Wednesday Morning, November 2, 2005

Surface Science
Room 203 - Session SS2-WeM

Reactions on Metals & Oxides

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

8:20am SS2-WeM1 Reactivity of Oxygen on Au(111) in CO Oxidation, *B.K. Min*, *A.R. Alemozafar, D.S. Pinnaduwage, X. Deng, C.M. Friend,* Harvard University

Characteristics of oxygen on Au(111) related to reactivity in carbon monoxide oxidation were investigated by X-ray photoelectron spectroscopy (XPS), high resolution electron energy loss spectroscopy (HREELS) and scanning tunneling microscopy (STM). Oxygen was deposited on the Au(111) surface between 200 K - 400 K via exposure to ozone. Depending on the adsorption temperature, different characteristics of oxygen (chemisorbed and oxidic) and surface morphologies were observed. The reactivity of the oxygen-covered Au(111) surface is strongly dependent on reaction temperature; highest reactivity is observed at 200 K. Additionally, oxygen deposited at 200 K is more reactive than oxygen deposited at 300 K and 400 K. These results suggest that both reaction temperature and characteristics of oxygen are important for the reactivity of Au(111) in carbon monoxide oxidation.

8:40am SS2-WeM2 Modeling of Nanoscale Spatiotemporal Behavior in CO-oxidation on Pd(100), *D.-J. Liu, J.W. Evans,* Iowa State University

For CO-oxidation on metal surfaces, a few STM studies have begun to explore nanoscale spatial organization in titration reactions, and FIM studies have revealed propagation of near-atomically sharp reaction fronts. However, there has been almost no realistic atomistic modeling of such processes. Thus, we have developed such a model for CO-oxidation on Pd(100) exploiting DFT calculations and experimental data, e.g., on adspecies ordering, to accurately determine the small but significant lateral interactions between adspecies. Efficient kinetic Monte Carlo algorithms are developed to study model behavior. Below 300 K, the system can be characterized by coadsorption of CO and oxygen with different ordering structures. Between 300 K and 350 K, reaction occurs involving sharp moving fronts between domains of CO and oxygen. In this regime, chemical diffusion of CO is greatly inhibited due to strong interactions between adsorbates. (At higher temperatures, the interface between CO- and oxygen-rich domains becomes an extended chemical wave, familiar from PEEM studies, the profile reflecting the coverage dependent CO diffusion.) Finally, for nanoscale systems (such as field emitter tips or supported metal clusters), fluctuation-induced transitions between reactive and near-poisoned steady states were also analyzed.

9:00am SS2-WeM3 Surface Reactivity Tailored by Electron Confinement or Surface Modifiers Probed at Micro and Nano-Scales, *M. Kiskinova,* Sincrotrone Trieste, Italy **INVITED**

Most of the attempts to tailor the surface reactivity have focused on the creation of specific surface structures, where electronic perturbations are induced, or by chemical modification of the surface properties by adding small amounts of substances. Recently it has been shown that the chemical specific imaging, combined with laterally resolved structural characterizations is of vital importance for understanding key factors controlling the processes at the surface of complex systems and the related to that local reactivity. In the talk selected results obtained using chemical specific imaging, photoelectron micro-spectroscopy, low energy electron microscopy and scanning tunnelling microscopy will be presented and discussed. The effect of electron confinement in ultrathin films will be illustrated for Mg films with varying thickness at micrometer scales; they show sensible difference in the local oxidation rate, correlated to the periodic changes in the density of electronic states induced by quantum-well states crossing the Fermi level of the Mg film.@footnote 1@ The complexity of the realistic systems, where a rich variety of self-organized micro and/or nano-structures may form and coexist under reaction reactions will be illustrated using the results obtained with Rh surfaces modified with potassium or other metals.@footnote 2,3@. In will be shown that stabilization of the substrate surface reconstructions and mass transport driven self-reorganization processes are common phenomena, which may affect the composition and reactive properties of the surface at local microscopic scales. @FootnoteText@@footnote 1@ L. Aballe et al, Phys. Rev. Lett. 93, 2004, 196103. @footnote 2@ S. G@um u@nther et al, J.Chem. Phys. 117, 2002, 2923119; ibid. 119, 2003, 12503; J. Phys. Chem.

2005, in press. @footnote 3@ A. Locatelli et al, J. Am. Chem. Soc. 127, 2005, 2351.

9:40am SS2-WeM5 Rh-promoted Decomposition of Methanol Adsorbed on Cerium Oxide Thin Films, *J. Zhou,* *D.R. Mullins,* Oak Ridge National Laboratory

