Surface Science
Room: C-112 - Session SS3-TuM

Metals, Adsorbates, and Defects on TiO_2
Moderator: R.L. Kurtz, Louisiana State University

8:20am **SS3-TuM1 Effects of Cluster Size and Deposition Energy on Adsorption and Sintering Behavior of Metal Nanoclusters on Oxide Supports**, *M. Aizawa, S. Lee,* University of Utah, *J. Lee,* Seoul National University, Korea, ***S.L. Anderson***, University of Utah **INVITED**

Size-selected metal nanoclusters on oxide supports are prepared by deposition of pre-formed, mass-selected cluster ions, allowing impact energy to be varied over a wide range. The samples thus prepared, are probed by a combination of XPS, AES, ISS, and TPD, providing insight into changes in oxidation state, morphology, and chemical behavior, induced by varying deposition conditions, thermal processing, and exposure to adsorbates. Results will be presented for Ni_n and Ir_n on TiO_2. In both cases, the clusters appear to be stable with respect to breakup or sintering for a range of deposition energies on room temperature substrates. Significant morphology changes are observed following exposure to adsorbates. Both the adsorbate interation strengths and morphology changes are strongly size dependent.

9:00am **SS3-TuM3 Bonding of Gold Nano-Clusters to Vacancies on Rutile TiO_2(110)**, ***E. Wahlström***, *R. Schaub*, University of Aarhus, Denmark, *N. Lopez*, Technical University of Denmark, *A. Ronnau*, University of Aarhus, Denmark, *J.K. Norskov*, Technical University of Denmark, *F. Besenbacher*, University of Aarhus, Denmark

We have studied the early stages of Au cluster nucleation on defective rutile TiO_2(110) using scanning tunneling microscopy (STM). STM images and STM movies show a diffusion controlled growth mechanism. Room temperature STM movies show that the smallest stable clusters have a radius > 0.6 nm, while at 140 K not even single gold atoms seem to diffuse on the surface. It is also shown that a correlation exists between a decrease in density of bridging oxygen vacancies and growth of Au clusters at all investigated temperatures. This is direct evidence of a strong interaction between Au atoms and single atomic oxygen vacancies. Density functional theory calculations support these findings.

9:20am **SS3-TuM4 The Chemical and Catalytic Activity of Au/TiO_2(110) towards Sulfur Dioxide**, ***Z. Chang***, *J.A. Rodriguez, G. Liu, T. Jirsak, J. Hrbek, J. Dvorak,* Brookhaven National Laboratory, *A. Maiti*, Accelrys Inc.

Bulk metallic gold typically exhibits a very low chemical and catalytic activity. Recently gold has become the subject of a lot of attention due to its unusual catalytic properties when dispersed on some oxide supports. Gold particles supported on titania are active catalyst for the low temperature oxidation of CO, the selective oxidation of propene, and photocatalytic oxidations used for environmental cleanup. We used synchrotron-based high-resolution photoemission and first-principles density-functional slab calculations to study the interaction of gold with titania and the chemistry of SO_2 on Au/TiO_2(110) surfaces. Au/TiO_2 is much more chemically active than metallic gold or stoichiometric titania. On Au(111) and rough polycrystalline surfaces of gold, SO_2 bonds weakly and desorbs intact at temperatures below 200 K. For the adsorption of SO_2 on TiO_2(110) at 300 K, SO_4 is the only product. In contract, Au/TiO_2(110) surfaces fully dissociate the SO_2 molecule under identical reaction conditions. Interactions with titania electronically perturb gold, making it more chemically active. Furthermore, our experimental and theoretical results show quite clearly that not only gold is perturbed when gold and titania interact. The adsorbed gold, on its part, enhances the reactivity of titania by facilitating the migration of O vacancies from the bulk to the surface of the oxide. In general, the complex coupling of these phenomena must be taken into consideration when trying to explain the unusual chemical and catalytic activity of Au/TiO_2. The research was carried out at BNL under Contract No. DE-AC02-98CH10086 with the U.S. DOE (Division of Chemical Sciences).

9:40am **SS3-TuM5 STM Studies of Titanium Oxide Adlayers on a Pt(100) Surface**, ***T. Matsumoto***, University of Southern California, *M. Batzill*, Tulane University, *S. Hsieh, B.E. Koel*, University of Southern California

Pt supported on titanium oxide catalysts exhibit effects termed SMSI (strong metal support interaction). In order to probe aspects of this chemistry, thin films of titanium oxide on Pt single crystal surfaces have been observed by using surface science techniques, but most studies focused on titanium oxide films that fully covered the surface. In this study, submonolayer coverages and ultrathin films of titanium oxide on Pt(100) were observed by STM, LEED and XPS, and we report several new, ordered structures. These titanium oxide structures were produced by annealing to 800-1300 K after the deposition of Ti in an oxygen atmosphere or additional oxidation with NO_2 and O_3 after Ti deposition. A (3×5) structure of Ti_2O_3 was found after annealing above 800 K. This structure could also be produced by O_3 oxidation of the Pt_3Ti surface alloy produced on Pt(100). Our proposed structural model suggests that the thin film of titanium oxide with the (3×5) structure covers the Pt(100) surface fully. Several other locally ordered structures were found by annealing below 1000 K after additional oxidation of the (3×5) structure with NO_2 and O_3. These were more oxidized than Ti_2O_3, and were changed to the (3×5) structure after annealing to 1000 K.

