Monday Afternoon, October 2, 2000

Surface Science
Room 208 - Session SS1-MoA
Model Catalysts at High Pressures

Moderator: A.G. Sault, Sandia National Laboratories

2:00pm **SS1-MoA1 A New Mechanism for Hydrocarbon Dehydrogenation on Pt under Conditions of High Hydrogen Coverage***, J.C. Hemminger,* University of California, Irvine*; **D.A. Perry,*** University of Illinois

In 1978 Demuth and Ibach published the HREELS vibrational spectrum of cyclohexane (C@sub 6@H@sub 12@) adsorbed on clean Pt(111) at low temperature showing strong softening of some C-H modes. Subsequently, data from several laboratories resulted in a consistent picture for the initial step in the dehydrogenation of cyclohexane on clean Pt. The mechanism of the dehydrogenation involves the weakening of one of the axial C-H bonds of the cyclohexane by interaction with a Pt 3-fold hollow site (leading to the soft C-H modes). This is followed by C-H bond breaking to form Pt-H and Pt-C bonds. The initial dehydrogenation product is cyclohexyl (C@sub 6@H@sub 11@). Work from our laboratory has shown that in the presence of high coverages of surface hydrogen the dehydrogenation actually occurs at a lower surface temperature, indicative of a 20% reduction in the activation energy for the initial step. In combination with our HREELS data, that shows no C-H mode softening, this reduction of the activation energy strongly indicates a different mechanism for the dehydrogenation in the presence of high surface coverages of hydrogen. The high surface coverages of hydrogen will effectively fill the 3-fold hollow sites on Pt(111). This leads to a more weakly adsorbed cyclohexane and the lack of softening of the C-H modes. Under these conditions we propose that the dehydrogenation occurs via a @sigma@ bond metathesis mechanism. In this mechanism, which is well established in metal-hydride organometallic chemistry, a hydrogen that is bonded to the Pt interacts strongly with a hydrogen of the cyclohexane. The metal-hydride hydrogen combines with the hydrogen from the cyclohexane to directly form H@sub 2@ at the same time that a C-Pt bond is formed. This concerted mechanism is consistent with our observations that the C-H modes are not softened when the 3-fold hollow sites are blocked with hydrogen and yet a lower activation barrier path to the initiation of the dehydrogenation exists.

2:20pm **SS1-MoA2 The Role of Surface Hydrocarbon Species during Palladium-Catalyzed Reactions at High Pressures***, **D.J. Stacchiola**, W.T. Tysoe,* University of Wisconsin, Milwaukee

It now appears clear that many, if not all, transition-metal-catalyzed hydrocarbon conversion reactions proceed in the presence of a relatively strongly bound carbonaceous layer adsorbed on the surface of the catalyst. In the case of Pd, ethylidyne species are present during ethylene hydrogenation, and vinylidenes in the case of reactions involving acetylene. In order to investigate adsorption on these carbonaceous-layer-covered surfaces, we have studied the adsorption of small molecules on both an ethylidyne-covered and a vinylidene-covered Pd(111) surface using molecular beam strategies and infrared spectroscopy under high pressure conditions. Results on the influence of carbonaceous layers on the hydrogenation kinetics of small hydrocarbons under high pressures are also discussed.

2:40pm **SS1-MoA3 Effect of the Environment on the Surfaces of Metals and Metal Oxides***, **M. Scheffler,*** Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

Surface Science UHV studies, in particular when concerned with metals or metal oxides, in some sense often investigate an artificial state. This means, the surface stoichiometry, and as a consequence the electronic properties, of the studied systems are significantly different to those that would exist in a realistic environment, which typically contains oxygen and water at higher pressure and temperature. This talk summarizes concepts for describing how the pressure and temperature of the environment or atmosphere affect surfaces.@footnote 1-3@ --- I will also describe recent developments in methodology: By combining density functional theory calculations with a lattice-gas Hamiltonian approach and the kinetic Monte Carlo method, surface phenomena can be described over time scales of the order of seconds and length scales of the order of micron.@footnote 4,5@ Examples of such calculations consider long-ranged adsorbate-adsorbate interactions,@footnote 5@ island formation and crystal growth, as well as surface structures with disorder, and thermal desorption.@footnote 4@ --- Using Ru as the main example (but also mentioning Al, Cr, Fe, Rh, Ag) I will show that the interaction with an oxygen atmosphere gives rise to a dramatic restructuring of the surface, yielding to mesoscopic domains of different stoichiometry and very different chemical activity.@footnote 1, 6-8@ The results will be discussed in view of their possible relevance for oxidation catalysis. --- @FootnoteText@@footnote 1@X.-G. Wang et al., Phys. Rev. Lett. 81, 1038 (1998). @footnote 2@ X.-G. Wang, A. Chaka, and M. Scheffler, Phys. Rev. Lett. 84, 3650 (2000). @footnote 3@ X.-G. Wang and M. Scheffler, to be submitted to Phys. Rev. B. @footnote 4@C. Stampfl et al., Phys. Rev. Lett. 83, 2993 (1999). @footnote 5@K.A. Fichthorn and M. Scheffler, Phys. Rev. Lett., May (2000). @footnote 6@A. Böttcher, H. Conrad and H. Niehus, J. Chem. Phys. 112, 4779 (2000). @footnote 7@ A. Böttcher et al., submitted to Surf. Sci. Lett. @footnote 8@H. Over et al., Science 287, 1474 (2000).

