# Thursday Afternoon, October 28, 1999

## Surface Science Division
## Room 607 - Session SS2-ThA

### Adsorption at Surfaces

**Moderator:** T.E. Madey, Rutgers, The State University of New Jersey

2:00pm **SS2-ThA1 Dissociative Adsorption of H@sub 2@ on Si(001): Reaction Channels and Structure Sensitivity*, M.B. Raschke,*** *M. Dürr, U. Höfer,* Max-Planck-Institut für Quantenoptik, Germany

Making use of the high adsorbate sensitivity of second-harmonic generation (SHG) the dissociative adsorption of H@sub 2@ on Si(001) could be detected in previous experiments.@footnote 1@ The extremely small sticking coefficients were found to exhibit a pronounced dependence on surface temperature, which indicates the importance of dynamic lattice distortions. In the present investigations, by preadsorbing atomic hydrogen, configurations are realized where, e.g., one of the two dangling-bonds per dimer becomes hydrogen terminated. In contrast to the dissociation on the initially clean Si(001) surface this preparation scheme facilitates two additional inter-dimer reaction pathways occuring with either a neighboring identical half-hydrogen-terminated dimer in the cis-configuration or a clean Si-dimer. Studying the dependence of the reactivities with kinetic energy of the H@sub 2@ molecules using molecular beam techniques, in the first case the dissociation was found to be non-activated, whereas a barrier of 0.2 eV was determined for the second. Together with the barrier of 0.8 eV found for dissociation on the clean surface this corresponds to differences in reactivity up to seven orders of magnitude for a surface temperature of 400 K. Comparing the activation with surface temperature with the dependence on H@sub 2@ beam energy a complementarity between exciting surface and molecular degrees of freedom was found. These results are particularly remarkable because of the geometric similarities of the different configurations of the Si-atoms involved. This together with the results of the recent study of the dissociation at D@sub B@-steps on Si(001)@footnote 2@ provide a systematic understanding of the parameter governing the H@sub 2@/Si(001) interaction. @FootnoteText@ @footnote 1@P. Bratu, K.-L. Kompa, and U. Höfer, Chem. Phys. Lett. 251 (1996) 1. @footnote 2@P. Kratzer, E. Pehlke, M. Scheffler, M. B. Raschke, and U. Höfer, Phys. Rev. Lett. 81 (1998) 5596.

2:20pm **SS2-ThA2 Adsorption of Molecular Hydrogen on the Si(100)-2x1 Surface***, J.J. Boland,* ***E.J. Buehler,*** University of North Carolina

The mechanism of molecular hydrogen adsorption on the Si(100)-2x1 surface was studied using variable temperature scanning tunneling microscopy. The measured desorption barrier of ~2.5eV and the bond energies of Si--H (3.5eV) and H--H (4.5eV) predict a tiny barrier to adsorption. This agrees with data showing that desorbing molecules have no excess translational energy as they leave the surface. The magnitude of the room temperature sticking coefficient (<10@super -10@), however, shows that there is actually a large barrier to adsorption, suggesting a violation of detailed balance. We show that the origin of this discrepancy lies in the motion of the atoms of the Si dimers. The dimers of the clean Si(100)-2x1 surface are constantly tilting at room temperature. We have prepared a surface that contains clean Si--Si dimers that are frozen in a relatively untilted configuration. The room temperature sticking coefficient of molecular hydrogen at these sites is six orders of magnitude greater than that on a clean Si(100)-2x1 surface. The implications for hydrogen adsorption and detailed balance are discussed.

2:40pm **SS2-ThA3 Molecular Beam Study of the Adsorption and Desorption of Hydrogen Sulfide on Au(100)***,* ***St.J. Dixon-Warren,*** Washington State University

The adsorption and desorption of hydrogen sulfide on clean reconstructed Au(100)-(5x20) and sulfided gold, denoted Au(100)-(1x1)-SH, has been studied with a combination of temperature programmed desorption (TPD), low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and molecular beam methods. Precursor adsorption kinetics were observed for the adsorption of H@sub 2@S on the Au(100)-(5x20) between 80 and 100 K. The H@sub 2@S adsorbs reversibly into a weakly bound physisorbed state, which desorbs at ~107 K. At 110 K reversible Langmuir adsorption was observed for H@sub 2@S on the Au(100)-(5x20). The Au(100)-(1x1)-SH was prepared by electron irradiation of H@sub 2@S adsorbed on the Au(100)-(5x20) substrate. The adsorption kinetics for H@sub 2@S on the Au(100)-(1x1)-SH exhibited Langmuir adsorption kinetics at 80 K, in sharp contrast with the precursor adsorption kinetics observed on the clean Au(100)-(5x20) surface. The TPD of H@sub 2@S from Au(100)-(1x1)-SH and H@sub 2@S adsorbed on Au(100)-(1x1)-SH showed additional features at higher temperatures which are probably associated with the disproportionation of chemisorbed HS(ad). Finally, we have identified a further sulfided gold surface, denoted Au(100)-(2x2)-S which is prepared by annealing the Au(100)-(1x1)-SH to remove adsorbed hydrogen.

