Tuesday Morning, November 1, 2005

Surface Science
Room 202 - Session SS1-TuM

Vibrational Spectroscopy of Surfaces
Moderator: G.P. Williams, Jefferson Labs

8:20am SS1-TuM1 Direct Observation of Metathesis Reactions on a Carbide Surface: The Surface Chemistry of Multiple Bonds., *M. Siaj*, P.H. McBreen, Université Laval, Canada
Well-defined metal ligand complexes are a feature of organometallic chemistry, and have long served as a guide to understanding chemisorption systems. However, the entire area of metal-ligand multiple bond chemistry appears to have almost no counterpart in surface science. Reports of surface alkylidene species, M=CR1R2 where M is a single metal atom, are extremely rare. Metal-alkylidenes are catalysts for metathesis chemistry, one of the most powerful synthetic methodologies in modern organic, polymer and materials science. Hence, for a variety of applications, it is very important to develop metathesis chemistry on extended surfaces. An extensive set of surface spectroscopy data will be used to show that alkylidene groups can be prepared and isolated on the surface of molybdenum carbide. Futhermore, it will be shown that vibrational spectroscopy may be used to perform in-situ monitoring of cross-metathesis and ring opening polymerization reactions, isolating both initiator and propagator species. These results illuminate both the reaction mechanism for heterogeneous metathesis and the unique ability of the metal carbide surface to promote highly selective catalysis.

8:40am SS1-TuM2 Strategies for DFT Modeling of Experimental Surface Vibrational Modes, *P. Uvdal*, Lund University, Sweden; *M.P. Andersson*, Technical University of Denmark
We have explored and developed electronic structure calculations as a tool for the interpretation of experimental vibrational spectra of surface adsorbates. By combining high sensitive surface infrared spectroscopy and density functional calculations details in the spectra, beyond the harmonic level, can be analyzed. These details allow us to extract new information about the physical properties of adsorbed molecules, information not available using the harmonic or normal mode approximation. For instance the C-H stretch region of organic adsorbates contains often more than 50% of the informational content of the vibrational spectrum. Any proper assignment of this region can, however, not be done at the normal mode level. It requires a treatment, which includes anharmonic coupling between fundamental C-H stretch modes and binary/overtone modes of CH3 and CH2 bending modes. This complicates the comparison between calculations and experiments. Base on the concept of spectral moment or intensity weight average one can however obtain the unperturbed frequency of a vibrational mode, e.g. the C-H stretch mode in methoxy. This frequency can then directly be compared to the frequency determined by calculations in the absence of anharmonic coupling between fundamental and binary/overtone modes. This new concept is discussed and related to our recently determined new scaling factor for harmonic vibrational frequencies using the B3LYP density functional method with the triplezeta basis set 6-311+G(d,p)@footnote 1@. @FootnoteText@ @footnote 1@M. P. Andersson and P. Uvdal, J. Phys. Chem. A 109, 2937 (2005).

9:00am SS1-TuM3 Freidel Oscillations: S and CO Metal Mediated Interactions, *X.F. Hu, C.J. Hirschmugl*, University of Wisconsin-Milwaukee
The coadsorption of CO and S on Cu(100) is examined to gain a deeper understanding of metal-mediated interactions between co-adsorbates. Using a combination of IRAS, Auger Electron Spectroscopy (AES) and TDMS, we find that CO adsorbates do not occupy the first and second nearest-neighbor adsorption sites of S adatoms, but are strongly bound to third-nearest neighbor sites. Simple site-blocking can explain the absence of CO adsorption at first-nearest neighbor sites. However, we attribute the second- and third-nearest neighbor results to S-induced changes in the LDOS. A local minimum is induced at second-nearest sites, suppressing CO adsorption, but a local maximum at third-nearest sites enhances the C-metal bonding strength. Bonding to these sites is stronger than even on the clean Cu(100) surface. Furthermore, the C-O stretch frequency and the dipole-dipole coupling are affected by the S coverage. For a low S coverage, where dipole-dipole coupling is still dominant, a Coherent Potential Approximation (CPA) treatment of dipole-dipole coupling is used to estimate the spatial extent reffective of S and CO substrate-mediated interactions. reffective is found to be between 6 ~ 7 Å. This work shows that S affects the CO adsorption in three ways: making adsorption sites electronically unfavorable, affecting the interface bonding between CO and Cu, and reducing the CO intermolecular interaction.