10:00am **SS3-TuM6 Oxygen Vacancies on TiO_2(110) : An STM Study of Adsorbate Mediated Diffusion**, ***R. Schaub***, *E. Wahlström, A. Ronnau, E. Laegsgaard, I. Stensgaard, F. Besenbacher*, University of Aarhus, Denmark

Time resolved fast Scanning Tunneling Microscopy (STM) experiments reveal a spatially correlated diffusion of oxygen vacancies present on the rutile TiO_2(110) surface. The diffusion is observed to occur exclusively perpendicular to the oxygen bridging rows of the (1x1) reconstructed surface. This unexpected behavior is unambiguously assigned to trace amounts of adsorbates present on the surface which mediate the oxygen vacancy diffusion. Based on high resolution STM movies, a novel atomistic diffusion mechanism is proposed.

10:20am **SS3-TuM7 Oxygen Vacancies as Active Sites for Water Dissociation on Rutile TiO_2(110)**, ***P. Thostrup***, *R. Schaub,* University of Aarhus, Denmark, *N. Lopez,* Technical University of Denmark, *E. Laegsgaard, I. Stensgaard,* University of Aarhus, Denmark, *J.K. Norskov*, Technical University of Denmark, *F. Besenbacher,* University of Aarhus, Denmark

Water dissociation on TiO_2 is of fundamental interest as an example of a simple surface chemical process with significant applications. In addition, TiO_2 is the material of choice for photochemical hydrogen production from water and for biocompatible implants. Earlier experimental studies report a minor degree of water dissociation on TiO_2(110) while theoretical studies predict the dissociated state, or mixed dissociated-molecular states, to be most energetically favorable. Thus, even for this simple process we do not have a clear picture of the dissociation energetics and the active site for dissociation. Through an interplay between scanning tunneling microscopy experiments and density functional theory calculations, we determine unambiguously the active surface site responsible for the dissociation of water molecules adsorbed on rutile TiO_2(110). Oxygen vacancies in the surface layer are shown to dissociate H_2O through the transfer of one proton to a nearby oxygen atom, forming two hydroxyl groups for every vacancy. The amount of water dissociation is limited by the density of oxygen vacancies present on the clean surface exclusively. The dissociation process sets in as soon as molecular water is able to diffuse to the active site.[1]

[1] R. Schaub, P. Thostrup et al., Phys. Rev. Lett. 87, 266104 (2001).

10:40am **SS3-TuM8 The Influence of Subsurface, Charged Impurities on the Adsorption of Chlorine at TiO_2(110)**, ***M. Batzill***, *B. Katsiev,* Tulane University, *E.L.D. Hebenstreit,* Lawrence Berkeley National Laboratory, *W. Hebenstreit,* Optical Coating Laboratory, Inc., *U. Diebold*, Tulane University

A fundamental surface science study on the influence of single, subsurface dopants on the chemical surface properties is presented. In particular the adsorption of chlorine atoms on TiO_2(110) samples modified by low concentrations of impurities were investigated. Subsurface impurity atoms were identified by scanning tunneling microscopy and spectroscopy. This analysis established that positively charged impurity atoms, most likely substitutional vanadium atoms, are present in some samples. Areas of about 2 nm in diameter around these impurities are imaged as protrusions in empty state STM images. This is consistent with a downward band bending induced by positively charge impurity atoms. Adsorption studies of Cl at room temperature on these samples showed that Cl atoms avoid chemisorption in the vicinity of these impurity atoms. Cl is an acceptor-like adsorbate that is negatively charged at the surface. The suppressed adsorption is explained by an increased local electron affinity due to the only partially screened positively charged impurities. This lowers the energy gain for adsorption of Cl at the surface and thus renders adsorption sites close to impurities as energetically disfavored compared to unaltered surface areas.

11:00am **SS3-TuM9 Lower 3-fold Hollow Site of K on TiO_2(110)1x1**, ***G. Thornton***, *C.L. Pang, C.A. Muryn,* Manchester University, UK, *V.R. Dhanak*, Daresbury Laboratory, UK

