

Thursday Afternoon, November 16, 2006

Surface Science

Room 2002 - Session SS1-ThA

Reactivity of Oxide Surfaces II

Moderator: Z. Dohnalek, Pacific Northwest National Laboratory

2:00pm **SS1-ThA1 Effect of Pt on Clean and Oxidized Surfaces of (Ni, Pt)@sub3@Al**, F. Qin, Iowa State University; J.W. Anderegg, C.J. Jenks, Ames Laboratory; C. Jiang, B. Gleeson, Iowa State University; D.J. Sordelet, Ames Laboratory; P.A. Thiel, Iowa State University

We have used experimental techniques (XPS, AES, LEED LEIS and STM) and a theoretical technique (DFT) to investigate the clean and oxidized surfaces of ternary (Ni, Pt)@sub3@Al single crystals. Regarding the clean surface, our experiment results indicate that Pt segregates to the surface. Density functional calculations in the dilute limit confirm that Pt segregation is favored energetically. Regarding the oxidized surface, we systematically examined the amount, chemical nature, and spatial distribution of the oxide that forms upon saturation at oxygen pressures in the range of 10@super-8@ to 10@super-6@ Torr, as a function of oxidation temperatures (300 to 900 K) and as a function of Pt content. We found that the predominant oxide between about 300 and 700 K is NiO, covered by a thin top layer of aluminum oxide, whereas between 700 and 900 K the predominant oxide is aluminum oxide. Pt exerts four effects: (a) Pt decreases the maximum amount of NiO; (b) Pt shifts formation of Al@subx@O@suby@ to lower temperatures; (c) Pt decreases the maximum amount of Al@subx@O@suby@; and (d) Pt slows the oxygen adsorption on the clean surface.

2:20pm **SS1-ThA2 The Hydrogen Cycle on the CeO@sub 2@ Surface**, M. Watkins, University College London, UK; A.S. Foster, Helsinki University of Technology, Finland; A.L. Schluger, University College London, UK

The ability of Cerium atoms to exist in varying charge states permits facile surface oxidation/reduction allowing ceria to mediate oxygen concentration when part of a mixed metal oxide catalyst. There is an extensive literature on the reduction/oxidation behaviour, however, experimental conditions and uncertainties in sample preparation make interpretation of experimental data difficult. We present density functional calculations implementing the generalized gradient approximation (GGA) and on site coulomb interactions (GGA+U) on the most stable surface of Ceria, specifically focusing on its interactions with hydrogen and water. Our calculations allow us to consider the process of surface reduction and the probable state of lightly reduced surfaces in the presence of water, allowing insight into surface processes in a variety of conditions. Several interesting properties of the Ceria surface are brought to the fore - the dissociation of water molecules on the ideal surface, the rapid dissociation of water at vacancy sites and the strongly exothermic dissociation of H@sub 2@ on the ideal surface. These results have strong implications for the interpretation of experimental data, and the construction of reaction schemes for this technologically important metal oxide surface.

2:40pm **SS1-ThA3 Microscopic Studies on Dynamic Processes on Metal Oxide Surfaces Relevant to Oxide Catalyses**, K. Fukui, Tokyo Institute of Technology, Japan

INVITED

Scanning probe microscopy (SPM) has great potential to understand site specific surface processes while preparation of catalysts and the role of surface defects in chemical reactions, which are key issues for developing metal oxide catalyses. In this talk, I will review our SPM studies on CeO@sub 2@(111) and Al@sub 2@O@sub 3@/NiAl(110) surfaces. CeO@sub 2@ is used for catalysts, fuel cells, etc., and their high oxygen transport and storage capacities are important for the applications. By using noncontact atomic force microscopy (NC-AFM), we have succeeded in visualizing various kinds of surface oxygen defects and highly mobile oxygen atoms around metastable multiple defects that are not reconstructed for stabilization.@footnote 1@ Activation energy for hopping of the mobile surface oxygen was estimated to be about 30 kJ mol@super -1@ from the consecutive SPM imaging of a slightly reduced CeO@sub 2@(111) at 300-400 K. We have also observed high reactivity of oxygen atom facing to the oxygen defect for extraction of hydrogen atom from the methoxy intermediate. We have been applying nonvolatile precursors for preparation of catalyst model surfaces. Water solution of [Rh(OAc)@sub 2@]@sub 2@ is ejected through a pulse-valve to a well ordered Al@sub 2@O@sub 3@/NiAl(110) under ultrahigh vacuum. By slowly annealing the precursor- adsorbed surface to 493 K, the Rh precursor decomposed and homogeneous metal clusters that contain 2-4

Rh atoms were observed by STM. It can be explained by decomposition kinetics of the precursor molecules. Finally, I will briefly introduce chemical identification of surface intermediates by using a single 'molecular tip' that can be switched by external light irradiation.@footnote 2@ @FootnoteText@ @footnote 1@ K. Fukui, S. Takakusagi, R. Tero, M. Aizawa, Y. Namai, and Y. Iwasawa, Phys. Chem. Chem. Phys. 5, 5349-5359 (2003).@footnote 2@ D. Takamatsu, Y. Yamakoshi, and K. Fukui, J. Phys. Chem. B 110, 1968-1970 (2006).

