Surface Science
Room 2002 - Session SS1-ThM

Reactivity of Oxide Surfaces I
Moderator: M.A. Henderson, Pacific Northwest National Laboratory

8:00am SS1-ThM1 Interaction of Gold Atoms and Clusters with Color Centers on the Surface of MgO(001) Thin Films, *M. Sterrer, T. Risse,* Fritz-Haber-Institute of the Max-Planck-Society, Germany*; G. Pacchioni,* University of Milano-Bicocca, Italy*; H.-J. Freund,* Fritz-Haber-Institute of the Max-Planck-Society, Germany

Catalytic activity of metal clusters may strongly be influenced by the properties of the underlying oxide support. The Au/MgO system has emerged to a prototype example in this respect because of the possibility for charge transfer from surface trapped electron centers (color centers) to adsorbed metal atoms and clusters, thus forming negatively charged metal particles. In this contribution, experimental results on the properties of single gold atoms nucleated on regular as well as color center containing MgO(001) surfaces will be presented and compared with calculated data. Electron Paramagnetic Resonance (EPR) spectroscopy and low-temperature (5K) Scanning Tunneling Microscopy (STM) has been applied to characterize single gold atoms, as well as color centers formed by electron bombardment, on the surface of MgO(001) thin films. The interaction of Au atoms and clusters with surface color centers has been monitored with infrared spectroscopy using CO as a probe for the charge state of gold particles. For single atoms and small clusters adsorbed onto color centers the observed redshift of the CO stretching frequency in comparison to CO adsorbed on neutral Au clusters is indicative for negatively charged entities. However, an even larger redshift is observed for CO on single Au atoms adsorbed on regular MgO sites. The origin of this unusual behavior will be discussed.

8:20am SS1-ThM2 Calcium Adsorption on MgO(100): Calorimetric and Structural Studies, *C.T. Campbell, J.F. Zhu, N. Ruzycki,* University of Washington

The adsorption of Ca on the MgO(100) surface at 300 K has been studied using microcalorimetry, in combination with LEED, AES, ISS, work function and sticking probability measurements. The sticking probability of Ca on MgO(100) at 300 K is unity. The growth of Ca on MgO(100) follows the Stranski-Krastanov mode (i.e, 2D growth and thereafter followed by 3D islands). No ordered structure can be found in LEED during Ca adsorption. Initially, Ca adsorbs cationically at defect sites (~ 6% of the surface) with a high heat of adsorption (~ 425 kJ/mol). After these sites fill, Ca grows to complete the first layer with a heat of adsorption of 167 kJ/mol. Afterwards, it grows 3D islands and its heat approaches that of Ca's bulk heat of sublimation (179 kJ/mol). Ion sputtering of the MgO surface generates O vacancies which adsorb Ca with a heat of ~350 kJ/mol.

8:40am SS1-ThM3 Probing of the Surface Chemistry and Binding Modes of DL-proline on TiO@sub2@(110) Single Crystal Surface: A Study via High Resolution X-ray Photoelectron Spectroscopy and Temperature Programmed Desorption, *G.J. Fleming,* The University of Auckland, New Zealand*; K. Adib, J.A. Rodriguez,* Brookhaven National Laboratory*; M.A. Barteau,* University of Delaware*; H. Idriss,* The University of Auckland, New Zealand

The use of titanium metal as a biomaterial has become common place in modern medicine due to its desirable mechanical properties and the relative chemical inertness.@footnote 1,2@ This has lead to the use of titanium in many medical applications ranging from hip replacements to aiding in the healing of fractures that occur in teeth and bones. When the titanium implant is placed inside the body's aqueous environment an oxidation process occurs, where an oxide layer forms in the range of approximately 10-100 nm thick. This layer is crucial since it prevents the Ti metal from further reacting with the biological molecules. However, it is the nature of the interaction of the bio-molecule with this thin TiO@sub2@ surface which ultimately determines the molecules final conformation. In this work we discus the surface chemistry and the nature of the interactions of DL-proline, a major constituent of the main structural protein in the body collagen I, on both oxidised and reduced TiO@sub2@(110) single crystal surfaces using High Resolution X-Ray Photoelectron Spectroscopy (HR-XPS) and Temperature Programmed Desorption (TPD). Upon adsorption on to the oxidised surface at 300 K, the N 1s spectrum revealed that proline is present as two distinct species: molecular (-NH-) and zwitterionic proline (-NH@sub2@@super+@-). Via the use of variable temperature XPS, the zwitterionic species was found to be only weakly adsorbed and removed form the surface by approximately 600 K. On the reduced surface, an increase in the amount of zwitterionic species adsorbed to the surface was found and can be attributed to the loss of bridging oxygen atoms from the (110) surface. TPD experiments show a very complex reaction pathways, in particular on the reduced surfaces, similar in nature to previous studies performed on the TiO@sub2@(011) surface.@footnote 3@. @FootnoteText@@footnote 1@F.H Jones, Surf. Sci. Rep. 2001 42, 75. @footnote 2@B. Kasemo, Surf. Sci. 2002, 500, 656 @footnote 3@G.J. Fleming and H. Idriss, Langmuir, 2004, 20, 7540.

