Wednesday Afternoon, October 4, 2000

Surface Science Room 209 - Session SS2+VT-WeA

Adsorption and Desorption Phenomena I

Moderator: C.M. Friend, Harvard University

2:00pm SS2+VT-WeA1 The Role of Two-dimensional Compressibility in Physisorption, Competitive Adsorption and Dynamic Displacement, G.A. Kimmel, Z. Dohnálek, R.S. Smith, B.D. Kay, Pacific Northwest National Laboratory INVITED

We have investigated the physisorption of gases (Ar, N@sub 2@, CH@sub 4@, etc) on Pt(111) with modulated beam techniques, beam reflection measurements and temperature programmed desorption (TPD). The kinetics of adsorption and desorption for systems where the coverage is larger than ~0.8 monolayer (ML) is dominated by the two-dimensional compression of the adsorbate layer. In particular, at coverages near 1 ML the repulsive interaction between adsorbates increases causing an approximately linear decrease in binding energy as the coverage increases. The formation of the first monolayer is complete when the binding energy of the adsorbates in the compressed first layer is equivalent to the binding energy of an adsorbate in the second layer (i.e. when the chemical potential of the first and second layers are equal). Evidence for this compression arises in the TPD of physisorbed gases from Pt(111) which reveal a non-zero, nearly constant desorption in the temperature range between the desorption peaks of the "first" and "second" monolayers. Modulated beam experiments also support this interpretation. In that case, the Pt(111) surface is pre-covered with ~1 ML of gas and then exposed to gas pulses of varying duration (~0.05 s - 1.0 s) and the desorbed/reflected flux is monitored. Another example where the two dimensional compression of the adsorbate layer is important occurs when the "competitive" adsorption of two gases is examined. In these experiments, an adsorbate can be displaced/desorbed when the surface is exposed to a gas which has a higher binding energy to the substrate. We will present a simple model for the binding energy as a function of coverage which explains the observed adsorption/desorption kinetics for a variety of systems.

2:40pm SS2+VT-WeA3 Molecular Adsorption and Growth of n-butane Adlayers on Pt(111), *J.F. Weaver*, University of Florida; *M. Ikai, A. Carlsson, R.J. Madix*, Stanford University

The molecular adsorption of n-butane and the growth of n-butane adlayers on Pt(111) have been investigated using molecular beam techniques, temperature-programmed desorption and low-energy electron diffraction. Our results indicate that four adlayer phases develop sequentially as the nbutane coverage increases from the submonolayer to second layer ranges at surface temperatures near 98 K. The structural properties of the adlayer and the kinetics for adlayer growth will be discussed in detail. Interestingly, although the changes in adlayer structure significantly affect the rates of nbutane desorption and surface diffusion, the adsorption probability of nbutane on Pt(111) is found to increase smoothly with increasing coverage. This finding indicates that the long-range arrangements and orientations of molecules in the n-butane adlayer have a negligible influence on the intrinsic adsorption dynamics, suggesting that the energy transfer processes that facilitate adsorption are highly localized.

3:00pm SS2+VT-WeA4 Optical Effects of Monolayer and Multilayer Adsorption: Formic Acid and Methanol on Cu(100), C.-L. Hsu, E.F. McCullen, R.G. Tobin, Tufts University

We have studied the adsorption of formic acid (HCOOH) and methanol on epitaxial Cu(100) films at 125 K in both the monolayer and multilayer regimes, using infrared reflectance and dc resistance measurements and visible-light ellipsometry. The results are analyzed using an electron scattering model for reflectance changes due to chemisorbed monolayers, and a macroscopic three-layer model for physisorbed multilayers. For methanol, which is only physisorbed on Cu, the infrared reflectance increases linearly with film thickness (determined ellipsometrically) in agreement with the three-layer model. For formic acid the first monolayer is chemisorbed and scattering of conduction electrons from the adsorbates leads to an initial decrease in reflectance, together with an increase in the electrical resistance of the Cu film. At higher formic acid exposures physisorbed multilayers form, leading to a reflectance increase similar to that observed for methanol. This behavior is qualitatively consistent with expectations, but there are some surprising features. As formic acid exposure increases, the initial reflectance drop continues even after the

resistance change is largely complete, even though both effects are believed to result from the same process. The subsequent rapid rise in reflectance suggests that the sticking coefficient is much lower for the first layer than for subsequent layers. Possible explanations for these effects will be discussed.