3:20pm **SS1-ThA5 Oxidation of NiAl(111)**, E. Loginova, F. Cosandey, T.E. Madey, Rutgers University

Our research is focused on faceting of Al@sub 2@O@sub 3@/NiAl(111) and is motivated by the possibility that alumina thin-film-covered NiAl facets might be used as oxide templates for transition metals in heterogeneous catalysis. We have performed a series of experiments aimed at understanding the adsorption of oxygen and oxygen-induced faceting of NiAl(111) using LEED, AES, SEM, AFM and high-resolution soft XPS (HRXPS, by means of synchrotron radiation at NSLS). The atomically rough NiAl(111) surface remains planar at room temperature when exposed to oxygen. However, the oxygen-covered surface changes its morphology and becomes faceted upon annealing at 1100K and higher; nucleation and growth of nanoscale {110} facets are observed. The adsorption and reaction of oxygen are characterized by HRXPS measurements of Al 2p and Ni 3p core levels for the faceted and planar surfaces. Moreover, after prolonged exposure to oxygen at elevated temperatures unusual three dimensional features exhibiting three-fold symmetry erupt from the surface and are oriented along low index directions; their dimensions are several micrometers in length, and 250 to 400nm high. A SEM X-ray EDS mapping study indicates that these are spinel (NiAl@sub 2@O@sub 4@) structures. A proposed qualitative model of spinel formation is as follows: when the oxygen-covered surface is annealed to elevated temperatures, oxygen diffuses below the surface and aluminum oxide nanoclusters may nucleate together with neighboring Ni-rich regions. Upon further annealing, a subsurface nucleation of NiAl@sub 2@O@sub 4@ spinel takes place at the Al@sub 2@O@sub 3@/Ni interface. Lattice strain is relieved by eruption of the spinel structures above the surface.

3:40pm **SS1-ThA6 Substrate-controlled Limiting Thickness for Nanoscale Alumina Film Growth on Single Crystal Nickel Aluminides under non-UHV Conditions**, J.A. Kelber, N.P. Magtoto, M. Jain, C. Vamala, University of North Texas

Nanothin ordered alumina films exposed to H@sub 2@O at partial pressures above UHV reach limiting thicknesses governed entirely by the structure of the nickel aluminide substrate (NiAl(110) vs. Ni@sub 3@Al(110)). This work provides a basis for developing quantitative predictive models of the Mott-Cabrera mechanism, and also indicates that such nanothin films have important differences from bulk oxides in non-UHV environments. Auger, LEED, and STM were used to characterize alumina films grown on single crystal substrates in UHV, and exposed to 10@super -7@ Torr < p@sub 2@O < 10@super -3@ Torr/300 K in an adjacent environmental chamber. Film thickness was characterized by Auger spectroscopy. Films grown on NiAl(110) reach a limiting thickness of 17±1 angstroms independent of initial thickness or roughness, while films grown on Ni@sub 3@Al(110) displayed a limiting thickness of 12± 1 angstroms. The different thicknesses correspond to different energies for transfer of an Al atom from the substrate into the oxide, with the larger number of Ni-Al bonds for Ni@sub 3@Al leading to a higher barrier on that substrate. The implications of these results for ultrathin alumina films as model catalyst supports and in nanoelectronics will be discussed.

4:00pm **SS1-ThA7 NOx Storage Capacity and Thermal Aging of BaO/theta-Al2O3/NiAl(100) Model Catalyst**, J. Szanyi, E. Ozensoy, C.H.F. Peden, Pacific Northwest National Laboratory

NOx storage behavior of a BaO/θ-Al₂O₃/NiAl(100) model catalytic system during NO₂ adsorption was studied via X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) techniques; and compared to that of the θ-Al₂O₃/NiAl(100) support material and a thermally-aged BaO/θ-Al₂O₃/NiAl(100) model catalyst at 1100K. At T > 300 K, adsorbed NO₂ is converted to nitrates on all of the surfaces studied. Nitrates that are residing on the alumina sites of the model catalyst surfaces are relatively weakly bound and typically desorb within 300 K-600 K, leading to NO(g) evolution; while nitrates associated with the baria sites are significantly more stable and desorb within 600 K- 850 K, resulting in NO(g) or NO(g)+O₂(g) evolution. NOx uptake by the baria sites of the BaO/θ-Al₂O₃/NiAl(100) model catalyst surface was found to be as high as a

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factor of five with respect to that of the γ -Al₂O₃/NiAl(100) support material. Thermal aging of a BaO/ γ -Al₂O₃/NiAl(100) model catalyst surface at 1100 K prior to NO_x uptake experiments, brings about a significant (70 %) reduction in the NO_x storage capacity of the model catalyst surface.

