

Surface Science

Room 209 - Session SS2+VT-ThM

Adsorption and Desorption Phenomena II

Moderator: J.C. Hemminger, University of California, Irvine

8:20am **SS2+VT-ThM1 Alkali Metal and H@sub 2@O Co-adsorption and Reaction on Graphite(0001)**, *M.A. Gleeson, D.V. Chakarov, B. Kasemo*, Chalmers University of Technology and Göteborg University, Sweden

A comparative study of alkali metal (Na, K, Cs) adsorption, co-adsorption and reaction with H@sub 2@O on the basal plane of graphite has been performed. Water molecules are stabilised by interaction with alkali atoms, and undergo coverage and temperature dependent reactions. The surface solvation number is similar for all three alkali metals at low coverages (3 to 4 H@sub 2@O molecules per alkali atom). The critical alkali coverage for reactive co-adsorption at 98 K ranges between 0.1 to 0.25 ML. Reaction between H@sub 2@O and the alkali metals leads to the formation of hydroxide, hydride and oxide species on the surface. Additional peaks appear in the water desorption spectra due to alkali-stabilised H@sub 2@O and hydroxide decomposition. Decomposition of alkali oxides at high temperature can result in oxidation of the graphite and subsequent CO@sub 2@ evolution. Similarities and differences between the alkali metals are discussed.

8:40am **SS2+VT-ThM2 Adsorption of Hydrogen on Clean and Alkali-modified Low-index and Stepped Copper Surfaces**, *L. Thomsen*, Odense University/University of Southern Denmark; *J. Onsgaard*, Odense University/University of Southern Denmark, Denmark; *P.J. Godowski*, University of Wroclaw, Poland; *S.V. Hoffmann*, University of Aarhus, Denmark; *L. Bech, P. Moller*, Odense University/University of Southern Denmark

The interest for adsorption of low molecular gases like H and CO@sub 2@ on alkali-modified copper surfaces stems from the promoting role of the alkali metals in heterogeneous catalysis. Due to the substantial lowering of the work function with the addition of the alkali metal, pronounced changes in the adsorption and reaction properties of the copper surfaces are observed. The adsorption of atomic hydrogen on clean and potassium-modified Cu(110), Cu(100) surfaces and the stepped Cu(115), Cu(117) and Cu(112) surfaces has been studied. Typically, two hydrogen-induced states in the valence band have been found on the clean crystal and assigned to one state receding in the subsurface and another state at the surface of the crystal. Two states due to hydrogen are also observed on the potassium-modified surfaces and assigned to a potassium-hydrogen bond and a copper-hydrogen bond. Co-adsorption of H and CO@sub 2@ on the K/Cu surface results in formation of formate with high efficiency on the most corrugated surfaces.

9:00am **SS2+VT-ThM3 Angle Resolved Photoemission Study on Adsorption and Desorption of Cobaltocene on Cu(111)**, *J. Choi*, Louisiana State University; *P.A. Dowben*, University of Nebraska, Lincoln

The molecular adsorption and desorption of cobaltocene, Co(C₅H₅)₂, on Cu(111) have been studied by angle resolved photoemission spectroscopy (ARPES). We have measured the molecular orientation and bonding of adsorbed cobaltocene on Cu(111). Photoemission results indicate that the initially adsorbed surface species closely resembles that of molecular cobaltocene. The shift in photoemission binding energies relative to gas phase is largely independent of the molecular orbital. The molecule is adsorbed with cyclopentadienyl (C₅H₅) ring ligands parallel to the surface at 150K, and the molecular axis normal to the surface at the low coverage (below 10 Langmuir). The molecularly adsorbed cobaltocene loses the normal preferential orientation, at the higher coverages. Furthermore, molecular orientation is strongly affected by annealing temperature, indicating that there are more than one molecular adsorption states. With increasing of temperature, molecularly adsorbed cobaltocene on Cu(111) is desorbed.

9:20am **SS2+VT-ThM4 Angle Effects on the Nucleation of Polymeric Thin Films from Molecular Cluster Deposition: Molecular Dynamics Simulations**, *Y. Hu, S.B. Sinnott*, The University of Kentucky

Cluster beam deposition of organic material is thought to result in thin-film formation through rapid chemical reactions that occur at the impact site between the cluster and the surface. These reactions occur on the order of a few picoseconds and so are ideal for study with atomistic simulations. In this work, classical molecular dynamics simulations are used to investigate

the effect of incident angle on the nucleation and growth of polymeric thin films through organic molecular cluster deposition. The classical reactive empirical bond order method is used in the simulations. @footnote 1@ The specific system under study consists of clusters of ethylene being deposited on a diamond and amorphous carbon substrate at room temperature at various incident angles. The results show how the incident angle affects the nucleation of a thin film from the deposition. In addition, the dependence of this angle effect on substrate rigidity is investigated. This work is supported by the National Science Foundation (CHE-9708049). @FootnoteText@ @footnote 1@ S.B. Sinnott, L. Qi, O.A. Shenderova, D.W. Brenner, in Chapter 1 of Volume IV of ADVANCES IN CLASSICAL TRAJECTORY METHODS, Molecular Dynamics of Clusters, Surfaces, Liquids, and Interfaces, Ed. W. Hase (JAI Press, Inc., Stamford, CT, 1999), pp. 1-26.

