

Surface Science

Room: 201 A - Session SS-MoA

Metal Oxides: Reactivity and Catalysis

2:00pm **SS-MoA1 Controlling Surface Reactivity of an Ultrathin MgO Film by Interface Tuning**, Y. Kim, J. Jung, RIKEN, Japan, H.-J. Shin, UNIST, Republic of Korea, M. Kawai, University of Tokyo, Japan

Ultrathin oxide films grown on metal substrates have been a subject of great interest not only as a supporting material for chemically active nanoparticles but also as a catalyst in the field of heterogeneous catalysis. We have demonstrated that the chemical reactivity for water dissociation on an ultrathin MgO film supported by the Ag(100) substrate depends greatly on film thickness and is enhanced compared to that achieved with their bulk counterpart using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations [1]. The change of chemical reactivity of ultrathin MgO film depending on the film thickness can be explained by the strengthening of the interaction between the oxide and metal interface layers [2]. This result implies that the artificial manipulation of the local structure at the oxide-metal interface is expected to play a pivotal role in controlling the catalytic activity of oxide film. We have also examined and compared the water dissociation on various model systems with defects at the oxide-metal interface of the 2-ML MgO/Ag(100) using periodic DFT calculations [2]. Our results clearly show that such structural imperfections at the interface can improve the chemical reactivity of the MgO film supported by an Ag substrate. This is closely correlated with the accompanied change of charge distribution of the oxide surface due to the accumulation of transferred charge density at the interface. In addition, the chemical reactions on the ultrathin oxide film surface can be tuned by interface defects regardless of the charging of adsorbates. A recent result of coupling between molecular vibration and surface phonon in the CO hopping process on MgO/Ag(100) with tunneling electrons will also be introduced [3].

[1] H.-J. Shin, J. Jung, K. Motobayashi, S. Yanagisawa, Y. Morikawa, Y. Kim, and M. Kawai, *Nat. Mater.* 9, 442 (2010).

[2] J. Jung, H.-J. Shin, Y. Kim, and M. Kawai, *Phys. Rev. B* 82, 085413 (2010); *J. Am. Chem. Soc.* 133, 6142 (2011); *J. Am. Chem. Soc.* 134, 10554 (2012).

[3] H.-J. Shin, J. Jung, M. Kawai, and Y. Kim, submitted.

2:20pm **SS-MoA2 Energetics of Adsorption of D₂O on Fe₃O₄ (111) Studied by Microcalorimetry**, C.A. Wolcott, I.X. Green, C.T. Campbell, University of Washington

Metal oxides represent an important class of materials whose interfacial properties play an important role in chemical sensors, catalysis, environmental science, biology, and many other fields [1]. This poster presents for the first time the direct measurement of the heat of adsorption and reaction of a molecular species on an oxide surface. The energetics of the adsorption and reaction of D₂O with a Fe₃O₄ (111) surface were studied using single crystal adsorption calorimetry (SCAC). SCAC allows for the direct measurements of surface reaction heats by using a pulsed molecular beam, a thin sample, and a temperature transducer. A 4nm thick film of Fe₃O₄(111) was grown on a 1µm thick Pt(111) crystal using the method of Weiss and Ranke[1]. Following the work of Weiss et al. [2], water is expected to form three species on an Fe₃O₄ (111) surface. Initially water reacts and dissociates on the surface producing surface hydroxyls bound to iron sites and hydrogen bound to oxygen sites. Upon continued dosing some water is seen to adsorb molecularly on the surface before eventually forming multilayers. In the present work we explored the heat of adsorption of D₂O as a function of both surface temperature and surface coverage using a pulsed molecular beam and a liquid nitrogen cryostat. By analyzing how the heat of adsorption changes as a function of temperature and coverage and correlating with the surface species observed by Weiss and others, heats of reaction for the formation of surface hydroxyls and molecular water on Fe₃O₄(111) are calculated. These results are compared with the heats measured indirectly by Weiss et al using TPD and UPS [2] and with DFT results [3].

[1] Weiss W., Ranke W., **Progress in Surface Science**, 70, 2002, 1.

[2] Joseph Y., Kuhrs C., Ranke W., Weiss W., **Surface Science**, 433, 1999, 114.

[3] Yang T., Wen X.D., Cao D.B, Li Y.W, Wang J.G., Huo C.F., **J Fuel Chem Technol**, 37 (4), 2009, 506.

