Surface Science
Room 104E - Session SS+AS+HC-MoA
Metals, Alloys, and Oxides: Reactivity and Catalysis

Moderator: David Mullins, Oak Ridge National Laboratory

1:40pm **SS+AS+HC-MoA1 Scanning Tunneling Microscopy Studies of Hydrogen adsorption on the RuO$_2$(110) Surface**, ***Arjun Dahal***, *R. Mu, Z. Dohnálek, I. Lyubinetsky,* Pacific Northwest National Laboratory

Understanding of hydrogen/oxide interactions is important for a variety of fundamental and applied processes. By using high resolution scanning tunneling microscopy (STM), we probed the adsorption of H_2 (or D_2) on model catalyst RuO$_2$(110) surface, which has wide range of applications in heterogeneous catalysis, hydrogen storage, and many other energy related areas. Well-defined RuO$_2$(110) surface exposes alternating rows of bridge-bonded oxygen atoms (O_b) and five-fold-coordinated Ru atoms (Ru_{cus}). STM data indicate that hydrogen molecule dissociates even at 5 K, whereas one hydrogen adatom adsorbs on top of the Ru_{cus} site (producing a hydrate, H-Ru_{cus}, species) and the second on top of the adjacent O_b site (forming a bridging hydroxyl, H-O_b, species), generating an H-Ru_{cus}/H-O_b pair. For the low hydrogen coverage, the dissociated H-Ru_{cus}/H-O_b pairs adsorb on every alternate Ru_{cus}/O_b sites adopting a (2×1) registration. When RuO$_2$(110) surface adopts a such registration of the H-Ru_{cus}/H-O_b pairs locally, hydrogen starts to adsorb molecularly on top of the Ru_{cus} sites in between the adjacent dissociated hydrogen-pairs. With further increase of hydrogen coverage, linear arrays of H_2 molecules are formed along Ru_{cus} rows. The saturation coverage of the hydrogen on the RuO$_2$(110) surface is observed to be ~0.75 ML, where 1 ML is designated as the Ru_{cus} site density on the stoichiometric RuO$_2$(110) surface (5.06×10^{14} cm^{-2}). Upon annealing the hydrogen-covered RuO$_2$(110) surface, H_2 molecules from the linear array desorb around 110 K. On the other hand, the H-R_{cus} species of H-R_{cus}/H-O_b pair transforms (via a proton transfer) into another H-O_b group, across-row from original H-O_b group, producing crosswise H-O_b/H-O_b pair at temperatures above ~250 K.

2:00pm **SS+AS+HC-MoA2 Metal Vapor Adsorption Calorimetry on Layered Ca Niobate Nanosheets: Energetics and Adsorbate Structure**, ***Wei Zhang***, *J. Lownsbury,* University of Washington; *R. Uppuluri, T.E. Mallouk,* The Pennsylvania State University; *C.T. Campbell,* University of Washington

The metal/oxide interface is essential to many current and prospective technologies, including oxide-supported metal catalysts, fuel cells, photocatalysis, and nanoscale electronic contacts, so understanding the strength of metal – oxide bonding at such interfaces is of great interest. These strengths have been measured on single crystal oxide surfaces by single crystal adsorption calorimetry (SCAC) of metal atom adsorption in ultrahigh vacuum (UHV)[1] and on niobate and tantalate nanosheets by solution-based isothermal titration calorimetry during the deposition of transition metal oxide (or hydroxide) nanoparticles from their aqueous salt solutions[2,3]. These niobate nanosheets are very interesting since they are highly ordered and essentially like single crystal surfaces in that the ratio of terrace sites to defect and edge sites is huge. Furthermore, when used as supports for transition metal oxide nanoparticles, they have been shown to display unusual stability against sintering.[2,3] Here, we directly measure the adsorption energies of metal vapor on such niobate nanosheets using SCAC in UHV. Specifically, we study the adsorption of Ca and Ag vapor onto calcium niobate films that are 4 nanosheets thick (~4 nm total). Calcium atoms show a sticking probability near unity and an initial heat of adsorption of ~660 kJ/mol, much higher than the heat of bulk Ca(s) sublimation (178 kJ/mol). Low-energy ion scattering spectroscopy (LEIS), which is element-specific and probes only the topmost atomic layer, is used to investigate the resulting metal particle/film morphology. The possible chemical reactions between the metal vapor and the calcium niobate during adsorption are elucidated using X-ray photoelectron spectroscopy (XPS).

