol Adsorption and Reaction on Copper Clusters***, **W.-D. Hsu**, S.B. Sinnott,* University of Florida

The reaction of methanol molecules with size-selected Cu@sub n@ clusters, n=2-9, is investigated by first-principles molecular dynamics simulations. The simulations use density functional theory within the generalized gradient approximation and ultrasoft pseudopotentials. The molecules are deposited on the Cu clusters with an incident energy of 0.5 eV/molecule. The structure, dynamics, and reaction energy are studied as a function of the cluster size. Experiments by Kondow and co-workers@footnote 1@ find that the dominant reactions are methanol chemisorption, demethanation, and carbide formation, which are very different from the interaction of methanol with bare copper surfaces, where physisorption is the dominant outcome. The simulations detail the atomic scale mechanisms that are responsible for these differing behaviors. For example, they show that the adsorption energy of methanol to Cu@sub 7@ is about 0.5 eV, which is larger than the energy of adsorption of methanol on the Cu(111) surface@footnote 2@@super ,@@footnote 3@ by about 0.25 eV. The simulations also illustrate the differences in the interaction of methanol with copper clusters of various sizes. This work is supported by the National Science Foundation (CHE-0200838). @FootnoteText@ @footnote 1@M. Ichihashi, T. Hanmura, R. T. Yadav, and T. Kondow, J. Phys. Chem. A 104 (2000) 11885@footnote 2@J. R. B. Gomes, and J. A. N. F. Gomes, Surf. Sci. 471 (2001) 59@footnote 3@J. Greeley, and M. Marvrikakis, J. Cataly. 208 (2002) 291.

4:40pm **SS1-MoA9 Furan Decomposition Mechanism on Vicinal Pd(111) Studied by STM and DFT@footnote 1@***, A. Loui,** *C.Y. Fong, S. Chiang,* University of California, Davis

We have used scanning tunneling microscopy to investigate the behavior of furan (C@sub 4@H@sub 4@O) adsorbed intactly on stepped Pd(111) at 199 and 225 K, as well as aspects of its decomposition after heating to a maximum temperature of 415 K. Studies conducted on two substrates with relatively narrow and wide terraces reveal strikingly different behaviors. Furan is shown to preferentially adsorb at step edge sites on both surfaces, while evidence of molecular diffusion is seen only on the narrower vicinal planes. After heating to 288 K, 300 K, and 415 K, evidence of reaction can be observed in occupied-states STM images. Our observations support a furan decomposition mechanism wherein the heterocycle preferentially adsorbs and reacts at upper step edge sites. Although our data do not provide a complete picture of the surface reaction, the proposed model is consistent with previous studies of surface adsorption, diffusion, and reaction on vicinal, low-Miller-index transition metal surfaces. Ab initio calculations based on Hohenberg-Kohn density functional theory (DFT) have been performed for several high-symmetry adsorption modes of furan on flat Pd(111). These results, optimized with respect to planewave basis size and k-point sampling of the Brillouin zone, show that a two-fold chemisorption site is energetically preferred over the three-fold hollow and on-top sites. @FootnoteText@ @footnote 1@ Funded by NSF CHE-0111671.

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