3:20pm **SS1-MoA5 Low Temperature CO Oxidation on the Pt(111) Surface Studied Over an Extended Pressure Range***, **D.J. Burnett**, A.M. Gabelnick, A.T. Capitano, A.L. Marsh,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology*; J.L. Gland,* University of Michigan

In-situ Fluorescence Yield Soft X-ray methods and Temperature Programmed Reaction Spectroscopy (TPRS) experiments were used to characterize the oxidation of CO in the temperature range where molecular oxygen dissociates. Taken together, these experiments enable characterization of this reaction over an extended pressure range (UHV to 0.01 Torr). Coadsorbed molecular oxygen and carbon monoxide TPRS experiments show that molecular oxygen must be adsorbed prior to carbon monoxide in order for low temperature (145 K) carbon dioxide to be produced. When molecular oxygen is preadsorbed with CO, the leading edge of molecular oxygen desorption is lowered nearly 20 degrees with a shoulder emerging at 127 K. When CO is preadsorbed, the molecular oxygen desorption peak remains unchanged (single peak with maximum at 142 K). Temperature Programmed Fluorescence Yield Near Edge Spectroscopy (TP-FYNES) experiments, capable of monitoring reactions under reactive atmospheres, were performed in pressures up to 0.01 Torr. For preadsorbed molecular oxygen with a CO overlayer, the same amount of low temperature carbon dioxide is formed when heated in vacuum and in oxygen pressures up to 0.002 Torr. For preadsorbed partial CO monolayers, the low temperature CO oxidation channel can be reached using pressures of oxygen (0.0005 to 0.01 Torr), as opposed to UHV experiments. Based on these results, oxygen dissociation appears to be limited in the vicinity of CO. Since coadsorbed CO enhances molecular oxygen desorption, these results suggest that competition between desorption of molecular oxygen and dissociation limits the reaction with coadsorbed CO. Detailed isothermal kinetic studies were performed with preadsorbed CO to establish a more detailed understanding of the oxidation mechanism.

3:40pm **SS1-MoA6 Rapid Reactions on Nanofabricated Catalyst Pt Particles***, **L. Österlund**, S. Johansson, B. Kasemo,* Chalmers University of Technology, Sweden

The CO oxidation steady-state kinetics has been measured at atmospheric pressure on nanofabricated catalysts. The Pt/ceria and Pt/SiO@sub 2@ catalyst samples used in the present study were prepared by electron-beam lithography (EBL) technique as previously described.@footnote 1@ This technique offers unprecedented opportunities of preparing catalyst particles of well-defined size distribution. Simultaneously it opens the possibility of independently changing particle size, inter-particle distance and the interface between different components, respectively. Here we report results on fairly large, polycrystalline particles (700 nm diameter), as well as smaller crystalline particles formed by disintegration of Pt particles at well-controlled exposures to a H@sub 2@/O@sub 2@ gas mixture.@footnote 2@ The reaction kinetics of the CO oxidation, including the kinetic phase transition and the bistability region has been explored in detail theoretically.@footnote 3@ However, experimental results at high pressures are still by and large lacking. The results presented here fills this gap and provides new information of the kinetic parameters governing the reaction. Rapid reactions on nanometer particles can be very different from those on an infinite surface. Results of the reaction kinetics on the small Pt particles are discussed in this context . @FootnoteText@ @footnote 1@ S. Johansson et al. J. Vac. Sci. Technol. A 18, No 4 (2000). @footnote2@ K. Wong, S. Johansson, and B. Kasemo, Faraday Discuss. 105, 237 (1996). @footnote 3@ V. P. Zhdanov and B. Kasemo, Surf. Sci. Rep. 20, 111 (1994).

4:00pm **SS1-MoA7 Co-adsorption and Reaction of Ethylene and NO over Rh Loaded Ceria Surfaces***, D.R. Mullins, **S.H. Overbury,*** Oak Ridge National Laboratory