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2:20pm **SS+AS+HC-MoA3 Structure and Reactivity of Model Iron Oxide Surfaces**, ***Gareth Parkinson***, TU Wien, Austria **INVITED**

Iron oxides are abundant in nature and extensively utilized in modern technologies including heterogeneous catalysis [1]. Magnetite (Fe_3O_4), for example, is the active phase of the industrial water-gas shift catalyst, while hematite (Fe_2O_3) is used as the photoanode for photoelectrochemical water splitting. In this talk I will discuss our recent investigations of the Fe_3O_4(100) and Fe_2O_3(1-102) surfaces using a combined experiment/theory approach. The Fe_3O_4(100) surface forms a reconstruction based on an ordered array of subsurface cation vacancies that contains exclusively Fe^{3+}, and is relatively inert [2]. Although formic acid adsorbs dissociatively at regular lattice sites [3], methanol adsorption is restricted to defects containing Fe^{2+} [4]. The bulk of the talk will focus on a detailed study of water adsorption on Fe_3O_4(100) by TPD, STM, XPS, UPS, DFT+U and molecular dynamics calculations. In the remaining time I will demonstrate that a bulk terminated Fe_2O_3(1-102) surface can be prepared by annealing in 10^{-6} mbar O_2, and a reduced (2x1) surface forms rapidly when heating in UHV. The structure of the (2x1) reconstruction and its reactivity toward water will be discussed.

[1] G.S. Parkinson, Iron oxide surfaces, Surface Science Reports (2016), http://dx.doi.org/10.1016/j.surfrep.2016.02.001

[2] R. Bliem, E. McDermott, P. Ferstl, M. Setvin, O. Gamba, J. Pavelec, M.A. Schneider, M. Schmid, U. Diebold, P. Blaha, L. Hammer, G.S. Parkinson, Subsurface Cation Vacancy Stabilization of the Magnetite (001) Surface, Science 346 (2014) 1215-1218.

[3] O. Gamba, H. Noei, J. Pavelec, R. Bliem, M. Schmid, U. Diebold, A. Stierle, G.S. Parkinson, Adsorption of Formic Acid on the Fe_3O_4(001) Surface, The Journal of Physical Chemistry C 119 (2015) 20459-20465.

[4] O. Gamba, J. Hulva, J. Pavelec, R. Bliem, M. Schmid, U. Diebold, G.S. Parkinson, The role of surface defects in the adsorption of methanol on Fe_3O_4(001), Topics in Catalysis submitted (2016).

3:00pm **SS+AS+HC-MoA5 Structure and Ethanol Reactivity of Ti-modified CeO$_x$(111) Mixed Oxide Surfaces**, *E.W. Peterson,* ***Jing Zhou,*** University of Wyoming

Ceria has been widely studied as an oxidation-reduction catalyst due to its unique redox properties and oxygen storage capacity. There has been an interest to incorporate additional metal dopants such as Ti into ceria to potentially enhance the thermal stability as well as improve the redox properties for practical applications in catalysis. This paper focuses on the fundamental mechanistic understanding of the effect of Ti dopant on the structure and reactivity of ceria using scanning tunneling microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy and temperature programmed desorption techniques. In the study, submonolayer coverage of Ti was deposited on well-ordered CeO$_x$(111) ($1.5<x<2$) thin films at room temperature. XPS studies show that Ti is oxidized to Ti^{4+} at the cost of Ce^{4+} reduction. Observation of CO IR band at 2173 cm^{-1} further confirms the presence of titania on the ceria surface. At 300 K, small atomic-like features of Ti-O-Ce linkages are present on ceria, which can coalesce into chain structures after heating to 700 K. Upon ethanol adsorption at 300 K, ethoxy was the surface intermediate observed on both oxidized and partially reduced ceria surface. With heating, it can go through the dehydration or dehydrogenation process to form acetaldehyde, ethylene, water and hydrogen products. Our studies have demonstrated that addition of Ti in ceria can affect the dehydration and dehydrogenation selectivity. Furthermore, the nature of ceria supports associated with oxygen vacancies and Ti dopants can have a promotional effect in the stability of deposited metal nanoparticles, such as Ni, and the chemical behavior toward the adsorption and reaction of ethanol. The research is sponsored by the National Science Foundation Career Grant (Award Number: CHE1151846) and the Wyoming NASA EPSCoR (NASA Grant: NNX13AB13A).

