

## Surface Science Division Room 309 - Session SS2-MoM

### Molecular Adsorbates on Metals

**Moderator:** B.E. Koel, University of Southern California

#### 8:20am SS2-MoM1 An X-ray Absorption Study of Saturated Hydrocarbons Physisorbed on Metal Surfaces, K. Weiss, C. Wöll, Ruhr-Universität Bochum, Germany

Monolayers of linear and cyclic saturated hydrocarbons (n-hexane, cyclohexane, n-octane, n-hexatriacontane) physisorbed on several metal surfaces (Cu(111), Au(111), Ru(0001) and Pt(111)) have been investigated by K-edge X-ray absorption spectroscopy (XAS). Whereas the corresponding multilayer data qualitatively resembles the core excitation spectrum observed for the free molecules, a strong quenching of the Rydberg R-resonance at 287.7 eV is observed for molecules in direct contact with the substrate. The interaction with the metal surface is found to result in the formation of a new, sharp resonance which is assigned to a novel surface-induced Rydberg state. In addition the broad feature observed in the saturated hydrocarbon monolayer XAS-spectra at 285.1 eV is identified as a transition into metal-molecule hybrid orbitals, indicating a significant chemical interaction between saturated hydrocarbon and the metal surface. This C-H-activation is shown to correlate with the well-known soft C-H-stretch modes seen in IR-spectroscopy for many saturated hydrocarbon/metal surface combinations. @footnote 1@ @FootnoteText@ @footnote 1@ G. Witte, K. Weiss, P. Jakob, J. Braun, K.L. Kostov, and Ch. Wöll, Phys. Rev. Lett. 80, 121, (1998)

#### 8:40am SS2-MoM2 An Atom Specific Probe of the Surface Chemical Bond Using X-ray Emission Spectroscopy, J. Hasselstrom, A. Fohlisch, O. Karis, A. Nilsson, Uppsala University, Sweden; M. Nyberg, L.G.M. Pettersson, Stockholm University, Sweden; J. Stohr, IBM Almaden Research Division

When a molecule is adsorbed on a metal surface by chemical bonding new electronic states are formed. The direct observation and identification of these states is still an experimental challenge. In this contribution we will show how X-ray Emission Spectroscopy (XES), in spite of its inherent bulk sensitivity, can be used to investigate adsorbed molecules. We have applied XES to CO and NH@sub 3@ adsorbed on single crystal Cu surfaces. These molecules have lone pair orbitals in its @sigma@-systems and adsorb with these towards the substrate. Due to the localization of the core excited intermediate state, XE spectroscopy allows an atom specific probe of the valence electrons, i.e. the molecular contributions can be separated from those of the substrate. In combination with ab initio calculation, new details of the chemical bond formed at the surface can be revealed. It is, for CO adsorbed on Cu(100), found that the surface chemical bond formation can be related to the @pi@-system interacting with the metal d band. The overall interaction of the @sigma@-system, i.e. the 5@sigma@ lone pair, is found to be repulsive. In contrast, the @sigma@-system, involving the 3a@sub 1@ lone pair, of ammonia is found to comprise the main covalent contribution to the adsorption energy of the NH@sub 3@/Cu(110) system; the degenerated 1e orbitals, often referred to as the N-H @pi@-system preserve much of its molecular character. Our results indicate that the different bonding mechanisms can be related to the energy position of the lone pair valence orbitals as compared to the metal bands, and furthermore to the corresponding symmetries of the lowest unoccupied molecular orbitals.

#### 9:00am SS2-MoM3 The Role of Steps and Kinks in Catalytic Activity, L. Ford, P. Blowers, R. Masel, University of Illinois, Urbana

In the literature, there is the idea that steps and kinks are active sites for chemical reactions, but the experimental data is far from convincing. In this paper we see if there is a correlation between step and kink density and reactivity for a number of simple decomposition and hydrogenation reactions on platinum. We have examined the decomposition of ethylene, methanol, methylamine, ethanol, propanol, NO, the hydrogenation of ethylene, and the hydrogenolysis of ethylene, methanol, ethanol on Pt(111), Pt(110)(1x1), Pt(110)(1x2), Pt(100)-hex, Pt(100)(1x1), Pt(210), Pt(511), Pt(331). We find that in general stepped surfaces have different reactivity than closed packed planes, but some stepped surfaces are more active than Pt(111) while other stepped surfaces are less active than Pt(111). There is no correlation between step and kink density and catalytic activity. Calculations are done to understand the variations. We find that in general stepped surfaces relax to more stable geometries. The relaxation process lowers the electronic coordination number of the atoms in the

surface of the catalyst so after relaxation, there is not a large difference in the coordination of atoms in stepped surfaces and Pt(111).

#### 9:20am SS2-MoM4 Face Specificity and the Role of Metal Adatoms in Molecular Reorientation at Surfaces, C.C. Perry, S. Haq, University of Liverpool, United Kingdom; B.G. Frederick, University of Maine, U.K.; N.V. Richardson, University of St. Andrews, Scotland, U.K.