9:40am **SS2+VT-ThM5 Geometrical Structure and Orientation of Metal Tetrphenylporphyrins on Au (111)**, *K.W. Hipsps, L. Scudiero, D.E. Barlow*, Washington State University

Geometrical structure and orientation of metal tetrphenylporphyrins on Au (111). Metal (II) tetrphenylporphyrin (MTPP) complexes adsorbed on polycrystalline Au and Au (111) are studied by Fourier transform reflectance-absorption infrared (FT-RAIR), X-ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscope (STM). XPS and FT-RAIR data indicate that the chemical composition of those complexes is preserved when they are vapor deposited on Au. FT-RAIR data also suggests that the first few adsorbed layers are oriented with the porphyrin ring parallel to the Au surface. STM images are presented for several transition metal ions. At low coverage, STM images show monolayer islands randomly distributed on Au (111) and high-resolution images display a square unit cell.

10:00am **SS2+VT-ThM6 Experimental and Theoretical STM Imaging of Xylene Isomers on Pd(111)**@footnote 1@, *D. Futaba, J.P. Landry, A. Loui, S. Chiang*, University of California, Davis

We have performed both theoretical and experimental studies of the three isomers of xylene, C@sub 6@H @sub 4@(CH@sub 3@)@sub 2@, adsorbed on Pd(111). Simulated scanning tunneling microscope (STM) images, calculated using a relatively simple computational method based on extended Hückel molecular orbital theory (EHT), showed no observable differences in surface features between occupied and unoccupied states images, nor between adsorption on the various high symmetry binding sites. The calculated binding energies suggest that xylene molecules prefer to bind in particular orientations on hollow and bridge sites. The computed images for xylene on Pd displayed almost identical surface features and symmetries as those calculated on Rh(111).@footnote 2@ Using STM and low-energy electron diffraction (LEED), we imaged the characteristic surface structures and investigated the molecular ordering for the three isomers on Pd(111). Experimental STM images showed each of the isomers exhibiting the characteristic geometries predicted by EHT. Both meta(m-)xylene and ortho(o-)xylene are characterized by an overall triangular shape, with m-xylene nearly equilateral. Para(p-)xylene shows a distinct diamond shape. M-xylene molecules adsorbed to upper step edges, usually with one side of the molecule aligned with the step edge and parallel to the close-packed directions of the Pd lattice. Only the p-xylene isomer showed long range order, forming a hexagonal structure with the long axes of the molecules parallel to each other. Translation and rotation of p-xylene molecules between consecutive scans were observed for the saturated Pd surface, causing disorder in previously ordered regions. @FootnoteText@ @footnote 1@ Supported by NSF CHE-95-20366 and UCOP CLC. @footnote 2@ D. N. Futaba and S. Chiang, Surf. Sci., 448, L175 (2000).

10:20am **SS2+VT-ThM7 Reactions of cis-, trans-, and 1,1-dichloroethene on Pd(111) Studied by TDS, LITD, and STM**, *D.E. Hunka, D.M. Jaramillo*, University of California, Davis; *D.C. Herman*, University of North Carolina, Chapel Hill; *K.D. Lormand, D. Futaba, S. Chiang, D.P. Land*, University of California, Davis

Chloroethylenes are the among the most abundant groundwater and soil contaminants. Catalytic degradation on transition metal surfaces offers a promising method for the alleviation of this ubiquitous problem. Large differences in the reaction rates of the various compounds have been observed. However, little is known about the reaction mechanisms or the origin of these rate differences. In aqueous solutions, for example, cis-dichloroethylene (cis-DCE) reacts an order of magnitude more slowly on Fe than do trans- or 1,1-DCE. The reactivities do not follow any monotonic trends in dipole, solubility, or bond strength. Addition of Pd to Fe catalysts has been shown to increase the rate of reaction for some of these species by orders of magnitude. We have undertaken to study the reactivity of the

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three isomers of DCE on Pd(111). As in aqueous solution, the cis isomer reacts very differently from the other two isomers. Decomposition on Pd(111) occurs below room temperature and H@sub 2@ is evolved with C and Cl remaining on the surface to very high temperatures. In contrast, both trans- and 1,1-DCE rearrange to yield chlorinated intermediates that decompose in two steps above room temperature liberating HCl. Some subtle differences exist in the reaction mechanisms, but both are drastically different from the cis isomer. Laser-induced thermal desorption and conventional thermal desorption with FT mass spectrometry, infrared spectroscopy, scanning tunneling microscopy and other surface techniques are used to elucidate the surface reaction mechanisms and energetics.

10:40am **SS2+VT-ThM8 Wet Oxidation of CO on Pt(111)**, *J. Bergeld, D.V. Chakarov, B. Kasemo*, Chalmers University of Technology and Göteborg University, Sweden

Presence of small amounts of OH is found to initiate the CO oxidation on Pt(111) surface. We have studied water coadsorption with CO on atomic oxygen precovered platinum surface with temperature programmed desorption (TPD) and found distinct relationship between the low temperature, @beta@@sub 3@ peak intensity and the presence and amount of coadsorbed OH. High initial CO coverage is another prerequisite for the low temperature start of the reaction. We are proposing and discussing several feasible mechanisms of the phenomenon, giving preference to autocatalytic reaction between CO and OH at the boundaries of ordered CO and oxygen/hydroxyl islands.

