

Surface Science

Room 208 - Session SS1-WeM

Chemical Interactions and Surface Reactivity

Moderator: J.L. Gland, University of Michigan

8:20am SS1-WeM1 Increased Reactivity of Strained Ni Layers on Ru(0001), R.C. Egeberg, I. Chorkendorff, Technical University of Denmark, Denmark

Understanding the reactivity of metal surfaces and in particular how to control and manipulate this reactivity is the first step towards improved catalysts. From many surface science studies a detailed knowledge about the structures emerging from metal on metal growth has been gained whilst the link to the overall reactivity of such bimetallic structures has not been equally thoroughly investigated. We here present data showing how to utilize the growth properties of Ni on Ru(0001) to improve the ability of Ni to catalyze the reforming of methane. By growing a pseudomorphical Ni overlayer on Ru(0001) a strained Ni layer is formed with respect to Ni(111). As a result of the change in electronic configuration this procedure results in a more reactive Ni layer as it has been predicted from DFT calculations. In steam reforming catalysis the dissociation of methane is the rate-limiting step and we have therefore focused on the initial sticking of methane on this surface. Thermal experiments at 530 K show that the Ni overlayer is ca. 2 times more reactive than Ru(0001) and ca. 20 times more reactive than Ni(111). As more than 1 monolayer of Ni is deposited the sticking decreases and saturates at the value for Ni(111). The adsorption energy of CO which is used as a probe molecule follows the same trend as the CH@sub 4@ sticking. Supersonic molecular beam experiments support the picture of a lower activation barrier on the strained Ni overlayer. Finally, the ability of the surface to catalyze the partial oxidation of methane is under investigation.

8:40am SS1-WeM2 Suppression of NO Dissociation by Adsorbed Gold on Pt(335), D.C. Skelton, Michigan State University / General Motors; *R.G. Tobin,* Tufts University; *C.L. DiMaggio, D.K. Lambert, G.B. Fisher,* Delphi Automotive Research Labs

We have conducted a temperature programmed desorption study to compare the dissociation probabilities of oxygen and NO on a partially gold-covered stepped Pt(335) surface. NO dissociation takes place almost exclusively at step sites. It apparently requires either multiple adjacent open step sites, or special sites such as kinks, and is therefore unusually sensitive to modification of steps and defects. A gold coverage of 0.15 ML reduces NO dissociation by a factor of five compared to bare Pt, and increasing the gold coverage to 0.3 ML further reduces it to an undetectable level. Oxygen dissociation also occurs preferentially at step sites, but is far less sensitive to step blockage: At 0.3 ML gold, the saturation oxygen coverage is only 20% lower than on bare Pt. These results help explain the operation of a recently developed electrochemical NO@sub x@ sensor. @footnote 1@ An effective NO@sub x@ sensor is vital for pollution control in fuel-efficient lean-burn gasoline and diesel engines. The electrochemical sensor uses a platinum-gold alloy electrode in a pumping cell to remove oxygen from the exhaust gas without dissociating NO. For effective sensor operation, the electrode must be ~10@super 3@ more effective at dissociating oxygen than at dissociating NO. Our experiments suggest that a platinum-gold alloy electrode has this remarkable selectivity because gold blocks special sites that are needed for NO dissociation but not for oxygen dissociation. @FootnoteText@ @footnote 1@ N. Kato, Y. Hamada and H. Kurachi, SAE Paper 970858 (1997).

9:00am SS1-WeM3 Chemical and Electronic Properties of Ni/Pt(111) Bimetallic Surfaces: Unique Surface Reactivity at the Monolayer Ni Coverage, J.G. Chen, J. Eng, Jr., M.T. Buelow, H.H. Hwu, N.A. Khan, University of Delaware

INVITED

In a recent paper we reported the observation of an "anomalous" reactivity of Ni/Pt(111) bimetallic surfaces at Ni coverages around one monolayer (ML) [3]. For example, after a saturation exposure of D2 to a Ni/Pt(111) surface with one ML Ni, the desorption of D2 occurs at 220 K from the TPD measurements. This desorption temperature is lower than that of D2 desorption from either Pt(111) (294 K) or Ni(111) (379 K). The lower desorption temperature suggests that the D atoms are rather mobile on the one ML Ni/Pt(111) surface. We have tested this idea by investigating the hydrogenation of cyclohexene to cyclohexane, and the hydrodesulfurization of thiophene to 1,3-butadiene on the one ML Ni/Pt(111) surface. In both cases the hydrogenation reactions take place at

around 220 K under UHV conditions; these two reactions do not occur on either Pt(111) or Ni(111) under similar experimental conditions. In this talk we will present these latest TPD results, as well as our characterization of the chemical and electronic properties of the Ni/Pt(111) surfaces using high-resolution electron energy loss spectroscopy (HREELS), near-edge X-ray absorption fine structure (NEXAFS), and X-ray photoelectron spectroscopy (XPS).

9:40am SS1-WeM5 Coverage Dependent Selectivity and a New Approach to Tailoring Nanostructures on Single Crystal Surfaces, A.V. Teplyakov, H. He, A.T. Mathauser, University of Delaware

Here we report a remarkable chemistry exhibited by 6-bromo-1-hexene on a Cu@sub 3@Pt(111) surface. The dehydrocyclization reaction leading to the formation of benzene takes place at very low coverage; as the surface fills up the decomposition becomes a predominant pathway. Similar behavior was reported for other linear hydrocarbons on metals and metal alloys previously. However, further increase of surface concentration of 6-bromo-1-hexene leads to a different type of chemistry. The hydrogenation of 5-hexenyl produced as a result of C-Br bond dissociation leads to the formation of 1-hexene which is stable on a surface until the molecular desorption of this compound starts at 230 K. Molecular desorption from the monolayer becomes significant at even higher dose. All these processes occur within a specific coverage very clearly making the 6-bromo-1-hexene on a Cu@sub 3@Pt(111) surface extremely attractive to analyze the kinetics of coverage dependent processes. Steric requirements for each of the processes described here and the availability of the adsorption sites on the alloy surface are believed to govern the predominant reaction. Thermodynamics and potential applications of these chemical processes for masking and production of nanoscale features will be discussed.

