

Surface Science Division Room 309 - Session SS2-MoA

Surface Chemistry on Model Catalysts

Moderator: C.H.F. Peden, Pacific Northwest National Laboratory

2:00pm SS2-MoA1 Adsorption and Mass Transfer Processes on Stepped Metal Surfaces, J.E. Reutt-Robey, University of Maryland, College Park INVITED

We present experiments that explore the role of crystallographic steps in regulating the propagation of surface chemical processes. Using scanning tunneling microscopy as the primary structural probe, we track the evolution of step structures on clean metal surfaces, under chemical adsorption, and under reaction conditions. Substantial step motions are observed during these processes on vicinal Ag(110) and Al(111) substrates, even at room temperature, revealing these steps as efficient adatom sources and sinks. The interplay between these step motions and molecular events is further investigated. Atomically resolved STM measurements of adlayer structures, in conjunction with infrared spectroscopic characterization of the adsorbates, reveal the lateral distribution of adsorbates with respect to the step edge, and their chemical speciation. For the oxidation and hydrogenation reactions that we have investigated on these metallic substrates, steps serve two principal roles: They act as efficient adatom sources for the formation of adsorbate-substrate complexes. They introduce domain boundaries that facilitate mass flow in both adsorption and reaction.

2:40pm SS2-MoA3 Visualization of Heterogeneously Catalytic Processes, M. Bode, M. Getzlaff, R. Wiesendanger, University of Hamburg, Germany

The goal of this study is to get deeper insight into the understanding of heterogeneous catalysis by combining the special merits of scanning tunneling microscopy/spectroscopy (STM/STS) and ultra-violet photoemission spectroscopy (UPS). We report on the electronic structure and the development of the adsorption process of hydrogen covered Gadolinium films being exposed to carbon monoxide. Clean Gd(0001) films were epitaxially grown on W(110). These films were exposed to hydrogen which leads to a local quenching of the d_z2_{super}2-like surface state being characteristic for the clean Gd(0001) surface. Due to the high spatial resolution of STM and its sensitivity to the local density of states at close to the Fermi-level, the adsorption process can be visualized and directly be correlated to the electronic properties measured by from UPS. The adsorption process at room temperature consists of five steps. At the very beginning the total amount of CO causes a removal of hydrogen from the surface. In the next two steps the rest of the adsorbed hydrogen atoms is removed and carbon and oxygen remains at the surface. In the intermediate regime CO dissociates and carbon and oxygen is adsorbed at or near the surface. This information is corroborated by investigations of clean Gd(0001) being exposed to CO and oxygen, respectively. The last step demonstrates the oxidation to Gd₂O₃ acting as catalyst for the transformation of CO to CO₂ which creates stable carbonate species at the surface.

3:00pm SS2-MoA4 Studies of Oxygen Species on a Heated Silver Membrane, R.J. Beuhler, R.M. Rao, M.G. White, Brookhaven National Laboratory

Oxidation reactions catalyzed by silver are a multi billion dollar enterprise worldwide. Such reactions have been investigated extensively by conventional surface science techniques, however, applications using state- or species-selective laser techniques are difficult to carry out for practical reasons specific to Ag surfaces. For example, the dissociative adsorption cross section of O₂ on Ag is on the order of 10⁻¹⁴ cm², which means that the high pressure of O₂ impinging on a silver surface makes state-selective detection of reaction products under collision free conditions nearly impossible. As a step towards understanding of the dynamics of oxidation reactions on Ag, we have undertaken a study of the oxygen species and reactions on the high vacuum side of a heated silver membrane. High surface coverages of O-atoms are produced by dissociative adsorption of molecular oxygen on the high-pressure side of a heated Ag-foil through which the O-atoms diffuse to the surface. Reactions at the high vacuum side can be studied under conditions that allow energy and spectroscopic analysis of the products. Preliminary results have been obtained for the recombination reaction O₂(a) + O₂(a) = O₂(g) using (2+1) REMPI laser spectroscopy to probe state and energy distributions of the desorbing molecules. Initial measurements on

the yield and temperature dependence of the oxidation reactions of CO and ethylene at intermediate pressures (10⁻⁵ to 10⁻⁴ Torr) have also been performed. These results and limitations in the foil experiment will be discussed.

