

Surface Science

Room 327 - Session SS1-FrM

Catalysis IV: Reactivity of Complex Systems

Moderator: S. Semancik, National Institute of Standards and Technology

8:20am SS1-FrM1 Surface Chemistry of Carburization and Embrittlement of Fe, *D.E. Jiang¹, E.A. Carter*, University of California, Los Angeles

High temperature and pressure, as well as reactive gases such as CO and H₂, erode steel. Experimental observations of eroded steel show that carburization and embrittlement are potential causes for the erosion. We investigate the surface chemistry behind this problem via spin-polarized periodic density functional theory. In this talk, we will discuss C and H adsorption on Fe(110) and C and H diffusion into and through bulk Fe. Static properties including site preference, solution enthalpies, and adsorption energies, are predicted with increasing system size and compared with experiment. For adsorption, different 2-dimensional structures will be compared. Barriers for diffusion of C and H into and through bulk Fe will be presented. Our predictions generally agree very well with experiment, though we do make some predictions which suggest further experimental studies. C and H show very different behavior both in bulk Fe and on Fe(110). For example, H prefers the tetrahedral site in bulk Fe, while C prefers the bulk octahedral site. H prefers the quasi three-fold site on Fe(110), while C prefers the long bridge site. Our study provides a clear picture of structures and energetics of C and H in bulk Fe and on Fe(110).

8:40am SS1-FrM2 Surface Science Studies of Tungsten Carbides as Potential Electrocatalysts, *M.B. Zellner, H.H. Hwu, J.G. Chen*, University of Delaware

The purpose of this research is to examine the feasibility of tungsten carbides 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/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. The reactions of CH₃OH, H₂O, H₂ and CO over tungsten carbide surfaces are studied with temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). Thus far, investigations on the C/W(111) and Pt/C/W(111) have been completed. The results show that the carbide surfaces possess characteristics critical to the potential application as DMFC and hydrogen 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. In order to bridge the materials gap from model surfaces to realistic systems, thin films of WC and W₂C have been deposited on carbon paper and glassy carbon substrates by means of PVD to be tested as electrocatalysts for hydrogen oxidation. Electrochemical testing on the PVD electrocatalysts is currently underway.

9:00am SS1-FrM3 Chemical Properties of Bimetallic and Metal Carbide Surfaces by Theoretical and Experimental Studies, *J.R. Kitchin, M.A. Barteau, J.G. Chen*, University of Delaware

The optimal catalyst balances the adsorption energies of all surface species involved, ensuring adequate concentrations of important intermediates, while preventing poisoning by strongly bound intermediates. Multi-component catalysts, such as transition metal carbides and bimetallic catalysts, are one solution to these problems, as the adsorption properties of molecules can be tuned by the composition of the catalyst. However, it is difficult to know a priori how the chemical properties of a particular carbide or bimetallic catalyst will be modified relative to the parent metals. Advances in Density Functional Theory (DFT) now allow many of these systems to be explored from first principles with desktop computers. We have used DFT to calculate electronic properties and adsorption energies of small molecules and atoms on idealized bimetallic and carbide catalyst surfaces. These electronic properties were then used to establish correlations with experimental data and the calculated adsorption energies. For example, we calculated the electronic structure and adsorption energy of H atoms (HBE) on 13 different monolayer, bimetallic catalyst surfaces and showed a near linear correlation between the calculated HBEs and the surface d-band center of the catalyst. We have

calculated the surface d-band centers of more than 25 other monolayer, bimetallic combinations and some carbide surfaces. Using the HBE/d-band correlation established above we could use these calculations to predict promising new bimetallic catalysts with desirable H and CO binding energies. These correlations, along with a growing database of calculated d-band centers for bimetallic and carbide catalysts, should be considered a starting point for the rational design of bimetallic and carbide catalysts with desired chemisorption properties.

9:20am SS1-FrM4 HREELS Measurements of Iodine Vibrations on Cu(111) and Cu(221), *D. Sung, A.J. Gellman*, Carnegie Mellon University

Density functional theory calculations have shown that iodine atoms adsorb at the tops of the step edges on stepped Cu single crystal surfaces. In order to try to corroborate this prediction, we have measured and compared vibrational frequencies of iodine atoms adsorbed on the flat Cu(111) surface and the stepped Cu(221) surface using High Resolution Electron Energy Loss Spectroscopy (HREELS). Energy losses at 136 cm⁻¹ and 235 cm⁻¹ are observed on both surfaces. We assign these two frequencies to in-plane and out-of-plane vibrations of iodine on the (111) terrace sites. On a stepped surface one would expect the in-plane mode perpendicular to the step edge to be higher in frequency than the in-plane mode on the Cu(111) surface, if the atom is adsorbed at the bottom of the step edge. It would be expected to appear at a lower frequency if the atom is adsorbed at the top of the step edge. On the Cu(221) surface, an additional peak appears at 80 cm⁻¹, corresponding to the vibration of iodine adsorbed on the step edges of Cu(221). The fact that this new mode is at a lower frequency than the in-plane mode on the Cu(111) surface is consistent with the expectation that the iodine atom is adsorbed at the top of the step edge. The experimental results are consistent with the theoretical prediction that iodine atoms adsorb at the top of the step edges on the Cu(221) surface.

