Friday Morning, October 29, 1999

Surface Science Division Room 607 - Session SS2-FrM

Adsorption on Metals and Silicon

Moderator: A.A. Baski, Virginia Commonwealth University

8:20am SS2-FrM1 Quantitative Determination of Adsorbate Interactions on an Iron Surface, L. Österlund, M.O. Pedersen, I. Stensgaard, E. Laegsgaard, F. Besenbacher, University of Aarhus, Denmark

We introduce a new concept of Configuration Distribution Analysis (CDA) to extract quantitative values of the adsorbate-adsorbate interaction potential from Scanning Tunneling Microscopy (STM) data. By analyzing atomically resolved nitrogen islands on a Fe(100) surface, we show that the propensity of small, compact c(2x2) islands is due to a many-body effect in combination with elastic interactions. It is shown that the nearest and nextnearest neighbour interactions are strongly repulsive and weakly attractive, respectively, where the latter is modulated by the nearest neighbour coordination. Accurate determination of adsorbate-adsorbate interactions are essential to understand a variety of surface phenomena, and until now, there has been a lack of reliable experimental results. The results presented here promise to provide a new tool to bridge this gap.

8:40am SS2-FrM2 CO Adsorption on Mn Films on Cu(100), M. Grüne, Universität Bonn, Germany; G. Boishin, Bulgarian Academy of Sciences, Bulgaria; R.-J. Linden, T. Pelster, J. Breitbach, A. Frey, C. Becker, K. Wandelt, Universität Bonn, Germany

The adsorption of carbon monoxide on Mn films on Cu(100) at 100 K was studied by means of UPS, HREELS, LEED, TDS, and work function change measurements. On the c(8x2) Mn monolayer, two stages of adsorption can be separated. The first type of molecularly adsorbed CO increases the work function by 0.9 eV. HREEL spectra resolve at least 4 different adsorption states, which cannot be separated by dosing or annealing. We assign these to side-on CO, step sites, and different kinds of bridge-bonded sites. The substrate superstructure remains intact in this low-coverage range. No adsorbate-induced LEED spots can be observed. Further CO adsorption beyond a critical exposure leads to a destruction of the Mn film order accompanied by a change of the CO-metal interaction as revealed by UPS and a decrease of the work function by 0.16 eV. In HREELS an additional CO state can be identified, presumably ontop-CO. At submonolayer Mn coverages, CO adsorbs simultaneously on both Cu and Mn patches. A thick polycrystalline Mn film exhibits molecular adsorption preferably in the side-on geometry. Annealing of CO-covered monolayer films leads to a restructuring of the surface around 220 K, subsequent dissociation of CO around 300 K, accompanied by desorption with a maximum at 350 K. It is not possible to re-establish the ordered film structure by annealing. At submonolayer Mn coverages, an additional desorption maximum at 420 K can be attributed to CO desorption from the Mn island edges. If the surface has not been saturated with CO, molecules change from Cu to Mn sites upon annealing to 160 K. Annealing a CO-covered thick polycrystalline Mn film leads to complete CO dissociation around 210 K.

9:00am SS2-FrM3 STM Tip Induced 1D Chains on H-covered Ni(100) Surface, T. Komeda, M. Kawai, The Institute of Physical and Chemical Research (RIKEN), Japan

The adsorption of H on metal surfaces is considered as a weak chemisorption in general, based on its low desorption temperature. Due to its weak bonding, the surface reconstruction on H adsorption is observed only for very open surface, such as (110) surface of fcc transition metal. It has been shown that the H saturated Ni(110) surface at room temperature shows streaky (1x2) superstructure, on which high resolution STM observation showed added and missing rows as the origin of its structure. In this paper, we show STM tip can create very characteristic 1D chains of protrusion and depletion on H-saturated Ni(100) surface; Ni(100) surface is believed to be stable for H adsorption and forms no reconstruction. The 1D structure is apparently similar to the added and missing row structure on H saturated Ni(110) surface. Experimentally clean Ni(100) surface was exposed to 10 L(1L=10-6 torr s) of H2 at 100 K and observed with low temperature STM which is cooled with liquid nitrogen. When the surface is scanned with a very small gap between the tip and the sample (scanning condition such as -1 mV biased on the sample and tunneling current of 4nA), straight protruded rows accompanying depleted rows besides them appear. The height of the protruded row is 0.3-0.5 A, and the high resolution image shows it is composed of a chain of single atoms spaced with 2x1 periodicity. The characteristic 1D structure is similar to the added