9:00am SS1-ThM4 Density Functional Study of the Dissociative Adsorption of Formic Acid on the TiO@sub 2@ Rutile (0 1 1) Surface, *P.R. McGill, H. Idriss,* University of Auckland, New Zealand

Titanium dioxide is used or present (as a consequence of oxidation of a titanium metal surface) in a range of applications, such as catalysts and medical implants, where its interaction with small adsorbed molecules is of considerable interest. While a number of studies have been conducted in this area, the majority of these have focused on the rutile (1 1 0) surface. The rutile (0 1 1) surface and its interaction with adsorbed species, while being the subject of a number of practical investigations, has until recently been neglected by computational studies. LEED evidence@footnote 1@ suggests that the (0 1 1) surface undergoes a 2x1 reconstruction as opposed to being bulk-terminated. Recently, a computational study@footnote 2@ has proposed a model for this 2x1 surface, and shows it to have several unique features such as Ti=O double bonds. In this work, periodic density functional calculations employing the PBE exchange-correlation functional and plane wave basis sets,@footnote 3@ are carried out on the adsorption of formic acid to the bulk-terminated and 2x1 models of the TiO@sub 2@ (0 1 1) surface. The 2x1 model is found to be more reactive, producing larger adsorption energies. A variety of interactions are possible for formic acid. Dissociative modes are considered because of the many experimental results which show their stable presence at room temperature. The acidic proton is thus assumed to transfer to a surface oxygen, while the remaining formate species interacts through its oxygens with one surface titanium in a monodentate or chelating fashion, or two surface titaniums in a bridging fashion. Stable conformations are found for the bridging and monodentate configurations. @FootnoteText@ @footnote 1@L. E. Firment, Surf.Sci. 116, 205 (1982)@footnote 2@T.J. Beck, A. Klust, M. Batzill, U. Diebold, C. Valentin, A. Selloni, Phys.Rev. Lett. 93, 036104 (2004)@footnote 3@Calculations performed using PWSCF, by S. Baroni, S. de Gironcoli, A. dal Corso, P. Giannozzi.

9:20am SS1-ThM5 Structure and Catalytic Activity of Model Oxide Systems, *O. Bondarchuk, Z. Zhang,* University of Texas at Austin*; J. Kim,* Pacific Northwest National Laboratory*; J.M. White,* University of Texas at Austin*; B.D. Kay, Z. Dohnalek,* Pacific Northwest National Laboratory
INVITED

The rutile form of titania, and particularly the [110] surface has become the prototypical substrate for studies of model system metal oxide surface chemistry. We combined atomically resolved imaging and ensemble averaged techniques to examine the adsorption, dissociation, and partial oxidation of alcohols on TiO@sub 2@(110) and (WO@sub 3@)@sub 3@/TiO@sub 2@(110) model catalysts. On clean TiO@sub 2@(110) the images obtained from the same area before and after adsorption show that alcohols adsorb preferentially on oxygen vacancies and that their dissociation occurs via O-H bond scission. The dynamics of proton diffusion was examined as a function of alcohol coverage. Model (WO@sub 3@)@sub 3@/TiO@sub 2@(110) systems were prepared using direct sublimation of WO@sub 3@ and characterized using high resolution Scanning Tunneling Microscopy, X-ray photoelectron spectroscopy and N@sub 2@ physisorption. Reactivity studies of this system towards alcohol dehydration and formaldehyde polymerization have been carried out in an ensemble averaged manner using molecular beam scattering and temperature programmed desorption techniques. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

10:00am SS1-ThM7 Point Defect and Adsorbate Identification on TiO$_2$(110) by Non-Contact AFM, *J.V. Lauritsen*, G.H. Olesen, M.C. Christensen, University of Aarhus, Denmark; *A.S. Foster,* Helsinki University of Technology, Finland; *M. Reichling,* University of Osnabruck, Germany; *F. Besenbacher,* University of Aarhus, Denmark