2:40pm **SS-MoA3 Surface Chemistry of PdO(101)**, J.F. Weaver, University of Florida, A. Asthagiri, The Ohio State University, C. Hakanoglu, A. Antony, F. Zhang, University of Florida **INVITED**

The formation of palladium oxide (PdO) is thought to be responsible for the exceptional activity of supported Pd catalysts toward the complete oxidation of alkanes under oxygen-rich conditions. In this talk, I will discuss our investigations of the surface chemical properties of a PdO(101) thin film, focusing particularly on the adsorption and selective activation of alkanes. We find that *n*-alkanes adsorb relatively strongly on the PdO(101) surface by forming σ -complexes along rows of coordinatively-unsaturated Pd atoms, and that this adsorbed state acts as the precursor for initial C-H bond cleavage. I will discuss characteristics of the binding and activation of alkane σ -complexes on PdO(101) as determined from both experiment and density functional theory calculations. I will also discuss elementary processes involved in adsorbate oxidation and surface reduction of PdO(101), and make comparisons with the chemical reactivity of other late transition metal oxides.

3:40pm **SS-MoA6 Elemental Steps in Dehydration of Diols on TiO₂(110)**, D. Acharya, Y. Yoon, Pacific Northwest National Laboratory, Z. Zhang, Baylor University, Z. Li, X. Lin, L. Chen, R. Mu, B.D. Kay, R. Rousseau, Z. Dohnalek, Pacific Northwest National Laboratory

Simple diols (ethylene and propylene glycols) are employed as models for deoxygenation reactions of biomass. TiO₂(110) is selected as a prototypical oxide catalyst to attain detailed mechanistic understanding of such reactions. In these studies atomically resolved imaging by scanning tunneling microscopy (STM) is combined with ensemble-averaging spectroscopic techniques such as temperature programmed desorption (TPD) and theoretical investigations via density functional theory (DFT). STM studies reveal that at low temperatures (140 K), diols adsorb on five-fold coordinated Ti⁴⁺ sites. The molecules readily dissociate via O-H bond scission forming Ti-bound hydroxyalkoxy and bridging hydroxy (HO_b) species. The reverse reaction leading to molecularly bound diols is also observed indicating the attainment of a dynamic equilibrium between these conjugate acid/base pairs. Above 250 K, diols readily diffuse to oxygen vacancies and irreversibly dissociate via O-H bond scission of one of the OH groups forming geminate pairs of hydroxyalkoxy and hydroxyl species, both anchored on bridging oxygen (O_b) rows. The hydroxyalkoxy species rotate around their O_b anchor, switching the position of their OH between the two adjacent Ti rows. The rotating species are also found to assist cross-O_b row HO_b hydrogen transfer. The OH group of the hydroxyalkoxy species is further observed to dissociate forming a dioxy species and an additional HO_b. Annealing to ~450 K results in the formation of new dioxy intermediates that are centered on top of the O_b rows. Alkenes as final products are observed to desorb between 600 and 700 K. For ethylene glycol, our coverage dependent TPD studies further show acetaldehyde as a second carbon containing product at high coverages. Detailed theoretical calculations yield a deep insight into the mechanism and energetics of the observed reaction steps.

4:00pm **SS-MoA7 Site-specific Chemistry in Aqueous Solutions Produces Atomically Flat Rutile (110)**, D. Jing, A. Song, M.A. Hines, Cornell University

The high photocatalytic reactivity of nanocrystalline TiO₂ has attracted widespread interest for applications ranging from next-generation solar cells to self-cleaning surfaces; however, surface science investigations of these materials under technically relevant conditions have been hindered by a number of experimental difficulties. Moreover, the correlation between the chemical properties of clean TiO₂ surfaces produced in vacuum by repeated sputter-and-anneal cycles, the standard surface science technique, to those present in solution or in humid environments is unclear. We have used STM to investigate the atomic-scale reactivity of the most commonly studied TiO₂ polymorph, rutile, in pH-controlled aqueous solutions. Clean, atomically flat rutile (110) surfaces with well controlled step structures can be prepared using a simple aqueous solution. After mild heating (~150°C) to remove adsorbed water, STM reveals atomically flat surfaces of comparable quality to those produced using standard sputter-and-high-temperature-anneal cycles. The nature of the highly site-specific chemical reactions that produce these surfaces is revealed by kinetic simulations of pH-dependent changes in the etch morphology. A chemical mechanism for the production of atomically flat surfaces that is consistent with the inorganic chemistry of Ti(IV) compounds and the observed anisotropic reactivity is proposed.