3:00pm **SS2-ThA4 Decomposition of Nickelocene on Single Crystal Surfaces***,* ***D.L. Pugmire,*** *C.M. Woodbridge, M.A. Langell,* University of Nebraska, Lincoln

The decomposition mechanisms of nickelocene on several surfaces of varying reactivity have been elucidated by use of high resolution electron energy loss spectroscopy (HREELS), x-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD). Exposure of nickelocene to the reactive Ni(100) surface at 135 K results in its decomposition into fragments containing C-C triple bonds. When this substrate is warmed to 273 K, carbide contamination is observed. Exposure of nickelocene to NiO(100) at 135 K also yields decomposition, but with different products than those observed on Ni(100). There is no evidence for the formation of species containing C-C triple bonds on NiO(100). Instead, species with C-C double bonds result upon adsorption at 135 K and as the NiO(100) substrate is warmed to 273 K, all carbon-containing species desorb. In contrast to the reactive nature of Ni(100) and NiO(100), Ag(100) molecularly adsorbs nickelocene at 135 K with its molecular axis perpendicular to the substrate surface. When this substrate is heated, nickelocene desorbs molecularly at approximately 210 K, leaving a surface free of residual carbon. Mechanisms of nickelocene decomposition on the reactive surfaces are proposed based on the HREELS, XPS and TPD results.

3:20pm **SS2-ThA5 New Opportunities in Surface Studies using High Brilliance Synchrotron Radiation***,* ***N. Mårtensson,*** Uppsala University, Sweden **INVITED**

Synchrotron radiation is a most powerful source for electromagnetic radiation with wide applications in a variety of research areas. With synchrotron radiation one can span in a continuous manner a large photon energy range. The radiation is intense and stronly polarized, linearly or circularly. The third generation synchrotron radiation sources which are now coming into operation are optimized for the utilization of insertion devices, i.e. undulators and wigglers, in the straight sections of the storage rings. The utilization of resonant spectroscopies will be discussed. The element specificity at core level thresholds can be used to focus on specific elements or even chemically different species of the same element in complex environments, e.g. at buried interfaces or in adsorbed molecules. The utilization of such techniques will be discussed in different regimes of the electronic structure. The characterization of the electronic states in CuNi systems will be discussed. Resonant photoemission, autoionization or resonant x-ray scattering also allow one to study dynamic properties of the excited states, e.g. probing charge transfer processes between weakly adsorbed molecules and surfaces. It is also shown how X-ray photoelectron spectroscopy at a resolution of 50 meV of adsorbed molecules make it possible to resolve vibrational fine-structure, thereby enhancing the information contents in the spectra considerably. The new way of studying chemical bonding at surfaces using x-ray emission spectroscopy will also discussed

4:00pm **SS2-ThA7 The Surface Chemistry of Iron Pentacarbonyl on Palladium (111)***,* ***M.N. Rocklein,*** *D.P. Land,* University of California, Davis

The interaction of organometallic compounds with surfaces can lead to catalytically-active surface moieties or to metal deposition. This is important to industries concerned with supported metal catalysts, magnetic storage, and microelectronics. Depending of the exposure, iron pentacarbonyl desorbs from the close-packed palladium surface in ultra-high vacuum at 153 and 170 K. This corresponds to multilayer and saturation coverage desorption. However, approximately 30% of the first saturation layer decomposes on the surface during the temperature programmed desorption (TPD) experiment. This implies that some reaction was initiated below 170 K. Laser-induced thermal desorption Fourier transform mass spectrometry (LITD-FTMS) is capable of showing time-resolved changes in molecular surface composition. Interestingly, LITD shows that submonolayer coverages react at 150 K with further decomposition near 200 K. This study represents the first LITD-FTMS temperature survey of an organometallic/substrate system. TPD further shows evolution of carbon monoxide by a reaction-limited process near 260 K. The simplest explanation of this behavior involves a stepwise decarbonylation and the existence of surface intermediates up to at least

260 K. The proposed mechanism is further supported using reflection-absorption infrared spectroscopy (RAIRS).

4:20pm **SS2-ThA8 Adsorption Driven Displacement of N@sub 2@ from Pt(111)***, **G.A. Kimmel**, K.P. Stevenson, B.D. Kay,* Pacific Northwest National Laboratory