and missing row structure formed on H saturated Ni(110) surface, and apparently slight touch of the STM tip on the substrate can dig a single row and the released NiH species form added row. As can be seen in the apparent low height of 0.3-0.5 A for the added row on the terrace, the added row and the missing row shows strong bias dependence in the STM image, which indicates very characteristic electronic structures appeared on this quasi 1D structure.

9:20am SS2-FrM4 Morphology and Electronic Structure of 1D Ca-induced Rows on the Si(111) Surface, *M.S. Turner, K.M. Jones, A.A. Baski, J.A. Carlisle,* Virginia Commonwealth University

Deposition of highly reactive alkaline-earth adsorbates (Ca, Sr, Ba) onto semiconductor substrates leads to reconstructions which are row-like in nature. The Ca/Si(111) system has been studied using RHEED, STM and synchrotron radiation photoemission. For Ca coverages less than 0.5 ML, a series of odd-order nx1 (n=3,5,7...)reconstructions have been observed. The most stable of these is a (3x1) phase that occurs at 0.33 ML. Various models have been proposed for the general metal/Si(111)-(3x1) system, and we discuss the accuracy of these models as they apply to this system.@footnote 1@ In particular, we discuss how well the models can be altered to account for the higher-order reconstructions that are observed at higher Ca coverages, and for commonly observed defect structures in the (3x1) phase. These objectives are accomplished through comparison between the surface morphologies observed in STM images and the electronic structure of the different surface phases observed in highresolution core-level and valence-band photoemission. @FootnoteText@ @footnote 1@S.C. Erwin and H.H. Weitering, Phys. Rev. Lett. 81, 2296 (1998).

9:40am SS2-FrM5 STM Study of Metal Row Growth on Si(5 5 12), K.M. Saoud, I. Samanta, K.M. Jones, A.A. Baski, Virginia Commonwealth University

The high-index Si(5 5 12)-2x1 surface has recently gained interest as a template for overlayer growth, primarily because of its highly anisotropic row reconstruction. Our recent STM studies have shown that a noble metal such as Ag forms well-ordered overlayer rows on this surface.@footnote 1@ At coverages below 0.25 ML and moderate annealing temperatures (450°C), Ag forms monatomic rows with an inter-row spacing of ~5 nm. These Ag rows nucleate along the more reactive tetramer rows of the surface reconstruction, and are separated by isolated @pi@-chains remaining from the clean surface. At higher temperatures and coverages (>500°C, >0.25 ML), these @pi@-chains are removed and the Ag rows become wider with a strong 3x periodicity. We now have preliminary studies of more reactive metals such as Au and Ca on Si(5 5 12). At moderate annealing temperatures, both metals form overlayer rows that still preferentially nucleate along the tetramers. However, these rows are less well-ordered and are shorter at a given coverage, indicating the enhanced reactivity of these adsorbates. As expected, both metals change their growth behavior at higher annealing temperatures. The Au grows in 3x rows that become substantially more ordered and longer at a given coverage, whereas Ca rearranges the surface into a more complicated undulating row-like structure. In both cases, no remaining structures from the underlying reconstruction are visible. This work clearly demonstrates the utility of the Si(5 5 12) surface as a template for the 1D growth of a variety of metals. @FootnoteText@ @footnote 1@ H.H. Song, K.M. Jones, and A.A. Baski, J. Vac. Sci. Technol. A Jul/Aug 1999.