3:20pm SS2-MoA5 Promotion through Gas Phase Induced Surface Segregation: Methanol Synthesis from CO, CO₂ and H₂ over Ni/Cu(100), I. Chorkendorff, J. Nerlov, Technical University of Denmark, Denmark

The synthesis rate of methanol formation over Cu(100) and Ni/Cu(100) from various gas mixtures of CO, CO₂ and H₂ have been studied. It was found that the presence of submonolayer quantities of Ni leads to a strong increase in the rate of methanol formation from mixtures containing all three components whereas Ni does not influence the rate from mixtures of CO₂/H₂ and CO/H₂, respectively. The influence of the partial pressures of CO and CO₂ on the rate indicates that the role of CO is strictly promoting. From temperature programmed desorption spectra it follows that the surface concentration of Ni depends strongly on the partial pressure of CO. In this way the increase in reactivity was interpreted as a CO-induced structural promotion introduced by the stronger bonding of CO to Ni as compared to Cu. It is suggested that this type of promotional behavior will be of general importance in existent catalysts and perhaps even more relevant in the development of new or improved bimetallic catalyst

3:40pm SS2-MoA6 Carbon-Sulfur Bond Activation in Adsorbed Methylthiolate on Ni(100) with Gas Phase Atomic Hydrogen at 120 K, A.T. Capitano, J.L. Gland, University of Michigan

Low temperature carbon-sulfur bond activation has been observed during reaction with both gas phase atomic and subsurface hydrogen. These results show for the first time that hydrogen can directly induce C-S bond activation in an adsorbed species. This new surface reaction provides exciting new opportunities for examining fundamental mechanisms of hydrodesulfurization on surfaces under UHV conditions. Gas phase atomic hydrogen breaks the C-S bond in methylthiolate resulting in the formation of methane even at 120 K on the Ni(100) surface. These results indicate that the energy for C-S bond activation is furnished by the atomic hydrogen. In contrast, coadsorbed hydrogen causes no C-S bond activation in methylthiolate. For a constant flux of gas phase atomic hydrogen, the rate of methane formation is first order in methylthiolate coverage indicating a direct Eley-Rideal reaction. Some adsorbed methyl and methylthiolate can remain on the surface after reaction, depending on atomic hydrogen exposure. During subsequent TPD experiments, addition of hydrogen to these intermediates results in three methane formation processes. Subsurface hydrogen breaks the C-S bond in methylthiolate at 200 K. Methyl hydrogenation by coadsorbed hydrogen occurs at 250 K. Or, thermal activation of the C-S bond by the surface is observed at 320 K. Taken together, these results demonstrate that energetic forms of hydrogen can break C-S bonds by direct addition to adsorbed thiols on metal surfaces. The new mechanistic information generated using this approach may have substantial implication in fields ranging from catalytic hydrodesulfurization to stability of microelectronic devices.

4:00pm SS2-MoA7 Propylene Oxidation on the Pt (111) Surface over an Extended Range of Coverages, A.M. Gabelnick, J.T. Sipowska, J.L. Gland, University of Michigan

The reactions of propylene and oxygen coadsorbed on the Pt (111) surface have been characterized over an extended range of coverages using TPRS. Unexpected modification of the oxidation process is observed for high coadsorbed coverages. Initiation of propylene oxidation results in water formation at 200K which appears to involve abstraction of the acid methyl hydrogens. This low temperature reaction becomes increasingly important for high coadsorbed coverages suggesting that direct interaction between propylene and coadsorbed atomic oxygen may play an important role for high coadsorbed coverages. For the highest coadsorbed coverages and excess propylene we were surprised to observe acetone and acetic acid partial oxidation products. Large coverages of coadsorbed propylene also cause the formation of a new low temperature molecular oxygen peak at 140 K. For both coadsorbed molecular and atomic oxygen, the primary products observed are water, carbon dioxide, and carbon monoxide. Following initial water formation near 200 K, the dominant water peak appears at 300 K over the entire range of coverages. Further increase in temperature results in carbon dioxide formation at 350K. Oxidation of propylidyne has a larger activation energy and occurs in one step at 370K. At higher temperatures further propylidyne oxidation and decomposition

resembles that of propylene. Large coadsorbed coverages result in low temperature reaction and modified reaction selectivities.