3:20pm **SS+AS+HC-MoA6 New Insights into the Coverage-Dependent Structure and Desorption Kinetics of CO on Palladium(111)**, ***Pan Xu,*** Stony Brook University; *S.-Y. Hong,* Brookhaven National Laboratory; *S. Liu,* Stony Brook University; *N.R. Camillone, M.G. White, N. Camillone,* Brookhaven National Laboratory

Carbon monoxide adlayers on palladium surfaces have, since the early days of ultrahigh-vacuum surface science, served as model systems for the study of molecule–surface interactions, structure and dynamics. As part of a recent study of the dynamics of ultrafast molecule–surface energy transfer we have revisited the CO/Pd(111) system and found that it continues to teach us about the complexities of molecule–surface interactions. Specifically, it has long been known that CO adlayers assume a wide range of ordered structures on Pd(111) at low temperature (~80 K). In fact, between the (√3×√3)R30° 0.33-ML and (2×2) 0.75-ML (saturation) structures, at least 17 well-ordered structures have been identified. Until now, however, a comprehensive correlation between these structures and the thermal desorption kinetics has not been reported. In this talk we detail a systematic investigation that correlates individual temperature-programmed desorption (TPD) features with specific adlayer structural phase transitions. We report that in addition to the spectrum of previously-observed structures we have observed for the first time, to the best of our knowledge, a well-developed, ordered domain-boundary structure at a coverage just below saturation. We have assigned this structure as a c(16×2) adlayer comprised of stripes with local (2×2) structure and used density functional theory to investigate the adsorption site preferences within the adlayer. We show how our results, in combination with existing data, can be interpreted in terms of a compromise between the energy minimization that accompanies binding at high-symmetry sites and lateral repulsive interactions. Furthermore, we describe how quantifying the coverage using the integrated desorption yield areas is problematic due to difficulties in growing a fully-saturated adlayer. We attribute these difficulties to a kinetic limitation of the structural phase transitions at high coverage, and show that this limitation is easily addressed by preparing the adlayer at a somewhat elevated temperature. We also detail use of the inversion-optimization method to extract the coverage dependence of the desorption activation energy from the TPD measurements. We compare the resultant simulated TPD line shapes with those derived using the "leading-edge" analysis method.

4:00pm **SS+AS+HC-MoA8 Combined Experimental and Computational Study of Water on Fe_3O_4 (001)**, ***Jan Hulva,*** Vienna University of Technology, Austria*; M. Meier,* Universität Wien, Austria*; J. Pavelec, S. Maaß, R. Bliem, M. Schmid, U. Diebold,* Vienna University of Technology, Austria*; C. Franchini,* Universität Wien, Austria*; G.S. Parkinson,* Vienna University of Technology, Austria

The interaction of water with metal-oxide surfaces is an important topic for a wide range of technological and environmental applications. This is particularly true for the iron oxides because of their abundance in nature and their use in chemical processes where water is involved e.g. the water-gas shift reaction [1]. Recent studies of water on iron oxide surfaces have found significant complexity, with evidence for pressure dependent adsorption, mixed-mode adsorption and coverage dependent hydrogen bonding [2-4]. Here we use a multi-technique experimental approach combined with ab-initio calculations including molecular dynamics to disentangle the coverage and temperature dependent behavior of water on the reconstructed Fe3O4(001)-(√2x√2)R45° surface [5].

Temperature programmed desorption shows that the first monolayer of water desorbs from the surface in four distinct peaks between 150 K and 250 K. Based on XPS, STM images and ab-initio calculations, we conclude that the first three peaks originate from molecular water desorbing from a coverage-dependent hydrogen-bonded network, while the last peak results from recombinative desorption from a partially dissociated water trimer species. Two additional desorption states at 340 K and 520 K are ascribed to desorption from surface defects and recombinative desorption of the surface surface hydroxyl groups, respectively.

[1] Parkinson, G.S., " Iron oxide surfaces", *Surface Science Reports* (2016)

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[3] Mulakaluri, N., et al. "Partial dissociation of water on Fe_3O_4 (001): Adsorbate induced charge and orbital order." *Phys. Rev. Lett.* 103 (2009): 176102.

[4] Kendelewicz, T., et al. "X-ray photoemission and density functional theory study of the interaction of water vapor with the Fe_3O_4 (001) surface at near-ambient conditions." *J. Phys. ChemC* 117 (2013): 2719-2733.

[5] Bliem, R., et al. "Subsurface cation vacancy stabilization of the magnetite (001) surface." *Science* 346 (2014): 1215-1218.