9:20am SS1-TuM4 Attenuated Total Reflection Infrared Spectroscopy and Nanoparticles: A New Tool for Probing Adsorption (CO, NH@sub 3@) on Planar Model Catalysts (Rh), *C.M. Leewis*, M.C.M. Van De Sanden, Eindhoven University of Technology, The Netherlands; *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands, Netherlands; *J.W. Niemantsverdriet*, Eindhoven University of Technology, The Netherlands
Attenuated total internal reflection Fourier transform infrared spectroscopy (ATR-FTIR) is used to study adsorption and/or decomposition of CO and NH@sub 3@ on Rh nanoparticles. The silicon ATR crystal (25 reflections, 45°) with a 50 nm thick hydroxylated thermal SiO@sub 2@ layer acts as the support for the nanoparticles. These are spincoated from a RhCl@sub 3@ solution in water followed by reduction in H@sub 2@ at 200°C. X-ray Photoelectron Spectroscopy (XPS) shows the reduction to Rh@super 0@ and the removal of Cl. Atomic Force Microscopy (AFM) shows a distribution of 200 particles per μm@super 2@, which are ~3 nm in height. The ATR-FTIR experiments are performed in UHV without exposing the crystal bevels and backside (both without oxide and Rh) to the gases. For a 4 cm@super -1@ resolution, a sensitivity of reflectance as low as 5x10@super -5@ absorbance units in the region 2000-3500 cm@super -1@ can be reached. CO exposure validates the detection of species on the nanoparticles, since CO does not interact with the support. Linearly adsorbed CO on Rh is observed at 2023 cm@super -1@. No bridged CO or geminal dicarbonyls are observed. For ammonia, interaction with the silica OH groups is observed around 2900 cm@super -1@ in combination with negative unperturbed OH peaks between 3500 and 3700 cm@super -1@. In addition, N-H bend (1634 cm@super -1@) and stretch (3065, 3197 cm@super -1@) vibrations are observed for substrate temperatures between 20°C and 150°C. The latter correspond to N-H on Rh, as verified with a sample without Rh, and remained after evacuation, suggesting strongly bound species. For 75°C and 100°C, additional peaks at 3354 and 3283 cm@super -1@ are observed, possibly due to NH@sub 2@ intermediates. ATR-FTIR is therefore a powerful technique for probing adsorbates on supported nanoparticles.

9:40am SS1-TuM5 Formation of C-H and N-H bonds on the Pt(111) Surface as Studied with Reflection Absorption Infrared Spectroscopy, *R. Deng, E. Herceg, K. Mudiyanselage, J. Jones, M. Trenary*, University of Illinois at Chicago **INVITED**
The reaction of hydrogen with atomic species adsorbed on transition metal surfaces is a key step in many important catalytic processes. However, many surface probes are not sensitive to hydrogen so the detection and characterization of processes in which hydrogen forms bonds to other elements on surfaces has been difficult. Recent advances in the sensitivity of surface infrared spectroscopy allows surface intermediates with very weak IR absorption bands to be unambiguously detected. It is well known that the complete dehydrogenation of various hydrocarbons eventually leads to graphitic monolayers on platinum surfaces, although the exact forms of the surface carbon prior to graphite formation are still undetermined. Surface carbon has been prepared by the dehydrogenation of ethylene and acetylene on Pt(111) through exposure at 750 K. Subsequent hydrogen exposure leads to clear infrared features due to methylidyne (CH), ethylidyne (CCH@sub 3@), and ethynyl (CCH). These results demonstrate that C atoms and C@sub 2@ molecules exist as stable species on the surface. An ordered (2x2) layer of N atoms can be prepared on Pt(111) through the oxidation of ammonia in which all of the hydrogen and oxygen are removed through the desorption of water. Subsequent hydrogen exposure leads to a sharp and intense infrared band at 3320 cm@sup -1@ due to the NH species. Quantitative determinations of the NH and N coverages through temperature programmed desorption measurements indicate that only a small fraction of the surface N atoms are reactive towards hydrogen. The NH species can not be further hydrogenated to NH@sub 2@ or NH@sub 3@ under the conditions used in these experiments.

10:20am SS1-TuM7 RAIRS Signature of the Ordered Methyl Bromide Monolayer on Pt(111), *I. Samanta*, T. Schwendemann, University of Virginia; *T. Kunstman*, University of Essen, Germany; *I. Harrison*, University of Virginia
Scanning tunneling microscopy (STM) reveals that methyl bromide (CH@sub 3@Br) adsorbed on a Pt(111) surface can order into a relatively close packed monolayer of upright molecules even though the dipole moment of these rod-like molecules is substantial (1.8 Debye in the gas

phase). The formation kinetics of the ordered (3 x 5) structure can be slow at temperatures less than 100 K. The unit cell contains four CH_3Br molecules of two kinds oriented with C-Br axis along the surface normal. The CH_3Br saturation coverage is estimated to be 0.27 ML by STM. Other ordered structures are observed at lower coverages. The evolution of ensemble-averaged reflection absorption infrared spectroscopy (RAIRS), thermal programmed desorption (TPD) spectroscopy, and photochemical dynamics experiments on $CH_3Br/Pt(111)$ as a function of coverage will be discussed in light of the microscopic structures observed by STM. The RAIRS signature of the ordered CH_3Br monolayer is the disappearance of the ν_5 asymmetric CH_3 deformational mode near 1411 cm^{-1} and the adsorption-site induced splitting of the ν_2 symmetric CH_3 deformational mode into a doublet at 1271 cm^{-1} and 1277 cm^{-1} with fwhms of just 3 cm^{-1}.