3:20pm SS2+VT-WeA5 Precursor-mediated Dissociation and Trapping Desorption of Oxygen on Cu(001)-2@sr@2x@sr@2-O, M. Yata, Y. Saitoh, National Research Institute for Metals, Japan

The adsorption and desorption of oxygen on Cu(001)-2@sr@2x@sr@2-O has been studied by molecular beam method. Angular and time-of flight distributions have been measured for scattering oxygen from the surface. The time-of flight distributions can be fitted by nonshifted Boltzmann distributions. This means that the oxygen molecules are trapped at the surface in a precursor state and subsequently desorb from the surface. The translational temperature of the desorbing oxygen is lower than the surface temperature, which suggests that there is no barrier for desorption from the precursor state. The dissociative sticking probability of oxygen increases as the translational energy of incident oxygen decreases. This probability also increases with increasing surface temperature. These results suggest that the adsorption of oxygen on the Cu(001)-2@sr@2x@sr@2-O surface proceeds via a precursor-mediated dissociation process rather than by a direct activation process. This is contrast to the dissociative adsorption of oxygen on clean Cu(001) in which the dissociation occurs by direct collisional activation. There exists a competition between dissociation reaction and desorption once the oxygen molecule is trapped in the precursor state. We have estimated the difference in activation energies between the dissociation and desorption of 330 meV. The effect of tensile stress on the dissociative adsorption reaction of oxygen on the Cu(001)-2@sr@2x@sr@2-O surface will be also discussed.

3:40pm SS2+VT-WeA6 The Effect of Deposition Pressure on Adsorbate Structure and Coverage: Oxygen on W(110)@footnote 1@, D.E. Muzzall, University of California, Davis; C.S. Fadley, University of California, Davis and LBNL; S. Chiang, University of California, Davis

In most prior surface science studies, it has been assumed that total exposure, rather than pressure and time as independent variables, controls the types of adsorption structures formed. The importance of deposition pressure as a variable, however, was recently suggested in a study of the kinetics of the low pressure adsorption of oxygen on W(110) using X-ray photoelectron spectroscopy (XPS)and diffraction.@footnote 2@ As a more quantitative measure of such effects, we have used ultrahigh vacuum scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and XPS to explore the adsorbate structures and the coverage dependence of O/W(110) as a function of deposition pressure at room temperature. For the same total adsorbate exposure in Langmuirs (L), we find that changes in deposition pressure of as little as a factor of 3 cause significant changes in the apparent structures, domain sizes (e.g., of (1x2)O), and adsorbate coverage in monolayers. Total coverages derived from STM data using a software thresholding technique indicate that a critical dosing pressure exists for both the (2x1) and (2x2) structures, 1 x 10@sup -9@ and 3 x 10@sup -9@ torr respectively, below which coverage does not increase with increasing exposure time. This indicates that an equilibrium condition has been reached, from which surface free energies for both of these structures can be derived.@footnote 3@ Finally, in addition to the ordered (1x2), (2x2), and (1x1) structures for O/W(110), we have characterized a new fourth ordered structure by LEED and STM. The structure formed for oxygen exposure of 3 to 6 L and coexisted with the (1x2) structure. The primitive unit cell is a rectangle, 0.77nm x 1.37nm, with 15 W and 6 O atoms and has the matrix notation ((3,-1),(0,5)) relative to the W(110) substrate. @FootnoteText@ @footnote 1@ Supported by NSF DMR-9522240. @footnote 2@ Y. X. Ynzunza et al, Surf. Sci., in press. @footnote 3@ P. Liu et al, Surf. Sci. 417 (1998) 53.

4:00pm SS2+VT-WeA7 STM Investigation of Benzene Adsorption on Ag(110), K.F. Kelly, J.J. Jackiw, Pennsylvania State University; J.I. Pascual, H. Conrad, H.-P. Rust, Fritz Haber Institute, Germany; P.S. Weiss, Pennsylvania State University

We have investigated the adsorption of benzene on Ag(110) using the scanning tunneling microscope. We found that the molecules preferentially adsorb above step edges at 66 K. The preference for step edge adsorption is attributed to the Smoluchowski effect enhancing the empty states to which charge is donated from the @pi@ orbitals of the benzene. However, there is no adsorption at the [001] steps. A lack of free charge due to a gap in the Ag Fermi surface along that direction reduces the Smoluchowski

Wednesday Afternoon, October 4, 2000

effect and thus the adsorption at these steps. After further deposition at 4 K, we find that benzene forms a weakly adsorbed hexagonal monolayer. The monolayer is imaged at large tip-sample separations and is transparent upon closer approach. The interaction of benzene molecules with steps and point defects reduces this transparency.

4:20pm SS2+VT-WeA8 Scanning Tunneling Microscopy and Spectroscopy of Metal Tetraphenylporphyrins on Au(111), K.W. Hipps, D.E. Barlow, L. Scudiero, Washington State University

STM images of metal(II) tetraphenylporphyrin monolayers on Au(111) are presented for several transition metal ions. The constant current images clearly reflect the electronic nature of the metal ion used. Scanning tunneling spectroscopy (dI/dV curves) also allows one to differentiate between the metal complexes. The primary electroactive states, as shown by tunneling spectroscopy, are those involving both occupied and unoccupied molecular orbitals close to the Fermi energy of the Au(111) substrate. Scanning tunneling spectroscopy results for the negative sample bias region are compared to Ultra-violet photoelectron spectra of these same compounds on Au.