11:00am **SS2+VT-ThM9 The Behavior of Zirconium Surfaces in the Presence of Oxygen, Nitrogen, and Hydrogen Containing Adsorbates**, *Y.C. Kang, D.A. Clauss, R.D. Ramsier*, University of Akron

Zirconium and its alloys exhibit a unique combination of physical properties that have led to their widespread use as structural materials in fission reactors as well as in a variety of chemical engineering applications involving harsh environments. Common to these applications is the presence of oxygen, nitrogen, and hydrogen containing moieties. Mechanistic studies of the chemistry of such species on zirconium surfaces are necessary to answer fundamental questions which cannot be addressed by phenomenological models of environmentally assisted degradation in these systems. As part of an effort to address these questions, low energy electron diffraction (LEED) and temperature programmed desorption (TPD) techniques have been applied to the adsorption of water, nitric oxide, and ammonia on Zr(0001) surfaces. Water adsorption at 180 K at exposures above 0.75 L results in water desorption in a broad TPD feature near 550 K. Data from LEED indicate that this adsorption does not result in ordered layers until 700 K annealing, and that the formation of ordered structures depends on exposure and annealing conditions. Low exposures of nitric oxide and ammonia at 160 K results in essentially no thermal desorption features, but high (greater than 20 L) ammonia exposures results in the production of water during TPD experiments and the formation of complex residual LEED patterns. These TPD and LEED data indicate a competition between the kinetics of recombination and desorption with those of diffusion involving the near-surface regions.

11:20am **SS2+VT-ThM10 Chlorosilane Adsorption on Clean Si Surfaces: STM and FT-IR Studies**, *M. Nishizawa, T. Yasuda, S. Yamasaki*, Joint Research Center for Atom Technology (JRCAT), Japan; *M. Shinohara, Y. Kimura, M. Niwano*, Research Institute of Electrical Communication (RIEC), Japan

Understanding the interaction of silane and chlorosilane molecules, (SiH@sub n@Cl@sub 4-n@), with Si surfaces is the base for atomic-scale control of Si growth. A Si(111) surface exhibits the DAS structure which has 7 kinds of dangling bonds with different electron occupancy, while a Si(100) surface reconstructs to the asymmetric-dimer structure. We are interested in the interaction of chlorosilane with these qualitatively different surfaces. This paper discusses structures of SiH@sub 2@Cl@sub 2@-chemisorbed Si(111)-(7x7) and Si(100)-(2x1) surfaces. We have employed STM to identify reaction sites, and FT-IR to probe their local structure. In the STM topographs for adsorption on the Si(111)-(7x7) surface, reacted adatom sites appear darker than the unreacted ones. At a low coverage, we find that SiH@sub 2@Cl@sub 2@ molecules preferentially react with corner adatoms in the unfaulted half of the (7x7) unit cell to produce surface species - SiH@sub 2@Cl and -Cl. Komura et al. proposed a structural model in which the - SiH@sub 2@Cl group is adsorbed on the corner-hole atom.@footnote 1@ Our STM results agree with this model. On the other hand, FT-IR spectra measured for this surface showed two sharp peaks at 2108 cm@super -1@ and 2123 cm@super -1@. These peaks are

tentatively assigned to the symmetric and asymmetric Si-H stretching vibrations of the surface - SiH@sub 2@Cl group. However, the observed peak positions of the Si-H stretching vibrations are much lower than those predicted from the semi-empirical formula by Locovsky.@footnote 2@ The reason for this discrepancy is under consideration. Results for the Si(100) surface will be reported at the presentation. This study, partly supported by NEDO, was performed at JRCAT under the joint research agreement between NAIR and ATP. @FootnoteText@ @footnote 1@ T. Komura et al., Appl Surf. Sci. 130 (1998) 23. @footnote 2@ G. Lucovsky, Solid State Commun. 29 (1979) 571.

11:40am **SS2+VT-ThM11 A Far-IRAS Study of Water Adsorption on V@sub 2@O@sub 3@(0001)**, *M.J. Pilling*, University of Wisconsin, Milwaukee; *D.S. Toledano*, Yale University; *C.J. Hirschmugl*, University of Wisconsin, Milwaukee; *V.E. Henrich*, Yale University

The high brightness of a synchrotron radiation source has been utilized to investigate adsorption occurring on a single crystal transition metal oxide surface with far infrared reflection absorption spectroscopy (IRAS). The adsorption of H@sub 2@O, H@sub 2@@super 18@O and oxygen on V@sub 2@O@sub 3@(0001) was investigated between 154K and 224K. Infrared absorption bands at 992 cm@super -1@ and 1040cm@super -1@ are observed in the spectra above and below the desorption temperature of multilayer water, indicating the presence of a chemisorbed surface species.

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