10:40am **SS1-TuM8 Adsorption on Carbon Nanotubes Studied Using Polarization-Modulated Infrared Reflection-Absorption Spectroscopy**, **V.M. Bermudez**, Naval Research Laboratory

Single-wall carbon nanotubes (SWNT's), deposited onto an Al substrate from a liquid suspension, have been cleaned by annealing in UHV. The effects of exposing the sample in situ to atomic H (or D) and/or to DMMP [dimethyl methylphosphonate, $(CH_3O)_2(CH_3)P=O$] were then studied using polarization-modulated infrared reflection-absorption spectroscopy. Atomic H reacts preferentially near strained or defective regions in the nanotube wall to produce a spectrum consistent with alkane-like species ($>CH_2$ and CH_3). Only a small fraction of the $>C=C<$ sites in the nanotube wall react with H, and there is no clear evidence for monohydride ($>C(H) C(H)<$) species. For DMMP, data were obtained under steady-state conditions in reagent pressures in excess of half the room-temperature vapor pressure. Adsorption occurs via the P=O group with a coverage that depends on the ambient pressure. Varying the DMMP coverage by changing the pressure causes changes in the spectrum that can be related to the strength of the DMMP/SWNT interaction. Pre-adsorbed H is seen to have little or no effect on the subsequent adsorption of DMMP. For DMMP, the molecular features are superimposed on a broad, smoothly-varying background that can be related to adsorption-induced changes in the Drude parameters characterizing the SWNT free-carrier density and scattering lifetime. Data were also obtained during exposure to $^{16}O_2$ or $^{18}O_2$. As in the case of atomic H, evidence is seen for preferential reaction near strained or defective regions, but no vibrational modes of adsorbed O or O_2 are detected.

11:00am **SS1-TuM9 Nanoporous Gold As a Novel Highly Active Substrate for Surface-Enhanced Raman Spectroscopy**, J. Biener, J.R. Hayes, S.O. Kucheyev, T. Huser, C.E. Talley, A.M. Hodge, **A.V. Hamza**, Lawrence Livermore National Laboratory

Surface-enhanced Raman-scattering (SERS) spectroscopy has attracted considerable interest in recent years due to the possibility to reach the single molecule detection limit. Colloidal solutions of gold or silver with particle sizes in the submicron range are most commonly used as SERS active substrates. However, the limited stability and reproducibility of metal colloids currently hampers their use as SERS substrates. Here, we report on the development of nanoporous gold (np-Au) as a novel, highly active SERS substrate. The SERS activity was probed using crystal violet as a test molecule. The significant Raman enhancement observed seems to be a consequence of the nanoscale surface roughness and curvature of np-Au. The material is prepared by dealloying Ag-Au alloys, and exhibits an open sponge-like morphology of interconnecting Au ligaments with a typical pore size distribution on the nanometer length scale. The dimensions of both pores and ligaments can be further fine-tuned by chemical and/or thermal treatments. Our ultimate goal is the development of an affordable, stable, reproducible, and highly active substrate for SERS-based chemical sensors. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

11:20am **SS1-TuM10 Vibrational and Photoelectron Spectroscopy of Formic Acid and Water Coadsorbed on Au(111) Surfaces: Chemical Interaction and Compound Formation**, **G. Pirug**, M. Kazempoor, Forschungszentrum Jülich GmbH, Germany

The coadsorption of formic acid (HCOOH) and water (H_2O) has been studied on Au(111) single crystal surfaces by means of vibrational spectroscopy (HREELS) and photoelectron spectroscopy (XPS) in the temperature range between 90 K and 200 K. Formic acid adsorbs at 90 K molecularly with vibrational modes characteristic for solid formic acid. Annealing results in a complete desorption at 190 K. Upon sequential adsorption of formic acid and water at 90 K no significant chemical interaction can be deduced from the vibrational signatures and the core level photoelectron binding energies. Independent of the sequence of exposure coadsorption or layered growth without intermixing is observed in the monolayer and the multilayer regime, respectively. Heating of the coadsorbed layer to about 140 K results in the formation of a new surface complex with characteristic vibrational losses at 190, 590 and 1000 cm^{-1}. Based on these frequencies and supported by the corresponding stoichiometries as deduced from XPS possible compounds will be discussed. Upon further annealing this complex decomposes leaving only molecularly adsorbed formic acid on the surface at 160 K. These results will be discussed in the light of recent findings for the electrochemical oxidation of formic acid on Au surfaces.

11:40am **SS1-TuM11 STS Vibrational Study of 1,3-cyclohexadiene on Si(100) Surface**, **B. Naydenov**, J.J. Boland, Trinity College Dublin, Ireland

Scanning tunnelling spectroscopy was performed on 1,3-cyclohexadiene modified Si(100) surface at 5K. Degenerated N-type semiconductor and platinum covered tungsten tips were used. For the first time a vibrational spectrum of chemisorbed molecule on semiconductor surface was obtained. The spectroscopic conditions involved small tip-sample separations, far from the normal imaging conditions, and for wish the simple tunnelling picture involving overlapping wave function tails is no longer valid. Under such conditions significant forces and weak chemical bond occurs between the tip and the surface. The vibrational features and the tunnelling barrier height variations with the tip-sample distance will be discussed.

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