10:00am SS2-FrM6 Chemisorption and Dissociation of O@sub 2@ on Pd(111) Studied by STM, M.K. Rose, Lawrence Berkeley National Laboratory; A. Borg, Norwegian University of Science and Technology, Norway; F. Besenbacher, University of Aarhus, Denmark; D.F. Ogletree, M. Salmeron, Lawrence Berkeley National Laboratory

A variable temperature STM study of chemisorption and dissociation of O@sub 2@ on Pd(111) is presented. Adsorption of O@sub 2@ on Pd(111) at 30K in the submonolayer range causes formation of a superoxo like and peroxo like molecular oxygen species. These two species image differently in STM, the superoxide appears to have weaker corrugation as compared to the peroxide. The superoxide is the more mobile species of the two at 30K. The peroxide display (2x2) structure in ordered areas, which grow in size upon annealing to 100K. Induced by the STM tip, individual O@sub 2@ molecules dissociate into pairs with a preferred separation of 2 lattice spacings, which is the equilibrium spacing in the (2x2)-O structure on Pd(111). Thermal O@sub 2@ dissociation is observed at about 150K. Our data show that the oxygen molecules evaporate from the peroxide island periphery onto the terrace before dissociation. Similar atomic oxygen pair

Friday Morning, October 29, 1999

spacings are observed in this case, but the distribution of oxygen on the surface is influenced by subsurface species present in the Pd(111).

10:20am SS2-FrM7 The Oxidation and Reduction of Pd(111), G. Zheng, E.I. Altman, Yale University

Palladium is a promising catalyst for oxidation reactions. Therefore, the oxidation of Pd(111) was characterized using STM, TPD, and LEED. Exposure of Pd(111) to O@sub 2@ resulted in a (2x2) structure, that saturated after exposure to 30 L. To increase the oxygen coverage, NO@sub 2@ was used. Initial exposure of Pd(111) to NO@sub 2@ also produced the (2x2) structure. Further exposure, however, resulted in additional diffraction spots, which persisted until the oxygen coverage reached approximately 1.0 ML. At oxygen coverages between 1.0 - 2.0 ML, a complicated LEED pattern was observed. This pattern could be explained as the superposition of two surface structures, one with a square surface lattice rotated 15° with respect to the Pd(111) substrate, the other with a rectangular surface lattice rotated 30° with respect to the Pd(111) substrate. In STM images, ad-islands and peninsulas were observed in this oxygen coverage regime. The rectangular structure was found on the original Pd(111) terraces, while the square structure was observed on the islands and peninsulas. A Moiré pattern due to lattice mismatch with underlying layers was also observed on the islands and peninsulas. The lattice constant for the square structure was 0.679 nm; and the two lattice constants for the rectangular structure were 0.394 nm and 0.638 nm, respectively, consistent with LEED observations. After further increasing the oxygen coverage, the complicated LEED patterns became faint. At the same time, a low temperature shoulder associated with bulk PdO developed in TPD traces. These results indicate that oxygen can exist in five different states on the Pd(111) surface. The reactivity of these states towards reduction is being characterized by monitoring the rate of disappearance of the different surface oxygen phases by recording STM movies during reduction by CO, H@sub 2@, and CH@sub 3@OH.

10:40am SS2-FrM8 Experimental and Theoretical STM Imaging of Molecules on Metal Surfaces@footnote 1@, D.N. Futaba, University of California, Davis; C.A. Pearson, University of Michigan; A. Loui, S. Chiang, D.M. Jaramillo, D.P. Land, University of California, Davis

We have imaged the surface structure of benzene coadsorbed with carbon monoxide (CO) on the Pd(111) surface in ultrahigh vacuum using a low temperature (90K) scanning tunneling microscope (STM). In conjunction with low-energy electron diffraction, three distinct overlayer structures have been observed to form as a function of various dosing conditions: two hexagonal structures when predosed with CO, (2@sr@3x2@sr@3)R30° and (3x3), and one rectangular structure. We are currently studying the mechanism by which one hexagonal layer transforms into the other as the benzene coverage increases. Our models of the structure give an overall molecular coverage of 1/3 for both hexagonal structures, suggesting molecular place exchange. We have performed laser induced thermal desorption and thermal desorption spectroscopy measurements to calibrate relative amounts of CO and benzene for the different structures. We also use a simple computational method, based on extended Hückel theory, to calculate STM images expected for the dehydrogenation of cyclohexene to benzene on Pd(111). Based on the proposed bonding geometry by Hunka et al.,@footnote 2@ we expect to see significant differences between the chemisorbed cyclohexene molecules and the resultant benzene molecules. Our calculated images of paraxylene and metaxylene on Rh(111) showed good agreement with existing experimental STM data by Cernota et al.@footnote 3@ Therefore, we expect good agreement between our calculations of orthoxylene on Pd(111) and our experiments in progress. @FootnoteText@ @footnote 1@ Funded by NSF (CHE-95-20366) and CLC Program of Univ. of California. @footnote 2@ D.E. Hunka, T. Picciotto, D.M. Jaramillo, D.P. Land, Surf. Sci., 421, L166 (1999). @footnote 3@ P.D. Cernota, H.A. Yoon, M. Salmeron, G.A. Somorjai, Surf. Sci., 415, 3511 (1998).