4:40pm SS2+VT-WeA9 Theory of Oxygen Adsorption on Ag(111): A DFT-GGA Investigation, W. Li, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany; C. Stampfl, Northwestern University; M. Scheffler, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

O/Ag(111) is an important system with unique catalytic behavior for several large-scale industrial processes, e.g., ethylene epoxidation and partial oxidation of methanol to formaldehyde. In spite of its importance, very little is known about the behavior of O at Ag(111) (which depends sensitively on pressure and temperature) on the microscopic level, and the precise atomic location and chemical nature of the various O species that form, e.g. on-surface, subsurface, in-surface. Using density-functional theory within the generalized gradient approximation, we investigate the interaction between oxygen and Ag(111). We found that the interaction between silver and oxygen is very weak. Adsorption becomes unfavorable for coverages between 0.33 and 0.50, with respect to the gas molecule O@sub 2@. Compared to hcp site, the fcc site is preferable, and the difference in adsorption energy differs by less than 0.17 eV/atom for the whole range of coverage considered. Strong charge transfer from silver to oxygen has been found due to the large difference in electronegativity between oxygen and silver, and results in a significant change in work function, which increases monotonically with oxygen coverage. Experimental studies report that at elevated temperatures two ordered phases form: a (4x4) structure (T@>=@400K),@footnote 1@ and a hightemperature (@sr@3 x @sr@3)R30° (T@>=@800K)@footnote 2@ structure. With respect to the latter, a surface substitutional site has been proposed. Our results show that this structure is unfavorable. For subsurface adsorption we find that oxygen prefers the octahedral site, but at coverage 0.33 it is also endothermic with respect to free O@sub 2@. We discuss alternative geometries for this phase. @FootnoteText@ @footnote 1@ G. Rovida et al., Surf. Sci. 43, 230 (1974); C. I. Carlisle et al., Phys. Rev. Lett. 84, 3899 (2000). @footnote 2@ B. Pettinger et al., Phys. Rev. Lett. 72, 1561 (1994); X. Bao et al. Phys. Rev. B 54, 2240 (1996).

5:00pm SS2+VT-WeA10 Adsorption of Propylene on Clean and Oxygen Covered Au(111) and Au(100), K.A. Davis, D.W. Goodman, Texas A&M University

The adsorption of propene on Au(111) and Au(100) was investigated using temperature programmed desorption (TPD) and high resolution energy loss spectroscopy (HREELS). A desorption activation energy of 9.4 kcal/mol and very small (< 25 cm@sup -1@) shifts of the vibrational frequencies from their gas phase values indicate that the interaction of propene with the surface is weak. Energy loss spectra suggest that propene adsorbs with its molecular plane tilted slightly with respect to the surface plane. Atomic oxygen, chemisorbed on the gold surfaces, was characterized using TPD and low energy electron diffraction (LEED), and its interaction with propene investigated. HREEL spectra of propene on the oxygen covered surfaces show shifts in the intensities and frequencies of the -CH@sub 2@ related vibrational features. Small amounts of product with masses 56 and 58 amu were observed for propene adsorbed onto a 0.4 ML oxygen-covered surface.

Author Index

Bold page numbers indicate presenter

- B --Barlow, D.E.: SS2+VT-WeA8, 2 - C --Carlsson, A.: SS2+VT-WeA3, 1 Chiang, S.: SS2+VT-WeA3, 1 Conrad, H.: SS2+VT-WeA7, 1 - D --Davis, K.A.: SS2+VT-WeA10, 2 Dohnálek, Z.: SS2+VT-WeA10, 2 - F --Fadley, C.S.: SS2+VT-WeA6, 1 - G --Goodman, D.W.: SS2+VT-WeA10, 2 - H --Hipps, K.W.: SS2+VT-WeA8, 2

Hsu, C.-L.: SS2+VT-WeA4, 1

Ikai, M.: SS2+VT-WeA3, 1 — J — Jackiw, J.J.: SS2+VT-WeA7, 1 — К — Kay, B.D.: SS2+VT-WeA1, 1 Kelly, K.F.: SS2+VT-WeA7, 1 Kimmel, G.A.: SS2+VT-WeA1, 1 -L-Li, W.: SS2+VT-WeA9, 2 -M-Madix, R.J.: SS2+VT-WeA3, 1 McCullen, E.F.: SS2+VT-WeA4, 1 Muzzall, D.E.: SS2+VT-WeA6, 1 - P --Pascual, J.I.: SS2+VT-WeA7, 1

- R --Rust, H.-P.: SS2+VT-WeA7, 1 - S --Saitoh, Y.: SS2+VT-WeA5, 1 Scheffler, M.: SS2+VT-WeA9, 2 Scudiero, L.: SS2+VT-WeA8, 2 Smith, R.S.: SS2+VT-WeA4, 1 - T --Tobin, R.G.: SS2+VT-WeA4, 1 - W --Weaver, J.F.: SS2+VT-WeA3, 1 Weiss, P.S.: SS2+VT-WeA7, 1 - Y --Yata, M.: SS2+VT-WeA5, 1