The AFM can provide atomic-scale insight into the surface structure of in principle any type of oxide. In order to apply AFM to study surface chemistry it is essential to understand the contrast patterns associated with surface defects and adsorbates. This is not trivial, since the atomic contrast is determined by interactions between the surface and the tip which is mostly in an undefined state. In this study, we successfully identify defects and adsorbates present on a reduced TiO$_2$(110) surface under UHV conditions by means of atom-resolved non-contact AFM images and theoretical simulations. We make use of the fact that we can image the TiO$_2$ surface with two well-defined tip states characterized by different short-range interactions reflecting a negatively or a positively charged tip, respectively. The details of the complementary images for the two types of tip allow us to unambiguously identify the Ti^{4+} and O^{2-} sub-lattices and hence investigate the exact structure and location of defects on the metal oxide surface. A detailed statistical analysis of atom-resolved AFM images shows that three different types of defects can be seen in the first hours after sample preparation. Interestingly, the same defects are imaged either as holes in the oxygen rows or as protrusion located between the Ti rows depending on the tip charge. By comparing the characteristic contrast patterns with detailed AFM simulations for both tips, we provide a qualitative and quantitative interpretation of the AFM images, including the identification of the three types of defects as bridging oxygen vacancies and two types of bridging hydroxyls (OH) resulting from water dissociation, respectively. The observation that the AFM tip can be functionalized in situ to discriminate between chemically different elements of an oxide surface is interesting and may provide an attractive method to perform adsorbate identification on other interesting metal-oxide systems.

10:20am SS1-ThM8 H$_2$O Dissociation and Proton Diffusion on TiO$_2$(110), *Z. Zhang*, O. Bondarchuk, J.M. White, University of Texas at Austin; *B.D. Kay, Z. Dohnálek,* Pacific Northwest National Laboratory

Rutile TiO$_2$(110) is a leading model oxide surface for the investigation of defect-related surface chemistry. The TiO$_2$ - H$_2$O system is of particular interest for both fundamental and applied science. We employed in situ Scanning Tunneling Microscopy (STM) to examine the adsorption and dissociation of water on bridge-bonded oxygen vacancies (BBO$_v$) of the TiO$_2$(110) surface. Provided the H$_2$O coverage (< 2.5%) is less than the BBOv concentration (~10%), atomically resolved images taken at room temperature before and after water dose confirm the titration of individual BBO$_v$ by dissociative adsorption of H$_2$O. The products are two hydroxyl species, one positioned at the BBO$_v$, denoted OH$_v$, and the other, denoted OH$_b$, formed by protonation at either of the two nearest-neighbor bridging oxygen atoms. The protons formed by water dissociation are observed to diffuse along the BBO row. Surprisingly, the probability of OH$_b$ diffusion is ~10 times higher than that of OH$_v$, demonstrating their inequality. The research described in this presentation was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

10:40am SS1-ThM9 Water Adsorption from Submonolayer to Multilayer Coverage on TiO2(110) and Fe2O3(0001) by In Situ Spectroscopy, *G. Ketteler,* Chalmers University of Technology, Sweden; *S. Yamamoto,* Stanford Synchrotron Radiation Laboratories; *H. Bluhm,* LBNL; *T. Kendelewicz,* Stanford University; *K. Andersson,* Stanford Synchrotron Radiation Laboratory; *D.E. Starr,* LBNL; *G.E. Brown Jr.,* Stanford University; *A. Nilsson,* Stanford Synchrotron Radiation Laboratory; *M. Salmeron,* LBNL

Despite their importance in environmental, chemical and biological sciences, the bonding structure of water at interfaces in equilibrium with vapor remains poorly understood. We have studied the adsorption of water on a rutile TiO$_2$(110) and hematite Fe$_2$O$_3$(0001) single crystal from submonolayer to several multilayer coverage by in situ X-ray photoemission at temperatures above 270 K in the presence of vapor pressures of up to 1.5 Torr. We find that water adsorption occurs in distinct steps that are determined by the availability of surface sites for hydrogen bonding. On TiO$_2$(110), very acidic sites such as O-vacancy defects present in high vacuum conditions disappear rapidly to form ~0.25 ML of OH species on bridging positions when the vapor pressure becomes larger than 10^{-4} Torr. A similar coverage of molecular water binds strongly to these acidic sites by charge transfer from the oxygen atom of water to the hydrogen atoms of the OH group (hydrogen bonding). This acts as a nucleation site for further water adsorption on both sides along the Ti troughs. We find no indication of a hydroxylation of regular terrace sites. The enthalpy and entropy of condensation over a wide coverage range were determined by analysis of equilibrium isobars. On Fe$_2$O$_3$(0001), defects as well as regular terrace sites are hydroxylated prior to water adsorption. Water adsorption occurred for higher relative humidity than on TiO$_2$(110) (5×10^{-3} vs. 10^{-6} % RH), and most likely it is bound to terrace OH groups. Based on these findings and NEXAFS we were able to propose a structure model for the H-bonded structures that determine water adsorption on rutile(110) and hematite(0001) from submonolaye to multilayer coverage. We will correlate the affinity of oxide surfaces to react with and bind water with the acido-basic properties of different surface functionalities.

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