Metal nanoparticles supported on single crystal oxides are important model systems for industrial catalysts. Research has found that the oxide substrates can greatly influence the catalytic activity of metal particles supported on them. In our study we have found that the reverse may also be true, i.e. that Rh nanoparticles may influence the thermal decomposition of methanol adsorbed on the oxide. All of the experiments were performed under UHV conditions by temperature programmed desorption (TPD) and synchrotron soft X-ray photoelectron spectroscopy (SXPS). Methanol decomposition was first carried out on the substrate ceria films to differentiate its chemistry from that when Rh is present. SXPS indicates that methanol deprotonates to form methoxy as the only intermediate on the ceria surface. On fully oxidized ceria, chemisorbed methoxy produced methanol and formaldehyde at about 560 K. However, on reduced ceria films methoxy decomposed further to produce primarily CO and H@sub 2@. When Rh nanoparticles were added to the ceria films, methoxy decomposed to CO and H@sub 2@ regardless of the ceria oxidation state and formaldehyde formation was suppressed. The desorption temperatures and intensities of CO and H@sub 2@ were found to be dependent on the reduction of the ceria films. These results indicate that the Rh promotes the decomposition of methanol adsorbed on the ceria and that decomposition may be influenced by the diffusion of methoxy intermediates across the oxide to the metal particles. Research sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

10:00am SS2-WeM6 Adsorption of NO2 on Ultrathin @theta@-Al2O3/AlNi(100) Film: the Formation of Nitrite and Nitrate Species, *J. Szanyi,* *E. Ozensoy, C.H.F. Peden,* Pacific Northwest National Laboratory

The interaction of NO2 with an ordered @theta@-Al2O3/NiAl(100) model catalyst surface was investigated using temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). The origin of the NOx uptake of the catalytic support (i.e. Al2O3) in a NOx storage catalyst is identified. Adsorbed NO2 is converted to strongly bound nitrites and nitrates that are stable on the model catalyst surface at temperatures as high as 300 and 650 K, respectively. The results show that alumina is not completely inert and may stabilize some form of NOx under certain catalytic conditions. The stability of the NOx formed by exposing the @theta@-Al2O3 model catalyst to NO2 adsorption increases in the order: NO2 (physisorbed or N2O4) < NO2 (chemisorbed) < NO2- < NO3-.

10:20am SS2-WeM7 Correlation Between Electronic Structure and Chemical/Catalytic Reactivity of TiO@sub 2@(110) Supported Vanadia Catalysts, *S. Lee,* Texas A&M University*; G.W. Zajac,* Innovene Corporation*; D.W. Goodman,* Texas A&M University

The adsorption and reaction of ethanol on model catalysts comprised of vanadium and vanadia deposited on rutile TiO@sub 2@(110) have been studied using temperature programmed desorption (TPD), X-ray and UV photoelectron spectroscopy (XPS and UPS), metastable impact electron spectroscopy (MIES), and low energy electron diffraction (LEED). Vanadium and vanadia films were prepared on TiO@sub 2@(110) under UHV conditions and the changes in their electronic properties were monitored following the adsorption and reaction of ethanol. Comparisons are made to Density of States generated from DFT calculations of small slabs of VO@sub x@/TiO@sub 2@ (Rutile) via the commercial codes of CASTEP and DMOL@super 3@ from Accelrys Inc. Dissociative adsorption of ethanol leads to the formation of ethylene at 650 K on TiO@sub 2@ supported vanadium. The activity for this reaction was found to depend markedly on the vanadium oxidation state.

10:40am SS2-WeM8 Catalytic Activity of WO@sub 3@ Clusters on TiO@sub 2@(110): Trimerization of Formaldehyde, *J. Kim,* Pacific Northwest National Laboratory*; O.A. Bondarchuk,* University of Texas, Austin*; Z. Dohnálek,* Pacific Northwest National Laboratory*; J.M. White,* University of Texas at Austin*; B.D. Kay,* Pacific Northwest National Laboratory

The catalytic activity of supported, high surface area transition metal oxides (TMO) catalysts have been extensively studied. In contrast, only a few studies have been conducted on transition metal oxide clusters supported on well-ordered, singe-crystalline oxide surfaces In this study,

the catalytic activity of WO@sub 3@ clusters deposited on a well-characterized TiO@sub 2@(110) surface was examined. The clusters were deposited via direct, thermal evaporation of WO@sub 3@. This deposition technique provides a reliable, carbon free source of W in the (6+) oxidation state as shown by X-ray photoelectron spectroscopy (XPS). Related scanning tunneling microscopy (STM) studies reveal that 600 K-annealed WO@sub 3@ clusters are monodispersed and ~1 nm in diameter. Temperature programmed desorption (TPD) of N@sub 2@ reveals that the structure of WO@sub 3@ does not changed significantly between 400 - 600 K. We have examined the adsorption of formaldehyde (H@sub 2@CO) on TiO@sub 2@(110) and on WO@sub 3@ (< 4 x 10@super 14@ WO@sub 3@/cm@super -2@) on TiO@sub 2@(110). On TiO@sub 2@(110), H@sub 2@CO adsorbs and desorbs molecularly for all coverages. On WO@sub 3@/TiO@sub 2@(110), the adsorption of H@sub 2@CO multilayers results in the catalytic formation of trioxane. The trimerization yield increases with the amount of adsorbed H@sub 2@CO and saturates for coverages exceeding ~10 ML. Submonolayer coverage of H@sub 2@CO do not yield any trioxane product. The yield increases linearly with the amount of deposited WO@sub 3@ and the reaction can be run repeatedly. @FootnoteText@ *Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

11:00am SS2-WeM9 Growth and Reactivity of Palladium Oxide Thin Films, *J. Wang, E.I. Altman,* Yale University