Using Reflection Absorption Infrared Spectroscopy (RAIRS), the coverage dependent reorientation of the benzoate species on the (110) and (111) faces of copper is compared and contrasted. Whereas on Cu(110), benzoate reorients from flat-lying to upright orientation with increasing coverage, on Cu(111), at all coverages, benzoate is aligned normal to the surface. The formation of periodic, flat-lying copper-benzoate structures has been attributed to the availability of metal adatoms, which differs dramatically between the (111) and (110) faces. We discuss the face specificity of molecular orientation by comparing calculated formation energies of adatom-vacancies from ledges and kink sites on (100), (110), and (111) faces. Further support for this model is given by the evaporation of sodium, either by pre- or post-dosing, onto low coverage benzoate/Cu(111), which induces benzoate to convert from perpendicular to parallel orientation. Likewise, coevaporation of Cu while dosing benzoic acid onto the Cu(111) surface also results in a majority of flat-lying benzoate species. Finally, for adsorption on the p(2x1)O/Cu(110) reconstruction, benzoate occurs only as the upright species, which is consistent with reducing the copper mobility and availability on the (110) face. We therefore suggest the possible role of metal adatoms as a new mechanism in controlling adsorbate orientation, and therefore face specificity, in surface reactions.

#### 9:40am SS2-MoM5 Theoretical Studies of Surface Reactions on Metals: I. Ethyl to Ethylene Conversion on Platinum; II. Photodissociation of Methane on Platinum, J.L. Whitten, North Carolina State University INVITED

An embedding method designed to provide a molecular level understanding of adsorbate energetics and surface reaction mechanisms is presented. Electronic structures, including relativistic effects, are described by an ab initio formalism that permits an accurate determination of energies and adsorbate structure. @footnote 1@ Applications to catalytic and photochemical reactions on transition metal surfaces are reported. I. In the catalytic conversion of ethyl adsorbed on platinum surfaces to ethylene, the minimum energy pathway for the transfer of hydrogen to the metal surface is calculated. A detailed description of the transition state is presented. II. In the photodissociation of methane physisorbed on platinum, results are reported for a methane molecule interacting with an embedded cluster model of Pt(111). Configuration interaction theory is used to sort out states resulting from electron attachment to methane from lower energy states that correspond to metal excitations. Energies of the ground and excited states of the Pt(111)CH@sub 4@ complex are calculated as a function of geometrical distortions and the distance of methane from the surface. Key steps in the photodissociation process are described. @FootnoteText@ @footnote 1@ J. L. Whitten and H. Yang, Surf. Sci. Repts., 218 (1996) 55.

#### 10:20am SS2-MoM7 Chemistry of SO@sub 2@ on Ru(001): Formation of SO@sub 3@ and SO@sub 4@, T. Jirsak, J.A. Rodriguez, S. Chaturvedi, J. Hrbek, Brookhaven National Laboratory

The interaction of SO@sub 2@ with Ru(001) at 300 and 100 K was studied using synchrotron-based high-resolution photoemission, INDO/S MO calculations, and a thermochemical analysis based on the bond-order conservation Morse-potential (BOC-MP) formalism. At 300 K and small exposures of SO@sub 2@, sulfur dioxide completely decomposes (SO@sub 2@ -> S@sub a@ + 2O@sub a@). Several coordination modes for adsorbed SO@sub 2@ were examined using INDO/S and the BOC-MP formalism. It was found that adsorption geometries in which the molecule is di-coordinated via O,O or S,O are the most probable precursors for dissociation. For large exposures of SO@sub 2@ at 300 K, SO@sub 3@ and SO@sub 4@ species appear on the Ru(001) surface confirming thus the theoretical predictions derived from the BOC-MP method which indicate that formation of SO@sub 3@ and SO@sub 4@ can take place only when the number of empty adsorption sites is limited. This prediction was also proved during the adsorption of SO@sub 2@ on a O/Ru(001) surface with @theta@@sub O@ = 0.25 ML, producing similar types of species as at saturation of SO@sub 2@ on Ru (S@sub n@+O, SO@sub 4@ and S). When a Ru surface partially covered by sulfur (@theta@@sub S@ = 0.2 ML) was exposed to molecular oxygen at 300 K, formation of SO@sub 3@ and SO@sub 4@ species was not observed. Experiments performed at a

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surface temperature of 100 K showed a very rich surface chemistry. Five different surface species were observed after SO@sub 2@ dosing: atomic S, S@sub n@+O, SO@sub 2@, SO@sub 3@ and SO@sub 4@. The S 2p spectrum of a Ru(001)surface saturated at 100 K is dominated by a very intensive peak of a multilayer of SO@sub 2@, which entirely disappeared upon annealing to 160 K. Further annealing to 260 K leaves mainly atomic S and SO@sub 4@ on the surface and the latter is completely decomposed by 350 K.