10:00am SS1-WeM6 The Near Edge X-ray Absorption Fine Structure of n-octane Adsorbed on Cu(110): New Insights Into the Type of Chemical Interaction, K. Weiss, L. Triguero, H. Öström, A. Nilsson, Uppsala University, Sweden

Using near edge X-ray absorption fine structure (NEXAFS) spectroscopy we have investigated the electronic structure of n-octane adsorbed on Cu(110). The molecule is found to be well oriented on the surface, which is seen from the high degree of NEXAFS dichroism. The NEXAFS spectra, which display the density of unoccupied molecular states, reveal large changes in the electronic structure of the adsorbed octane relative to the free molecule. We find that the molecular Rydberg states are strongly quenched upon adsorption and that there is a significant hybridization of molecular valence orbitals with the metal bands. In order to understand these adsorption induced electronic structure changes we have performed cluster model calculations in the framework of density functional theory. The calculations show nice agreement with the experimental results. In addition to a precise interpretation of the NEXAFS spectra, we present details on the geometric structure of the adsorbed octane molecule and the molecular orbital structure. The results are complemented by calculations of the X-ray emission spectra, which provide information on the occupied valence states. Our study gives new insights into the type of chemical interaction experienced by saturated hydrocarbons adsorbed on metal surfaces, which is of importance for the understanding of the C-H bond activation mechanism.

10:20am SS1-WeM7 Direct Experimental Measurement of Donation/Backdonation in Unsaturated Hydrocarbons Bonding to Metals, L. Triguero, Uppsala University, Sweden; *A. Föhlisch,* Universität Hamburg, Germany; *P. Väterline, J. Hasselström,* Uppsala University, Sweden; *M. Weinelt,* Universität Erlangen, Germany; *L.G.M. Pettersson,* Stockholm University, Sweden; *A. Nilsson,* Uppsala University, Sweden

Soft X-ray emission spectra (XES) from C@sub 2@H@sub 4@/Cu(110) and C@sub 6@H@sub 6@/Cu(110) have been obtained for two excitation energies, resonant and non-resonant, and resolved in all three spatial components (x, y, z). The one-step theory for resonant soft X-ray spectroscopy and Raman scattering is extended to adsorbates on metal surfaces and is implemented within a density functional theory framework. A combination of these experimental and theoretical works are used to examine the electronic structure of chemisorbed ethylene and benzene on the Cu(110) surface in order to investigate the suitability of the donation/backdonation bonding model given by Dewar, Chatt and Duncanson for the interaction of unsaturated hydrocarbons with metal surfaces. We give an experimental verification of the DCD model and find donation/backdonation to be twice as large for ethylene as for benzene. In particular, the degree of @sigma@-@pi@ mixing (rehybridization) is found to correspond to the amount of donation/backdonation, which is put

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into relation to the aromatic and non-aromatic π characters of benzene and ethylene, respectively.

10:40am SS1-WeM8 **Trapping-mediated Dissociative Chemisorption of Cycloalkanes on Ru(001) and Ir(111): The Influence of Ring Strain on the Activation of C-C and C-H Bonds**, *T.-W. Kim, C.J. Hagedorn, M.J. Weiss, W.H. Weinberg*, University of California, Santa Barbara

We have measured the initial probabilities of dissociative chemisorption of perhydrido and perdeutero cycloalkane isotopomers on the hexagonally close-packed (hcp) Ru(001) and Ir(111) single-crystalline surfaces for surface temperatures between 250 and 1100 K. Kinetic parameters (activation barrier and preexponential factor) describing the initial, rate-limiting C-H or C-C bond cleavage reactions were quantified for each cycloalkane isotopomer on each surface. Determination of the dominant initial reaction mechanism as either initial C-C or C-H bond cleavage was judged by the presence or absence of a kinetic isotope effect between the activation barriers for each cycloalkane isotopomer pair, and also by comparison with other relevant alkane activation barriers. On the Ir(111) surface, the dissociative chemisorption of cyclobutane, cyclopentane, and cyclohexane occurs via two different initial reaction pathways: initial C-C bond cleavage dominates on Ir(111) at high temperatures ($T > 600$ K), while at low temperature ($T < \sim 400$ K), initial C-H bond cleavage dominates. On the Ru(001) surface, dissociative chemisorption of cyclopentane occurs via initial C-C bond cleavage over the entire temperature range studied, whereas dissociative chemisorption of both cyclohexane and cyclooctane occurs via initial C-H bond cleavage. Comparison of the cycloalkane C-C bond activation barriers measured here with those reported previously in the literature, suggests that the difference in ring strain energies between the initial state and transition state for ring-opening C-C bond cleavage effectively lowers or raises the activation barrier for dissociative chemisorption via C-C bond cleavage depending on whether the transition state is less or more strained than the initial state. Moreover, steric arguments and metal-carbon bond strength arguments have been invoked to explain the observed trend of decreasing C-H bond activation barrier with decreasing cycloalkane ring size.

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