Pt(111) with beam reflection measurements and temperature programmed desorption (TPD). The interaction of weakly adsorbed species on surfaces is of fundamental interest since these systems provide a benchmark for more complicated systems. Our experiments involve the preparation of monolayer or sub-monolayer coverages of N@sub 2@ on Pt(111) followed by the adsorption of another species (e.g. CH@sub 4@, Kr and H@sub 2@O). Both species are monitored throughout the experiments, allowing for quantitative measurements of the coverages and sticking coefficients versus time. In all cases, N@sub 2@ is displaced from direct contact with the Pt(111) by the adsorbates which have higher binding energies. The fate of the displaced N@sub 2@ molecules is governed by the surface temperature and its interaction energy with the co-adsorbate. At higher temperatures, the N@sub 2@ desorbs as soon as it is displaced from the first layer. As the temperature is lowered, the N@sub 2@ desorbs when it is displaced from successively higher layers. This behavior results from the successively lower binding energy of N@sub 2@ to increasingly thick co-adsorbate layers. At "high" temperatures (~38 K), the N@sub 2@ desorption rate is approximately constant during the adsorption of the first monolayer of CH@sub 4@, falling abruptly to zero with its completion. This suggests that the mobility of the adsorbed CH@sub 4@ is high allowing it to rapidly find and displace N@sub 2@. The CH@sub 4@ sticking coefficient increases linearly with time as the surface layer is converted from N@sub 2@ to CH@sub 4@. TPD subsequent to the CH@sub 4@ exposure shows that the entire N@sub 2@ monolayer was displaced and desorbed during the CH@sub 4@ adsorption. At lower temperatures, lower diffusion rates lead to departures from zero-order desorption kinetics. The displacement of N@sub 2@ by H@sub 2@O is qualitatively similar, but quantitative comparisons are complicated by details of the N@sub 2@/H@sub 2@O interaction.

4:40pm **SS2-ThA9 The Vibrational Spectra of Adsorbed Alkoxies on Cu(100) and W(110): Experimental Data and ab initio Calculations***, **P. Uvdal**, R. Ásmundsson,* Lund University, Sweden*; A.D. McKerell, Jr.,* University of Maryland

Using surface FTIR spectroscopy we have measured the vibrational spectra of different alkoxies adsorbed on single crystal surfaces of Cu(100) and W(110). It is demonstrated how modification of the alkyl chain and the associated changes in the experimental vibrational spectra can be calculated with a high degree of accuracy using ab initio electronic structure calculations of an alkoxy-metal complex as the model. Analysis of the symmetry properties of the calculated normal modes allows for a determination of the geometry of the adsorbed species.

5:00pm **SS2-ThA10 Probing the Metal Sites of a V-oxide/Pd(111) "Inverse Catalyst": Adsorption of CO***, F.P. Leisenberger, G. Koller, S. Surnev, M.G. Ramsey, **F.P. Netzer**,* Karl-Franzens-Universität Graz, Austria

A vanadium oxide / Pd(111) "inverse catalyst" system, consisting of V-oxide island structures and bare Pd(111) patches in between, has been prepared by reactive evaporation of V onto Pd(111) at submonolayer to monolayer coverages and has been characterised by STM and high-resolution core level photoelectron spectroscopy. Here we report a study of the adsorption of CO on these "inverse" V@sub 2@O@sub 3@/ Pd(111) catalyst. Since CO does not adsorb on V-oxide at room temperature, this allows to probe the adsorption properties of free Pd(111) sites in the presence of the V-oxide phase boundary. The adsorption of CO has been followed by monitoring the C 1s core level signals as a function of the V-oxide coverage and the CO exposure at room temperature, using high-resolution XPS with synchrotron radiation. The amount of adsorbed CO, as determined quantitatively from the C 1s peak areas, decreases with the V-oxide coverage as a result of the blocking of Pd adsorption sites. The concomitant decrease of the CO saturation exposure, i.e. the CO exposure necessary to reach CO saturation of the various surfaces, indicates, however, that a precursor state exists on the V-oxide surface, from which CO can diffuse over the metal-oxide boundary on to Pd sites. This spill-over effect is also corroborated by the dependence of the initial sticking probability of CO on the V-oxide surface coverage. The difference of the C 1s binding energies of CO adsorbed on pristine and oxide covered Pd(111) suggests that Pd adsorption sites are electronically influenced by the presence of a V-oxide phase boundary. Supported by the Austrian Science Foundation.

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