Palladium has become the catalyst of choice for the catalytic combustion of hydrocarbons in low NOx gas turbines. Recent studies suggest that oxidized Pd is a more active catalyst for the complete oxidation of hydrocarbons. Our prior work on the oxidation of CO and C3H6 on oxygen-covered Pd(100) showed that on the more oxygen rich surface there existed a direct oxidation route for C3H6 that proceeds with a lower activation energy than dissociation to C followed by oxidation to CO2. It was impossible to increase the oxygen coverage much beyond the oxide-like monolayer by dosing with O2 or NO2 in UHV. Two approaches are carried out to access the regime where bulk PdO forms: oxidizing the Pd(100) using an oxygen plasma in UHV; and direct growth of PdO thin films. In the first approach, XPS showed that exposure to the plasma at 575 K created bulk PdO, while temperature programmed desorption (TPD) showed an order of magnitude increase in the amount of oxygen compared to NO2 exposure. The reactivity of C3H6 on such surfaces is studied using TPD, isothermal kinetic measurements, and LEED. TPD is used to measure adsorption/reaction kinetics; mass spectroscopy to search for potential reaction products. Isothermal oxygen titration studies are performed by loading oxygen and then exposing to the reductant at fixed temperatures, which yields reaction rates versus oxygen coverage at constant temperatures, repeating the experiments at different temperatures yields activation energies. In the second approach, single crystal PdO(001) films are grown on MgO(100) substrate using oxygen plasma assisted molecular beam epitaxy (OPA-MBE). In situ reflection high energy electron diffraction (RHEED) is used to monitor the growth. Ex situ XRD, LEED, XPS and UPS are used to study the bulk and surface orientation, the surface composition and chemical states. The reactivity of the epitaxial films towards C3H6 will be compared with that of the poorly ordered PdO formed by oxidizing Pd(100).

11:20am SS2-WeM10 Growth and Catalytic Activity of Epitaxial Palladium(111) Films, *Z. Dohnalek, J. Kim, B.D. Kay,* Pacific Northwest National Laboratory

Thin Pd films of various thickness were deposited on FeO(111) and Pt (111) substrates at 40 K. The morphology of the resulting films was characterized using low energy electron diffraction, Auger electron spectroscopy, and Kr and CO temperature programmed desorption as a function of annealing. The Pd layers deposited on Pt(111) are stable and develop into a well ordered Pd(111) films at annealing temperatures ranging from 500 to 1000 K. The Pd films deposited on FeO(111) can be ordered by annealing to 500 K but dewet upon heating to higher temperatures. The efficiency of ethylene hydrogenation was examined on these films as a function of their thickness and surface order. As the Pd(111) film thickness is decreased from 100 to 3 monolayers (ML), only a small increase (1 to 2%) in the hydrogenation efficiency is observed. This implies that H diffusion into the bulk does not play an important role for the films in this thickness range. A dramatic increase in the hydrogenation efficiency, resulting in yields up to 50%, occurs on the films covered with a disordered Pd layer (0-2ML) deposited at 40 K suggesting that the hydrogenation reaction is a structure dependent reaction. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

11:40am SS2-WeM11 Structure-Activity Relationship: The Case of CO and CO@sub 2@ Adsorption on ZnO(0001), H/ZnO(0001), Cu/ZnO(0001), *J. Wang, S. Funk, B. Hokkanen, E. Johnson,* North Dakota State University; ***U. Burghaus,*** North Dakota State University, Cass

Molecular beam scattering techniques were combined with thermal desorption spectroscopy (TDS) and applied to a number of different Zn-terminated ZnO systems; namely, clean ZnO(0001), defected ZnO(0001), H precovered ZnO(0001), and Cu precovered ZnO(0001). Furthermore, CO and CO@sub 2@ have been used as probe molecules with the goal to address the Structure-Activity Relationship (SAR). The CO@sub 2@-TDS curves consist of two distinct structures. By modifying the surface with Ar+ ion sputtering (more defects) and H-preadsorption (fewer defects), the two TDS structures could be assigned to adsorption of CO@sub 2@ on pristine and intrinsic defect sites with binding energies of 34.4 kJ/mol and 43.6 kJ/mol, respectively. Furthermore, He atom reflectivity curves indicated adsorption of CO@sub 2@ on defects. Thus, a kinetic SAR is evident. (See, Chemical Physics Letters 403 (2005) 42). Furthermore, a dynamic SAR was present in CO adsorption on the Cu/ZnO(0001) model catalyst. Whereas on small Cu sized-deposits, direct Langmuirian adsorption dynamics were observed; larger cluster sizes lead to the detection of precursor mediated adsorption dynamics of CO. Thus, the energy transfer processes governing the adsorption of a gas phase species on the surface depended distinctly on the morphology of the metal-on-metal oxide system. In the case of CO@sub 2@-Cu/ZnO(0001) a strong metal support interaction was observed; TDS and beam scattering data provide consistent hints that CO@sub 2@ populates predominantly along the rim of the Cu clusters. Monte Carlo Simulations have been applied for modeling of the molecular beam scattering data.

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