9:40am SS1-FrM5 Elucidating the Origin of Low-Temperature Reactivity of the Ni-Pt Bimetallic System, *N.A. Khan, J.G. Chen*, University of Delaware

Bimetallic surfaces possess unique physical, chemical and electronic properties unlike those of either parent metal. These surfaces have generated considerable interest as novel catalytic materials with higher reactivities and selectivities. As catalysts, they are used in numerous applications, such as fuel cells, hydrotreating (bimetallic sulfides and carbides) and hydrogenation catalysts. In our research, we have studied the Ni/Pt(111) and Pt/Ni(111) model bimetallic systems. We have found that the 1 ML Ni/Pt(111) surface demonstrates a low-temperature hydrogenation reaction pathway not present on either pure metal surface. DFT and LEIS studies indicate that this reaction pathway may be a result of Ni diffusing into the Pt(111) subsurface layers. In order to further study the interaction between Pt and Ni and the chemical properties of these bimetallic surfaces, we have also investigated the low-temperature reaction pathway on Pt/Ni(111). TPD studies reveal that the hydrogenation chemistry on the 1 ML Pt/Ni(111) surface is almost identical to that of the 1 ML Ni/Pt(111), revealing that the chemistry is independent of the order of metal deposition, i.e. Ni/Pt(111) or Pt/Ni(111). We will also demonstrate the strong correlation between model Ni-Pt surfaces and supported Ni-Pt bimetallic catalysts.

10:00am SS1-FrM6 Surface Reactions of Co-Adsorbed CH₂I and CF₃I on Ag (111), *K. Adib, H. Piao, J. Hrbek*, Brookhaven National Laboratory; *W. Huang, J.M. White*, University of Texas at Austin

Synchrotron X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) have been used to study the surface reactions of sequentially coadsorbed CH₂I and CF₃I on Ag (111). When adsorbed separately on Ag (111), CH₂I and CF₃I molecules undergo C-I bond cleavage at temperatures as low as 100 K to produce adsorbed CH₂ and CF₃, respectively, as well as I adatoms. In the case of CH₂I, upon subsequent thermal annealing of the surface, the dissociatively adsorbed CH₂ fragments may subsequently recombine and desorb primarily as C₂H₄. In the case of sequential co-adsorption in the submonolayer regime, the CF₃ and CH₂ fragments recombine to desorb as CF₂CH₂. Synchrotron XPS results indicate the presence of a surface bound species formed recombinatively in the temperature range of 200-250 K confirming that the CF₂CH₂ desorption is a two-step process. The first step involves methylene insertion to produce a surface bound species (CF₂CH₂) that can be detected by XPS. The second step involves fluoride elimination and the desorption of CF₂CH₂ as detected by TPD.

¹ Morton S. Traum Award Finalist

Friday Morning, November 7, 2003

10:20am **SS1-FrM7 Probing the Chemistry of CH₃I on Pt-Sn alloys**, E.C. Samano, CCMC-UNAM, Mexico; C. Panja, N.A. Saliba, B.E. Koel, USC
Adsorption and reaction of CH₃I (methyl iodide) on Pt(111) and the (2x2) and (√3x√3)R30° Sn/Pt(111) surface alloys was investigated primarily by using temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS). CH₃I adsorbs molecularly on Pt(111) at 100 K, and 34 % of the adsorbed CH₃I monolayer decomposes during heating above 200 K in TPD. Competition occurs during heating within the chemisorbed layer between hydrogenation to produce methane and dehydrogenation that ultimately leads to adsorbed carbon. Alloying Sn into the Pt(111) surface decreases the heat of adsorption and the amount of decomposition of CH₃I. Alloyed Sn slightly reduces the CH₃I adsorption bond energy from 13.4 kcal/mol on Pt(111) to 11.4 kcal/mol on the (2x2) alloy with θ_{Sn} = 0.25 and 9.3 kcal/mol on the (√3x√3)R30° Sn/Pt(111) alloy with θ_{Sn} = 0.33. More notably, the Sn-Pt alloy surface strongly suppressed CH₃I decomposition. Only 4% of the adsorbed CH₃I monolayer decomposed on the (2x2) Sn/Pt(111) surface, and no decomposition of CH₃I occurred on the (√3x√3)R30° Sn/Pt(111) surface during TPD. Methane was the only hydrocarbon desorption product observed during TPD. These results point to the importance of adjacent "pure Pt" three-fold hollow sites as reactive sites for CH₃I decomposition. Finally, we note that CH₃I, and presumably the other short-chain alkyl halides, are not reactive enough on Pt-Sn alloys to serve as convenient thermal precursors for preparing species small alkyl groups such as CH₃(a) for important basic studies of the reactivity and chemistry of alkyl groups on Pt-Sn alloys. Another approach is required such as the use of a CH₃-radical source or non-thermal activation of adsorbed precursors via photodissociation or electron-induced dissociation (EID).