In ceria containing emission control catalysts, such as three-way convertors in automobiles, the ceria plays an important role in oxygen exchange in both reduction and oxidation reactions. It is important to understand this role in catalytic reaction pathways. We have used soft x-ray photoelectron spectroscopy and TPD to study the co-adsorption and reaction of ethylene and NO on model catalysts surfaces composed of Rh deposited onto ceria films of controlled oxidation state. Studies focused on the effect of the oxidation state of the ceria upon the reaction pathways. The reactions occur predominantly on the Rh particles but are affected by oxygen spillover, interfacial reactions and modulation of the Rh reactivity by the ceria. Following adsorption at 100 K and subsequent programmed temperature increase, the ethylene decomposes in stages on the Rh particles leading to hydrogen evolution and leaving a reactive C species capable of reducing the ceria to produce CO. Correspondingly, NO reacts with both Rh and ceria. NO oxidizes the ceria resulting in N@sub 2@ evolution. NO dissociation occurs on Rh to an extent dependent upon the oxidation state of the ceria support. There is little interaction between co-adsorbed NO and ethylene when the ceria support is fully oxidized, except for site competition on Rh at low temperature. As temperature is increased water and N@sub 2@ are evolved followed by higher temperature CO evolution. However, for highly reduced ceria, water desorption is eliminated in favor of H@sub 2@, due to oxygen spillover onto ceria. Also, there is strong interaction between the N and C species on Rh which stabilizes them with respect to evolution of CO and N@sub 2@. Except for the absence of isocyanate and the presence of hydrogen and its branching between H@sub 2@ and water, the results are similar to reactions between CO and NO. Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, USDOE.

4:20pm **SS1-MoA8 Reducibility of Model Catalytic Converter Oxygen Storage Materials: Thin Ce@sub x@Zr@sub 2-x@O@sub 2@(111) Films Grown on Y-Stabilized Zirconia Single Crystals***, **C.H.F. Peden**, T. He, G.S. Herman,* Pacific Northwest National Laboratory*; Y.-J. Kim,* Taejon National University of Technology*; Y. Gao, S. Thevuthasan,* Pacific Northwest National Laboratory

Dramatic improvements have been made in automobile exhaust converter catalysts by the incorporation of oxygen storage (OS) materials, usually consisting of ceria (CeO@sub 2@) or modified ceria, that can effectively damp deviation in the exhaust air/fuel (A/F) ratio bringing the gas phase closer to the stoichiometric point. We have been growing and characterizing thin films of CeO@sub 2@ and ceria-zirconia (Ce@sub x@Zr@sub 2-x@O@sub 2@) for use as model materials for fundamental studies of their oxygen uptake, storage, and release properties. In this presentation, the growth and characterization (by x-ray diffraction, atomic force microscopy, reflection high-energy electron diffraction, low-energy electron diffraction, x-ray photoelectron spectroscopy (XPS) and diffraction, and low-energy ion scattering spectroscopy) of model CeO@sub 2@ and Ce@sub x@Zr@sub 2-x@O@sub 2@ thin films will be presented. A wide range of growth parameters using oxygen plasma-assisted molecular beam epitaxy have been used, and successful production of pure-phase, single-crystalline epitaxial oxide films has been achieved. We will also report results of XPS and temperature-programmed desorption experiments that have probed the rates of oxygen incorporation and removal from these materials. In particular, we have found that doping of the CeO@sub 2@ by Zr markedly enhances the kinetics of these processes.@footnote 1@ @FootnoteText@ @footnote 1@Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract number DE-AC06-76RLO 1830.

4:40pm **SS1-MoA9 Mocart: A Tool for Simulation of Heterogeneous Reactions Systems by a Monte-Carlo Method***, R. Kissel-Osterrieder, **F. Behrendt**, J. Warnatz,* Universität Heidelberg, Germany

A general purpose program called mocart for dynamical Monte-Carlo simulations of catalytic surface reactions has been developed. The stochastic model is based on the Master equation. Inputs for the program are the catalytic surface and its structure, the adsorbates and their initial distribution, the elementary reaction steps and their rate coefficients, and the adsorbate-adsorbate interactions, which can be defined for a variety of systems. The Monte-Carlo program is embedded in a computational fluid dynamics code for simulation of stagnation flow fields directed towards a reactive surface. Various aspects of performance improvements are discussed for three applications of this code. These cover the effects of defect sides on the evolution of reaction waves, the formation of spatio-temporal pattern, and models systems for supported catalyst. For all cases, the numerical results are compared with experimental observations.

5:00pm **SS1-MoA10 In Situ Soft X-ray Studies of CO Oxidation on Pt(411): Studies of Defect Reactivity***, **H.D. Lewis**, D.J. Burnett, A.M. Gabelnick, J.L. Gland,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology

The oxidation of preadsorbed CO on a Pt(411) single crystal surface has been studied over a temperature range of 100 to 600 K and in oxygen pressures up to 0.002 Torr using temperature-programmed fluorescence yield near-edge spectroscopy (TP-FYNES) above the carbon K edge. CO desorption from the Pt(411) surface shows that two-site desorption from step and terrace sites occurs. CO desorbs from terrace sites at 365 K and at 460 K from step sites, showing that CO is more strongly bound at the step sites. At low oxygen pressures (10@super-7@ Torr) oxidation occurs in two steps, beginning at terrace sites and then proceeding to step sites. At higher oxygen pressures (10@super-4@ Torr), one step oxidation at both the terrace and step sites is observed. Measuring surface carbon concentration it was determined that 60% of the CO adsorbed on the Pt(411) surface was on step sites, while the remaining 40% occupied the terrace sites. Isothermal kinetic studies were performed to establish a more detailed understanding of the oxidation mechanism. Kinetic parameters obtained in high oxygen pressures compare favorably to those on the Pt(111) surface.

Author Index

Bold page numbers indicate presenter