4:20pm SS2-MoA8 The Catalytic Chemistry of Small Hydrocarbons on Palladium: Cyclization, and Hydrogenation, W.T. Tysoe, H. Molero, M. Kaltchev, University of Wisconsin, Milwaukee

The reaction pathways for acetylene trimerization catalyzed by palladium is investigated using a range of surface-sensitive techniques. It is found that benzene is formed from acetylene via the intervention of a metallocyclic $C@sub4@subH@sub4@sub$ intermediate. This further reacts with a third acetylene to form benzene. However, the catalytic reaction proceeds in the presence of a carbonaceous layer, which consists of vinylidene species. At high pressures, acetylene is formed by reaction between acetylene adsorbed on the vinylidene-covered palladium surface and adsorbed vinylidene itself to form a $C@sub4@subH@sub4@sub$ intermediate. It is shown that the hydrocarbon part of this layer can be removed by reaction in high pressures (several Torr) of hydrogen. The activation energy for this process on molybdenum surfaces is about 6 kcal/mol. Correspondingly, the rate of acetylene cyclotrimerization is found to be accelerated by the addition of hydrogen to the reaction mixture. The implication of these phenomena on alkene and alkyne hydrogenation reactions catalyzed by transition metals will also be addressed and a model for hydrogenation reactions under high-pressure conditions is proposed that yield kinetic parameters in good agreement with those measured experimentally.

4:40pm SS2-MoA9 Dehydrogenation of Ethylbenzene Studied on Single Crystalline Iron Oxide Model Catalyst Films, W. Weiss, D. Zscherpel, M. Ritter, R. Schloegl, Fritz-Haber-Institut der MPG, Germany

We study the dehydrogenation of ethylbenzene (EB) to styrene over single crystalline $FeO(111)$, $Fe@sub3@O@sub4@(111)$ and $@alpha-Fe@sub2@O@sub3@(0001)$ model catalyst films grown onto $Pt(111)$ substrates. The epitaxial film growth and their atomic surface structures were studied by STM and LEED. 1-2 ML thick $FeO(111)$ films form oxygen terminated surfaces structures. The $Fe@sub3@O@sub4@(111)$ surface exposes iron atoms in the topmost layer, as determined by a dynamical LEED intensity analysis revealing a Pendry r -factor of 0.2. The $@alpha-Fe@sub2@O@sub3@(0001)$ surface exposes two different terminations, iron and oxygen, depending on the ambient oxygen partial pressure. With TDS and UPS a strong chemisorption of EB is observed on the iron terminated $Fe@sub3@O@sub4@$ and $@alpha-Fe@sub2@O@sub3@$ films, whereas only physisorption is observed on the oxygen terminated $FeO(111)$ film. Surface defects on the films were imaged by atomic resolution STM measurements, and the role of the oxide stoichiometry and surface defect concentrations for the model catalyst activities was studied by combining batch reactor experiments at total gas pressures of 1 mbar with pre- and post reaction surface analysis in UHV. No styrene is formed over $Fe@sub3@O@sub4@$ films. $Fe@sub2@O@sub3@$ films are catalytically active, and the styrene formation rate increases with increasing surface defect concentration on these films. This reveals $Fe@sub2@O@sub3@$ as the active oxide phase and atomic surface defects as catalytically active sites thereon. These defects can be steps, vacancies or adatoms. The formation of carbonaceous surface deposits that deactivate the model catalyst films after about 30 min reaction time was monitored with a PEEM microscope. A pattern formation is observed which indicates that the catalyst deactivation is a site selective process, which presumably starts at extended surface defects.

5:00pm SS2-MoA10 Chemisorption on and Modification of Molybdenum Carbide Surfaces, E. Zahidi, C. Morin, H. Oudghiri-Hassani, P.H. McBreen, Université Laval, Canada

Early transition metal carbides and nitrides are materials that combine a wealth of desired mechanical, electrical and chemical properties. Not the least of which is their catalytic activity and their resistance to poisoning by sulfur. RAIRS, XPS and TPD data will be presented for the interaction of simple molecules with bulk molybdenum carbides. The samples studied were prepared using the method typically used to synthesize high surface area carbide catalysts. Data for isotope labelled NO, CO and ethylene reveal how the carbide carbon may be either removed, replaced or deposited. RAIRS results for the cyclic molecules, cyclopropane, cyclohexane and cyclobutanone provide insight on the ability of molybdenum carbide to activate alkane molecules. The study also reveals methods for cleaning and preparing molybdenum carbide surfaces.

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