10:40am **SS2-MoM8 Low Temperature STM Imaging of Furan Molecules on Pd(111)**, C.A. Pearson, S. Chiang, A. Loui, D.N. Futaba, University of California, Davis

The cyclotrimerization reaction of acetylene to benzene is known to proceed readily in ultra high vacuum on the Pd(111) surface. Thermal desorption spectroscopy has measured furan (C@sub 4@H@sub 4@O)@footnote 1@ and thiophene (C@sub 4@H@sub 4@S)@footnote 2@ desorbing from the Pd(111) surface following the coadsorption of acetylene with oxygen and sulfur respectively. Using low temperature scanning tunneling microscopy (STM), we have imaged furan molecules adsorbed on the Pd(111) surface. Dosing and imaging of the sample was performed at 200 K. While no changes were evident with low energy electron diffraction (LEED), we observed localized ordering with the STM for monolayer coverage. Furan molecules form ordered rows in three different domains oriented 120° apart. The ordered regions are roughly 50 Å to 100 Å in size. Higher resolution images show individual molecules within the rows. Measurements of the intermolecular spacing in the images provide information about the molecular tilt on the surface. Images of individual molecules will also be compared with predicted theoretical STM images from extended Hückel molecular orbital theory. @FootnoteText@ @footnote 1@R.M. Ormerod, R.M. Lambert, Cat. Lett. 6, 121 (1990). @footnote 2@A.J. Gellman, Langmuir 7, 827 (1991).

11:00am **SS2-MoM9 Conformation and Orientation of Methyl Pyruvate on Ni(111)**, P.H. McBreen, M. Castonguay, J.R. Roy, Université Laval, Canada

Both the orientation and molecular conformation of adsorbed layers are determining factors in a variety of properties including chemical reactivity. The question of surface orientation and conformation are particularly important for methyl pyruvate since it possesses both a keto and an ester carbonyl and it can undergo cis-trans isomerization. Its hydrogenation to methyl lactate is one of the very few well documented cases of enantioselective heterogeneous catalysis. To the best of our knowledge this is first report of an investigation of the intrinsic adsorption of this prochiral molecule on a metal surface using surface science techniques. RAIRS data shows that methyl pyruvate is chemisorbed on Ni(111) at all coverages with its molecular plane perpendicular to the surface. Two different adsorption conformations are detected. The full monolayer is found to be exclusively in the bidentate cis-conformation. The results, and DFT calculations, indicate that the keto carbonyl metal surface interaction is stronger than the ester carbonyl metal surface interaction. Comment will be made on the fact that the observed molecular orientation and conformation are at odds with the model usually assumed in rationalizations of the enantioselective hydrogenation of methyl pyruvate.

11:20am **SS2-MoM10 Negative and Positive Adsorbate-Induced Reflectance Changes: Formic Acid on Cu(100)**, C.-L. Hsu, E.F. McCullen, R.G. Tobin, Tufts University

Adsorption on metal surfaces typically reduces the broadband reflectance of the surface, an effect that is usually attributed to diffuse scattering of the conduction electrons by the adsorbate. The resistance of the film typically increases. On the other hand, a dielectric film typically increases the broadband reflectance of a metal. Both effects are observed for the adsorption of formic acid (HCOOH) on epitaxial Cu(100) films at 125 K. Both the dc resistance and the infrared reflectance at 1500 cm@super -1@, away from any vibrational resonances, were measured during dosing. Upon initial exposure to formic acid, the film's resistance increases by 1% and its reflectance decreases by 0.5%. With continued exposure, leading to the growth of a multilayer formic acid film, the reflectance begins to increase and ultimately reaches a level more than 10% greater than the clean-surface reflectance. The resistance, however, scarcely changes after adsorption of the first monolayer. While the results are qualitatively consistent with expectations, there are discrepancies. The resistance and reflectance changes in the monolayer region are not proportional, and the increase in reflectance with thickness is more rapid than expected.

11:40am **SS2-MoM11 Ordering of Chemisorbed PF@sub 3@ on Cu(001)**, J. Braun, L.V. Goncharova, G.G. Bishop, A.V. Ermakov, Rutgers University; D.-M. Smilgies, Rutgers University, US; B.J. Hinch, Rutgers University

PF@sub 3@ adsorbs molecularly on many transition metal surfaces with P bonded at 'on top' positions. On close packed Pt, Ni and Ru crystal faces, PF@sub 3@ has been reported to adsorb with a high density @sr@3 x @sr@3 structure. In these cases steric interactions are believed to be strong enough to prevent rotational motion of the molecules about an axis parallel to the surface normal. On Cu(001), between 140K and 200K, a saturated(4x2) structure with at least two 90° rotated domains has been observed with both helium atom scattering and LEED. We shall discuss the implications of free rotational motion of these molecules in the c(4x2) and a close-packed, uniaxially-compressed, near-hexagonal phase that is found at higher coverages and lower temperatures. Evidence for PF@sub 3@ decomposition on Cu at temperatures above 500K will also be presented.

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