4:20pm **SS-MoA8 Coverage Dependence of Photocatalysis of Trimethyl Acetate on TiO₂(110)**, *Z.T. Wang, I. Lyubinetsky*, Pacific Northwest National Laboratory

Photocatalysis on titania (TiO₂) has attracted much attention due to the potential applications on water splitting and pollutant destructions. Various photocatalytic applications of TiO₂ often involve interfaces with carboxylate-anchored organic molecules. From the fundamental point of view, one of the most interesting carboxylate-anchored molecules in probing photochemistry on TiO₂ is trimethyl acetate (TMA). We employed the high-resolution scanning tunneling microscopy (STM) to investigate the coverage influence for the TMA photocatalysis on rutile TiO₂(110) at 300 K. TMA species were deposited through deprotonative dissociation of trimethylacetic acid (TMAA) on TiO₂(110). In the deprotonative process, the dissociated TMAA's generate an equal amount of TMA's and hydroxyl groups (OH_b) on TiO₂(110). We found that TMA's adsorbed at Ti sites exhibit the same photoreaction (complete hole-induced decomposition) at all coverages but coverage-dependent reaction dynamics, where the reaction rates decrease with increasing TMA coverages. Furthermore, our results reveal that pre-adsorbing hydroxyl groups on TiO₂(110) also suppress the TMA photodecomposition. We demonstrate that the coverage-dependence of TMA reaction rates should be attributed to the variation of hydroxyl group concentration on TiO₂(110). It appears that OH_b species likely being the surface electron-traps decrease TiO₂ reactivity toward hole-mediated reactions, which results in the decreasing of TMA photoreaction rates with increasing its coverages.

4:40pm **SS-MoA9 TiO_x Thin Films on Au(111): Water Dissociation Properties**, *M.H. Farstad*, Norwegian University of Science and Technology, Norway, *D. Ragazzon*, Uppsala University, Sweden, *A. Schaefer*, University of Bremen, Germany, *L.E. Walle, A. Borg*, Norwegian University of Science and Technology, Norway, *A. Sandell*, Uppsala University, Sweden

When TiO_x (x ≤ 2) thin films are deposited onto various metal substrates different structures with unique properties may form. This method therefore offers the possibility for guided design of TiO₂ structures, which can lead to new kinds of TiO₂-based materials for heterogeneous catalysis, photocatalysis and solar cells [1]. Since water is an integral part of these applications a solid understanding of the interaction between water and novel, supported titania structures is essential.

In the present work, we present results on water adsorption on ordered TiO_x structures on Au(111) grown in situ by chemical vapor deposition (CVD). Depending on the conditions during deposition four different ordered phases can be produced. These phases have previously been studied and characterized with high-resolution photoelectron spectroscopy (HR-PES), scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). Two phases, denoted honeycomb (HC) and wagon wheel (WW), are monolayer thick, reduced and wet the surface. The other two phases, denoted Star and Ring, are different forms of stoichiometric TiO₂. The Star phase is the thermodynamically stable form of titania on Au(111) and it grows in the form of islands that partially covers the surface. The Ring phase is a multi-domain structure that covers basically the whole surface. The analysis of the LEED pattern gives an oblique unit cell, strongly indicating the formation of TiO₂-B [2], a phase which surface properties are largely unknown.

Upon water adsorption all four TiO_x phases show evidence of dissociation. The maximum hydroxyl coverage for the 2x2 and Star phases is close to that formed on the rutile (110) surface [3], while the hydroxyl coverage on the Ring phase is significantly lower. On the defect free rutile (110) surface, nearly all hydroxyl groups are gone at 300 K. In contrast, the hydroxyls on the 2x2 and Star phases persists up to 500-600 K, that is, a temperature regime typically associated with recombination at defect sites. The Ring phase interacts weakly with water with little dissociation. The amount of dissociated water corresponds to an active site density of about 7%. The correlation between the water adsorption and dissociation behavior and the structural properties of the TiO_x phases will be discussed.

[1] U. Diebold, Surf. Sci. Reports 48, 53 (2003).

[2] A. Vittadini, M. Casarin, A. Selloni, The Journal of Physical Chemistry C 113 (44), 18973–18977 (2009).

[3] L. E. Walle, A. Borg, P. Uvdal, A. Sandell, Phys. Rev. B 80, 235436 (2009).