Recent calculations by San Miguel et al (J. Phys. Chem. B 105 (2001) 1794) and Bredow et al (Surf. Sci. 418 (1998) 150) both predict that the low coverage bond site of K on TiO2(110) is the so called lower three fold hollow site. This involves two bridging O atoms and an in-plane O. In our work we have tested this prediction at a K coverage of 0.15 ML using a combination of surface extended X-ray absorption fine structure (SEXAFS), scanning tunneling microscopy (STM), and non-contact atomic force microscopy (NC-AFM). The polarisation dependence of the SEXAFS data rules out the atop, bridge and upper three fold hollow sites, and are consistent with the lower three fold hollow predicted by theory, with a K-O distance of 2.63 Å±0.03 Å. In addition to elements of the clean surface STM image, images of the K dosed surface contain wide dark rows running along the [001] direction. These are about 3 nm in length and centered along the dark bridging oxygen rows such that the two adjacent 5-fold coordinated Ti rows are not imaged. These presumably arise from K-induced blocking of the tunneling current, either by charge transfer to Ti 3d states, or because there are no empty states of K near EF. The clustering of alkali metal sites is consistent with molecular dynamics simulations. In the absence of useful topographic information in STM, we turn to NC-AFM images of TiO2(110)1x1, where the [001] direction bright rows arise from bridging O atoms. In addition to straight rows characteristic of the clean surface, zigzag rows are observed on the K-dosed surface, presumably arising from K atoms alternately occupying sites on either side of a bridging O row, as predicted by theory.

11:20am **SS3-TuM10 Electronic and Geometric Structure of Anatase TiO_2(101) and (001) Single Crystals**, *A.R. Kumarasinghe, W.R. Flavell, A.G. Thomas, A.K. Mallick, D. Tsoutsou, G.C. Smith,* UMIST, UK, ***R.L. Stockbauer***, Louisiana State University, *M. Grätzel, R. Hengerer*, Swiss Federal Institute of Technology

Scanning tunnelling microscopy (STM), low energy electron diffraction (LEED) and resonant photoemission studies on single crystal anatase TiO_2 (101) 1x1 and (001) 1x4 surfaces are reported. The (101) surface exhibits triangular shaped large terraces/steps leading to a saw tooth like structure. The steps are monatomic and are ~ 4Å high. Atomically resolved STM images show that the (101) surface has a bulk (1x1) termination and is unreconstructed. Defect states which are clearly observed in atomically resolved images can be created on clean (101) surfaces following sputter anneal cycles. Bright features are seen on atomic rows are most likely due to adsorbed molecules.[1] A defect peak is observed near 1 eV BE in UPS and is thought to arise from the loss of surface oxygen. This state is investigated using I/V measurements from scanning tunnelling spectroscopy (STS). Ti 3p-3d resonant photoemission of the surfaces are compared with earlier work from rutile TiO_2 (110) and features in the valence band at around 6 and 8 eV BE are assigned regions of weak and strong Ti-O hybridisation respectively. The defect peak is observed at around 1 eV BE for both surfaces following surface defect creation and is thought to arise from Ti^{3+}. This peak can be removed by gentle heating in oxygen.[2] Constant initial state spectroscopy reveals differences in cation-anion hybridisation between the two surfaces, while repeated sputtering shows the (001) surface to be more resistant to the creation of O vacancies than the (101) face.

[1] W. Hebenstreit, N. Ruzycki, G. S. Herman, Y. Gao, and U. Diebold, Phys Rev B, 62, 24, (2000).

[2] A.G. Thomas, W.R. Flavell, A.R. Kumarasinghe. A.K. Mallick. D. Tsoutsou, G.C. Smith, R. L. Stockbauer, M. Grätzel and R. Hengerer (in preparation).

11:40am **SS3-TuM11 Interactions of Oxygenated Hydrocarbons with Stoichiometric and Defective $SrTiO_3$(100) Surfaces: Role of Surface Structures and Defects**, ***L.-Q. Wang***, *S. Azad, K.F. Ferris, M.H. Engelhard*, Pacific Northwest National Laboratory

Molecular interactions on metal oxide surfaces are influenced by the surface structures and by the presence of surface defets. Adsorption and reactivity of oxygenated hydrocarbons on metal oxide surfaces have recently received considerable attention due to the environmental concerns. In this study, we examined the interactions of a series of oxygenated hydrocarbons with stoichiometric and defective $SrTiO_3$(100) surfaces using x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and electronic structure calculations. The goal of this study is to have a fundamental understanding of the role of surface structures and defects on the adsorption and reactivity of these oxygenated hydrocarbons on metal oxide surfaces. $SrTiO_3$(100) was chosen as our model surface not only because of its heterogeneous and photo-catalytic activities but also because investigation of oxygenated hydrocarbons on single crystal oxide surfaces is very rare. This presentation compares the interaction of acetaldehyde with that of methanol, ethanol and formic acid on the same surface. Since aldehydes are weaker than carboxylic acids and stronger than alcohols, the comparison of their reactivity on the surface is very interesting. It was found that methanol, ethanol and acetaldehyde adsorb molecularly whereas formic acid goes through dissociative adsorption on stoichiometric $SrTiO_3$(100) surface. As comparable with studies on other oxides such as TiO_2, adsorption and protonation of weaker acids such as methanol, ethanol and acetaldehyde are found to depend more on the surface structures than stronger acids such as formic acid and these results are in good agreement with our theoretical calculations. However, decomposition and redox reactions of methanol, ethanol, and acetaldehyde take place when surface defects are created by Ar^+ sputtering. In addition, such surface defects change the reaction pathway for formic acid.

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