11:00am SS2-FrM9 In-Situ Soft X-ray Studies of Acetylene Oxidation on the Pt(111) Surface, *D.J. Burnett*, *A.M. Gabelnick*, University of Michigan; *D.A. Fischer*, National Institute of Standards and Technology; *J.L. Gland*, University of Michigan

In-situ studies of acetylene oxidation have been performed using Fluorescence Yield Soft X-ray methods for temperatures up to 600 K and pressures up to 0.01 torr. Absolute carbon coverages have been determined in steady-state and dynamic conditions on the Pt(111) surface over an extended pressure and temperature range using in-situ soft X-ray methods. Transient surface concentration measurements were used during these in-situ studies to provide direct measurement of surface reaction rates. Temperature-programmed oxidation of preadsorbed acetylene monolayers (TP-FYNES) on the Pt(111) surface was conducted in oxygen pressures up to 0.01 torr. Acetylene remains on the surface until skeletal oxidation occurs around 350 K, depending on the oxygen pressure. The onset temperature for skeletal oxidation decreased slightly with increasing oxygen pressures. Transient experiments with both acetylene and oxygen in the gas phase were performed over a wide range of pressures and temperatures. Further, detailed mechanistic studies were performed yielding a substantial amount of high quality kinetic rate data. These kinetic studies, coupled with the TP-FYNES results suggest a mechanism limited by C-H bond activation. In addition to the transient studies above, detailed spectroscopy was accomplished via in-situ, soft X-ray fluorescence yield methods to identify the dominant oxidation intermediates. Both acetylene and ethylene oxidation appear to involve the same surface intermediates since both processes are limited by the same rate-determining step. In both instances, oxidation intermediates have been identified and characterized using in-situ fluorescence yield methods.

11:20am SS2-FrM10 The Adsorption and Decomposition of Trimethylamine on Pt(111), D.-H. Kang, M. Trenary, University of Illinois, Chicago

Reflection absorption infrared spectroscopy (RAIRS) and temperature programmed reaction spectroscopy (TPRS) have been used to study the adsorption and decomposition of trimethylamine on Pt(111). In a series of previous RAIRS studies, it was shown that several different molecules containing CN bonds all rearranged on Pt(111) to form the same stable intermediate, aminomethylidyne, CNH@sub 2@. Aminomethylidyne was formed following the initial adsorption of azomethane, methylamine, hydrogen cyanide, and from the hydrogenation of surface CN that was produced from the dissociative adsorption of cyanogen. Furthermore, the hydrogenation of undissociated cyanogen was found to form the H@sub 2@NCCNH@sub 2@ species, which contains the same aminocarbyne functionality as in aminomethylidyne. This suggests that aminocarbynes of the general formula CNRR', where R and R' can be H or an alkyl group, may be common intermediates in surface chemical reactions involving CNcontaining molecules. Dimethylaminocarbyne (CN(CH@sub 3@)@sub 2@) is a well-known ligand in the organometallic literature. It could be formed on the Pt(111) surface through the removal of the three H atoms from one of the methyl groups of trimethylamine. The RAIRS and TPRS data obtained so far support the formation of dimethylaminocarbyne as a stable intermediate species formed from the partial dehydrogenation of trimethylamine on Pt(111). A key spectroscopic feature of CN(CH@sub 3@)@sub 2@ is an intense RAIRS band at 1471 cm@super -1@, which is characteristic of the CN stretch in aminocarbynes.