4:20pm **SS+AS+HC-MoA9 Water Desorption from Sulfur-Doped Oxide Thin Films on W (100)**, ***Anthony Babore***, *J.C. Hemminger,* University of California Irvine

Recent first principle calculations by Pacchioni and coworkers[1] suggest that sulfur dopants incorporated into the WO_{3-} lattice could favorably shift the band gap for enhanced visible light absorption. The present study aims to gain fundamental insight into the reactivity of a simple sulfur doped tungsten oxide system by using temperature programmed desorption (TPD) and water (D_2O) as a probe molecule. Furthermore, water desorption spectra were also obtained for pure oxide and pure sulfide films on W (100) for comparison. Auger electron spectroscopy (AES) was used to confirm the presence and relative amounts of sulfur and oxygen on the surface. TPD was then used to monitor the m/z 20, 19, and 18 signal intensity as a function of the temperature. To quantify the reactivity of water on the surface, activation energies of desorption were obtained. The results indicate distinct differences in the desorption spectra and desorption energies that exemplify the reactivity of each of the surfaces.

1. Wang F, Di Valentin C, Pacchioni G (2012) J Phys Chem C 116:8901–8909

4:40pm **SS+AS+HC-MoA10 Adsorption and Decomposition of Dimethyl Methylphosphonate on Metal Oxide Surfaces Under Atmospheric Conditions**, ***Ashley Head**, L. Trotochaud,* Lawrence Berkeley National Laboratory (LBNL)*; R. Tsyshevsky,* University of Maryland College Park*; O. Karslioglu,* Lawrence Berkeley National Laboratory (LBNL)*; M.M. Kuklja,* University of Maryland College Park*; H. Bluhm,* Lawrence Berkeley National Laboratory (LBNL)

Organophosphonates are used as corrosion inhibitors, pesticides, insecticides, and chemical warfare agents. This class of molecules has a range of acute toxicity, so dimethyl methylphosphonate is commonly used as a proxy for more toxic molecules. Metal oxides are used in applications for binding and decomposing organophosphonates despite little understanding of the chemistry and reactivity, especially in the presence of atmospheric molecules. With the ability to collect photoemission spectra at pressures up to about 25 Torr, ambient pressure XPS is well-suited to investigate the adsorption of DMMP in the presence of other molecules that have relevance to applications. Using MoO_x and CuO_x foils as model systems for chemical filtration materials, we have studied the adsorption and decomposition behavior of DMMP and how this behavior changes in the presence of atmospherically relevant molecules, including water, hydrocarbons, and NO_x. The effect of the small molecules on the substrate and the subsequent effects on DMMP binding, coverage, and decomposition will be discussed. APXPS results are interpreted with the aid of density functional theory calculations, which model DMMP adsorption, decomposition products, and reaction energies.

5:00pm **SS+AS+HC-MoA11 Oxygen Chemisorption and Thermal Oxidation of TiAlN High Power Pulsed Magnetron Sputtering Hard Coatings**, ***Martin Wiesing**, T. de los Arcos, G. Grundmeier,* University of Paderborn, Germany

The thermal oxidation of $Ti_{0.5}Al_{0.5}N$ hard coatings as deposited by High Power Pulsed Magnetron Sputtering was investigated at reduced oxygen partial pressures of 10^{-6} and 10^{-2} Pa in a temperature range from 298 to 800 K. Quasi in-situ X-ray Photoelectron Spectroscopy and Low Energy Ion Scattering studies revealed oxygen to bind selectively to Ti-sites on the surface [1] and oxygen migration into the near-surface region. Three dimensional oxidation leads to the formation of a double layered surface oxide including a TiAl(O,N) growth region [2] terminated with a Ti^{IV} containing surface oxide [3]. Based on Wagner plot analysis, the surface oxide layer formed at 800 K can be described by a mixed $Ti^{IV}Al^{III}O_x$ phase while a separated $(Ti^{IV}O_2)(Al^{III}{}_2O_3)$ phase preferentially forms at 298 K. Complementary Ultraviolet Photoelectron Spectroscopy revealed a high degree of nitrogen doping in both cases.

The results are of importance for the design of multi-layered nitridic hard coatings and for a thorough understanding of the high-temperature oxidation resistance of such coatings.

Acknowledgement: The authors gratefully acknowledge the German Research Foundation (DFG) for financial support (SFB–TR 87). We thank Prof. Dr. J. Schneider and Holger Rueß for providing the coated specimen.

References:

[1] C. Kunze, D. Music, M. to Baben, J.M. Schneider, G. Grundmeier, Temporal evolution of oxygen chemisorption on TiAlN, Appl. Surf. Sci. 290 (2014) 504–508. doi:10.1016/j.apsusc.2013.11.091.

[2] S. Hofmann, Formation and diffusion properties of oxide films on metals and on nitride coatings studied with Auger electron spectroscopy and X-ray photoelectron spectroscopy, Thin Solid Films. 193–194, Part 2 (1990) 648–664. doi:10.1016/0040-6090(90)90216-Z.

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