10:40am **SS1-FrM8 A Model Catalyst with Selectivity Controllable Functions: the Effects of Thickness Extensional Resonance Oscillation on the Catalytic Activities for Ethanol Decomposition of Thin AgAu Film Alloy Deposited on a Ferroelectric z-cut LiNbO₃ Crystal**, N. Saito, Y. Sato, Y. Yukawa, H. Nishiyama, Y. Inoue, Nagaoka University of Technology, Japan

In an attempt to design a heterogeneous catalyst that has artificially controllable functions for catalytic reactions, we have employed the resonance oscillation (RO) of acoustic wave generated on a poled ferroelectric crystal and demonstrated that the thickness extension mode resonance oscillation (TERO) has the ability to change the reaction selectivity over thin metal catalysts deposited on a z-cut LiNbO₃ crystal.¹ The effects of TERO are suggested to have strong influences on the electronic states of metal catalysts, and it is particularly interesting to apply the TERO for alloy catalysts consisting of more than one component surface metal atom with different electronic structures. In the present study, we investigated the TERO effects on catalytic ethanol decomposition on AgAu alloy catalysts. The AgAu alloy catalysts were prepared by consecutive deposition of Au and Ag, followed by heat treatment at high temperature enough to allow the metal phases to diffuse and to uniformly mix each other. In catalytic run on a Ag catalyst, the TERO increased ethylene activity without changes in acetaldehyde, indicating that the TERO activate only ethylene production on a single Ag metal surface. On the other hand, the TERO with AgAu catalysts increased the activity for acetaldehyde significantly. The activity enhancement increased with increasing Au content, passed through a maximum at 80% and decreased sharply. Laser Doppler measurement showed that lattice displacement generated by the TERO became the smallest at the same Au content (80%) as that where the TERO effect on the activity for acetaldehyde was the highest. This indicates that the nature and strength of Ag-Au bonds plays in an important role in the TERO-induced activity enhancement. Similar results were also observed for AgCu alloys. The mechanism of different TERO effects between Ag and Ag-based metal alloys is discussed. ¹ N.Saito and Y.Inoue, J.Phys.Chem.B, 107/9, 2040(2003).

11:00am **SS1-FrM9 Different Changes in Work Function of Low- and High-index Cu Surfaces with Lattice Displacement in Surface Acoustic Wave Propagation**, H. Nishiyama, N. Saito, Y. Inoue, Nagaoka University of Technology, Japan

Surface acoustic wave (SAW) generated on a poled ferroelectric crystal by applying rf electric power has been demonstrated to markedly enhance the catalytic activity of thin polycrystalline metal (Ag, Pd, Ni, Cu) films for different kinds of the metal-catalyzed reactions such as ethanol decomposition, ethanol and CO oxidation. The enhancement of the

catalytic activity and the changes in the selectivity with SAW suggest that the SAW could affect the work function of the catalyst metal surfaces. To confirm the view, in the present study, photoelectron emission spectroscopy (PEEM) was employed, since photoemission characteristics are directly related to the work function of the metal surfaces. Thin Cu metal films treated by either annealing or sputtering have been used, and their atomic scale surface structures were inferred by the characteristic CO stretch frequency obtained in infrared reflection absorption spectroscopy (IRAS). It was shown that annealing gave rise to a Cu(111)-like low index plane mainly, whereas sputtering produced a large density of step sites and high index planes such as (311) and (211). The different SAW effects on the low- and high-index Cu surfaces were observed: the SAW propagation decreased the PEEM intensity for the low-index plane such as Cu(111), whereas it increased the PEEM intensity for the high index planes and step sites. The results indicated that the SAW enhanced the work function of a densely packed Cu surface and reduced that of a less packed Cu surface with coordinatively-unsaturated metal atoms. Dynamic and vertical lattice displacement by SAW was proved to have prominent structure-sensitive effects enough to change the electronic structures of the metal surface.

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