11:40am SS2-FrM11 Investigation of the Adsorption and Reactions of Thiophene on Sulfided Cu, Mo and Rh Catalysts, *M.E. Bussell*, *P. Mills*, *D.C. Phillips*, *B.P. Woodruff*, *R. Main*, Western Washington University

Infrared (IR) spectroscopy and temperature programmed desorption (TPD) have been used to investigate the adsorption and reactions of thiophene on alumina-supported sulfided Cu, Mo and Rh catalysts over wide ranges of temperature (130-700 K) and pressure (10 @super-9@ - 10 @super3@ Torr). Following adsorption at 130 K, thiophene adsorbs on sulfided Mo and Rh catalysts in an @eta@@super 1@(S) geometry; it has not been possible to determine the adsorption geometry of thiophene on Cu sites of the sulfided Cu catalyst due to low coverage. The coverage of thiophene on sites in the supported metal sulfide particles is observed to increase in the order Cu < Mo < Rh, in agreement with CO chemisorption measurements. Little or no reactivity is observed when the different catalysts are heated in thiophene vapor alone at temperatures up to 700 K. In thiophene/H@sub 2@ mixtures, hydrogenated species are observed to form on sulfided Rh catalysts by 350 K, and by 550 K on sulfided Mo catalysts. Following evacuation to UHV pressures, TPD shows the major products to be butadiene, butenes and butane. The results of these experiments are in good agreement with flow reactor studies of thiophene hydrodesulfurization over these same catalysts.

Author Index

-A-Altman, E.I.: SS2-FrM7, 2 — B — Baski, A.A.: SS2-FrM4, 1; SS2-FrM5, 1 Becker, C.: SS2-FrM2, 1 Besenbacher, F.: SS2-FrM1, 1; SS2-FrM6, 1 Boishin, G.: SS2-FrM2, 1 Borg, A.: SS2-FrM6, 1 Breitbach, J.: SS2-FrM2, 1 Burnett, D.J.: SS2-FrM9, 2 Bussell, M.E.: SS2-FrM11, 2 - C -Carlisle, J.A.: SS2-FrM4, 1 Chiang, S.: SS2-FrM8, 2 - F --Fischer, D.A.: SS2-FrM9, 2 Frey, A.: SS2-FrM2, 1 Futaba, D.N.: SS2-FrM8, 2 — G — Gabelnick, A.M.: SS2-FrM9, 2

Bold page numbers indicate presenter Gland, J.L.: SS2-FrM9, 2 Grüne, M.: SS2-FrM2, 1 — J — Jaramillo, D.M.: SS2-FrM8, 2 Jones, K.M.: SS2-FrM4, 1; SS2-FrM5, 1 -K-Kang, D.-H.: SS2-FrM10, 2 Kawai, M.: SS2-FrM3, 1 Komeda, T.: SS2-FrM3, 1 -L-Laegsgaard, E.: SS2-FrM1, 1 Land, D.P.: SS2-FrM8, 2 Linden, R.-J.: SS2-FrM2, 1 Loui, A.: SS2-FrM8, 2 -M-Main, R.: SS2-FrM11, 2 Mills, P.: SS2-FrM11, 2 -0-Ogletree, D.F.: SS2-FrM6, 1 Österlund, L.: SS2-FrM1, 1

— P — Pearson, C.A.: SS2-FrM8, 2 Pedersen, M.O.: SS2-FrM1, 1 Pelster, T.: SS2-FrM2, 1 Phillips, D.C.: SS2-FrM11, 2 — R — Rose, M.K.: SS2-FrM6, 1 — S — Salmeron, M.: SS2-FrM6, 1 Samanta, I.: SS2-FrM5, 1 Saoud, K.M.: SS2-FrM5, 1 Stensgaard, I.: SS2-FrM1, 1 -T-Trenary, M.: SS2-FrM10, 2 Turner, M.S.: SS2-FrM4, 1 - w -Wandelt, K.: SS2-FrM2, 1 Woodruff, B.P.: SS2-FrM11, 2 — Z — Zheng, G.: SS2-FrM7, 2