4:20pm SS1-ThA8 Molecular Understanding of NO_x-Storage-Reduction Catalysts: NO₂ and H₂O Adsorption on BaO/ γ -Al₂O₃/NiAl(100), E. Ozensoy, J. Szanyi, C.H.F. Peden, Pacific Northwest National Laboratory

NO_x storage-reduction (NSR) catalysts were introduced very recently as an alternative way to treat NO_x emissions originating from diesel mobile sources that are operating with high air to fuel ratios where traditional three way catalysts fail to perform. Unfortunately current understanding of NSR technology is mostly based on the industrial combinatorial studies which are focused on the product development rather than the fundamental molecular aspects of these interesting systems. Therefore here in this work, we present the very first detailed surface science study on the NSR systems where BaO nanoparticles deposited on an atomically ordered γ -Al₂O₃ ultrathin film grown on a clean NiAl(100) surface, is used as a model catalyst to mimic the industrial counterpart. BaO growth behavior on Al₂O₃/NiAl(100) was studied using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), temperature programmed desorption (TPD) and low energy electron diffraction (LEED). Chemical and catalytic behavior of the BaO/Al₂O₃/NiAl(100) system is also investigated using H₂O and NO₂ as probe molecules in comparison with the clean γ -Al₂O₃/NiAl(100) surface. Preliminary results indicate that BaO deposition on γ -Al₂O₃/NiAl(100) at 300 K results in three dimensional BaO clusters which tend to wet the alumina surface upon heating up to 800 K. At higher temperatures (i.e. within 800-1200K), BaO desorption from the surface as well as interdiffusion of Ba into the Al₂O₃ lattice is observed. TPD studies indicate that NO_x storage capacity of the BaO phase is significantly higher than that of the Al₂O₃ support. Our XPS and TPD data reveals that in the BaO phase, NO_x is stored in the form of nitrates (NO₃⁻) and nitrites (NO₂⁻) that are stable up to 850 K. Co-adsorption of H₂O and NO₂ on BaO/Al₂O₃/NiAl(100) and γ -Al₂O₃/NiAl(100) surfaces was also studied using TPD to address competition for the different adsorption sites in NSR catalysts.

4:40pm SS1-ThA9 Oxygen-induced Surface Structures of Nb(110) Studied by LEED, AES and STM, B. An, S. Fukuyama, K. Yokogawa, AIST, Japan

Nb has attracted a great attention as a superconductive material and a hydrogen storage material; however, the material performance of Nb is extremely sensitive to surface oxides. Thus, the interaction of oxygen with Nb surface has been extensively studied by LEED-AES, XPS and EELS. Recently, we have studied the clean and oxygen-induced surface structures of Nb(100)¹ and Nb(111)² by STM with atomic resolution. In this study, we present the surface structures of Nb(110) formed during thermal cleaning in UHV and oxidation in low-pressure oxygen at 300 and 900 K by combined LEED, AES and STM. A quasi-periodically arranged sticklike structure, and the (3x1)-O, c(6x2)-O and clean (1x1) structures are sequentially observed on the Nb(110) surface at atomic resolution during thermal cleaning in UHV at temperatures from 1970 to 2500 K. At 300 K, the clean (1x1) surface is sequentially oxidized into the c(6x2)-O and (3x1)-O structures and the amorphous oxides in oxygen. At 900 K, the clean (1x1) surface is sequentially oxidized into the c(6x2)-O and sticklike structures in oxygen. The c(6x2)-O and (3x1)-O structures result from oxygen chemisorption and the sticklike structure results from the epitaxial growth of NbO_x oxide on Nb(110) surface. Atomic models for these oxygen-induced structures and the atomic-scale oxidation processes of the Nb(110) surface at 300 and 900 K are discussed. ¹B. An et al., Phys. Rev. B 68, 115423 (2003). ²B. An et al., 13th International Conference on Scanning Tunneling Microscopy/Spectroscopy and Related Techniques (STM2005), Abstracts, Sapporo, Japan, July 3-8, 2005, p. 81.

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