5:00pm **SS-MoA10 Probing Charge Transfer Following Molecular Adsorption on CeO₂(100) using Resonant Photoemission**, *D.R. Mullins, P.M. Albrecht*, Oak Ridge National Laboratory

Resonant photoemission excited at the Ce N_{IV,V}-edge was used to study electron transfer from molecular adsorbates to the Ce cation on fully oxidized CeO₂(100). Two features near the top of the valence band in CeO₂ are extremely sensitive to the oxidation state of the Ce cation. The O 2p

feature at a binding energy of 4 eV is proportional to the Ce⁴⁺ content in the surface. The Ce 4f peak at a binding energy of 1.5 eV is proportional to the Ce³⁺ content. The ratio of these two peaks at their respective resonance maxima provides a measure of the Ce³⁺/Ce⁴⁺ content. This ratio is extremely sensitive because the Ce 4f feature rises from a flat, low count background in fully oxidized CeO₂ to a peak with thousands of counts at even modest levels of Ce reduction. The kinetic energy of the valence electrons at resonance is ca. 120 eV which places them near the minimum for the electron mean free path and therefore provides excellent surface sensitivity.

A variety of molecules were adsorbed on CeO₂(100) at 190 K. CeO₂ is a reducible oxide and removal of O from the surface will result in a reduction of Ce⁴⁺ to Ce³⁺. At 190 K none of the molecules studied resulted in desorption from the surface and therefore reduction did not result from the removal of O but from charge transfer from the adsorbate to the Ce. At elevated temperatures products such as water and CO₂ were observed that clearly resulted in reduction of the Ce due to O removal.

Methanol and water undergo similar adsorption processes by breaking an O-H bond, depositing H on a surface O anion and adsorbing R-O- on the Ce cations. For methanol the methoxy adsorbate produced ca. 10% Ce³⁺ following adsorption whereas the hydroxyl adsorbate resulting from water exposure produced a negligible change in the Ce³⁺ content. This suggests that the C in the alcohol is partially oxidized following adsorption whereas there is no net transfer of charge from the H and O in the water to the Ce.

Acetaldehyde does act as a Bronsted acid by breaking an O-H bond yet it also produces a 10% reduction of the Ce. This may result from a partial oxidation of the C in the dioxy / η₂ adsorption state and also from an oxidation of a small amount of the acetaldehyde to acetate. Pyridine, a classic probe of acid sites through the lone-pair electrons on the N, results in no change in the Ce³⁺ content. N 1s XPS and C k-edge NEXAFS suggest that the pyridine may not bond to the surface through the N atom.

Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy.

5:20pm **SS-MoA11 Reactivity of Acetaldehyde on CeO₂(111) Surfaces and the Roles of Oxygen Vacancies**, *Y. Xu*, Louisiana State University, *F. Calaza, D.R. Mullins, S.H. Overbury*, Oak Ridge National Laboratory

Ceria is a widely used catalytic and functional catalyst support material, well known for its ability to store oxygen and change oxidation state. There is a growing body of evidence that the surface reactivity of ceria can vary significantly with the extent of reduction. We use acetaldehyde as a probe molecule to explore this phenomenon and to elucidate the roles of oxygen vacancies in redox reactions on ceria surfaces. Multiple surface characterization techniques and theoretical density functional theory (DFT) calculations have been applied in combination to elucidate the mechanism of the temperature-program desorption (TPD) of acetaldehyde on CeO₂(111) thin-film surfaces. In TPD, acetaldehyde desorbs without reaction from the stoichiometric CeO₂(111) surface at 210 K. When the surface is partially reduced, acetaldehyde loses its carbonyl bond character at low temperatures. Annealing to 400 K leads to the desorption of some of this strongly adsorbed species as acetaldehyde and the appearance of another species, conclusively identified by RAIRS and DFT to be the enolate form of acetaldehyde (CH₂CHO), which has not been captured previously on ceria surfaces. A microkinetic model based on the identified surface intermediates on CeO_x(111) and DFT energetics has been constructed to simulate the TPD, and finds close agreement with the experimental results. Our findings demonstrate that surface oxygen vacancies are key to activating acetaldehyde and stabilizing it for further reactions, and that the dominant surface reaction pathway changes as a function of vacancy concentration. This work has relevance to the conversion of biomass-derived oxygenates because enolate species are key intermediates in C-C coupling reactions including aldol condensation.

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