Surface Science
Room: 208 - Session SS+NC-MoA

Reactivity at Oxide Surfaces
Moderator: S. Chiang, University of California Davis

2:00pm **SS+NC-MoA1 Surface Structure and Chemistry of β-Ga_2O_3 Nanoribbons**, ***V.M. Bermudez***, *S.M. Prokes*, Naval Research Laboratory

β-Ga_2O_3 is an important material with applications as a catalyst support, as a transparent conducting oxide and as a critical component in chemical sensors. Much work has been done on high-surface-area powders and on polycrystalline thin films, but little is known about the surface properties of single crystals. We have carried out a series[1-3] of computational and experimental studies of β-Ga_2O_3 nanoribbons (NRs) which are single crystals with the (100) plane as the broad face. Ab-initio periodic slab calculations verify that the (100) surface is the lowest in energy and identify which of the two possible terminations ("A" or "B") is more stable. The (100)-B is very stable, and physisorption of molecular water, methanol or formic acid on this surface is found, computationally, to be energetically favored over dissociative adsorption. On the less stable (100)-A surface, physisorption of H_2O and CH_3OH is still somewhat more favorable than chemisorption, but formation of a bridging formate species is favored for HCO_2H. Infrared (IR) spectroscopy has been used to characterize the NRs and the interface with a gold substrate. The transmission spectrum of a thin layer of NRs shows an array of randomly-oriented single crystals. IR reflection-absorption spectra (IRRAS) suggest a reaction at the oxide/Au interface during annealing. IRRAS data for the adsorption of pyridine or 1-octanol are generally consistent with the computational results. Physisorption is the dominant effect; although, some chemisorption is also observed. This could indicate the presence of defects on the (100)-B surface or the co-existence of (100)-B and -A regions. For acetic or pentanoic acid, IRRAS clearly shows the formation of stable bridging carboxylate species which suggests that organic acids may be useful for functionalizing β-Ga_2O_3.

[1] V.M. Bermudez, Chem. Phys. 323 (2006) 193.

[2] V.M. Bermudez and S.M. Prokes, Langmuir 23 (2007) 12566.

[3] V.M. Bermudez, in preparation.

2:20pm **SS+NC-MoA2 Formaldehyde Reactions Over Rutile $TiO_2(110)$ Single Crystal**, *H. Qiu, Y. Wang,* Ruhr-University Bochum, Germany, *P. McGill,* ***H. Idriss,*** University of Auckland, New Zealand, *C. Woell*, Ruhr-University Bochum, Germany

The reaction of CH_2O with perfect and defective $TiO_2(110)$ surfaces (produced by over-annealing and Ar ion sputtering methods) was studied by thermal desorption spectroscopy (TDS), high resolution electron energy loss spectroscopy (HREELS) and DFT calculations. Exposing the perfect $TiO_2(110)$ surface to CH_2O at 100 K leads to the formation of physisorbed CH_2O and paraformaldehyde. The latter decomposes to CH_2O that desorbs at about 270 K. On the defective $TiO_2(110)$ surface CH_2O adsorbs more strongly on oxygen vacancy sites ultimately forming a diolate (-OCH_2CH_2O-) species, as demonstrated by HREELS. Upon heating to higher temperatures this species undergoes deoxygenation resulting in ethylene formation via a reductive coupling mechanism.

2:40pm **SS+NC-MoA3 Reactivity Studies on Oxide Supported Metal Nanoparticles**, ***H.-J. Freund***, Fritz-Haber-Institut, Germany **INVITED**

Metal nanoparticles supported on thin oxide films may be characterized at the atomic level. Typically it is assumed that reactions proceed on the surface of those particles. We report on results of hydrogenation and oxidation reactions where the interior as well as the metal-oxide interface participate. Several examples will be discussed on the basis of results on model systems characterized via STM, TPD, IRAS, r-NRA, molecular beam as well as high pressure studies.

3:20pm **SS+NC-MoA5 Transient Mobility of Oxygen Adatoms Resulting from O_2 Dissociation at Oxygen Vacancies of $TiO_2(110)$**, *Y. Du, Z. Dohnalek,* ***I. Lyubinetsky***, Pacific Northwest National Laboratory

The interaction of molecular oxygen with TiO_2–based materials affects many chemical and photochemical processes. We will present our recent discoveries in studying O_2 interaction with reduced $TiO_2(110)$ surface by scanning tunneling microscopy at 300K. By tracking the same surface area before and after O_2 exposure, we confirm the known O_2 dissociation channel occuring at the bridging oxygen vacancy (O_{vac}) sites, with one O atom healing an O_{vac} and other O bonding at the neighboring Ti site as an adatom (O_a). In addition, the lateral distribution and diffusion of O_a are studied. It is revealed that there are three possible configurations for the O_a in regarding to the position of the original O_{vac} site, which can not be explained by thermal diffusion. Through detailed study, we conclude that observed distribution of the O adatoms is attained through a nonthermal, transient mobility from the energy release during dissociation. Unlike for other known cases of the dissociation of diatomic molecules where both “hot” adatoms accommodate at equivalent sites, in this study, the O atoms filling the vacancies are locked into the bridging oxygen rows and only the O adatoms are relatively free to move. The transient motion of the hyperthermal O adatoms might bring an enhanced reactivity, thus affect surface chemistry.

4:00pm **SS+NC-MoA7 Direct Observation of O_2 Dissociation on Ti rows of Reduced $TiO_2(110)$**, ***Y. Du***, *Z. Zhang, Z. Dohnalek, I. Lyubinetsky*, Pacific Northwest National Laboratory

The interaction of molecular oxygen with TiO_2 plays a critical role in catalytic activity of TiO_2-based materials. It is generally agreed that reactivity of TiO_2, partially reduced by a vacuum annealing, is greatly influenced by surface oxygen vacancy defects. In particular, at room temperature, oxygen molecules were believed to dissociate only at vacancy sites with one O atom filling an oxygen vacancy and the other O atom residing at the neighboring Ti site as an adatom. In this talk, we will show that the oxygen dissociation process is much more complicated from our scanning tunneling microscopy studies. We will demonstrate that O vacancies are not the only sites to dissociate O_2 and reveal another O_2 dissociation channel, where an oxygen molecule dissociates on rows of five-fold coordinated Ti atoms to form an oxgyen adatom pair with two lattice constants spacing. We believe the discovery of the additional O_2 dissociation channel could have a considerable impact on the TiO_2 surface chemistry. It also calls for a partial reevaluation and/or reinterpretation some of the published experimental and theoretical results.

4:20pm **SS+NC-MoA8 Reactivity of Epitaxial Vanadia on TiO_2: Are Support Interactions Required for Reactivity?**, ***M. Li***, *E.I. Altman*, Yale University

The reactivities of vanadium oxide epitaxial thin films were studied using temperature programmed desorption (TPD). The vanadia films were grown on rutile $TiO_2(110)$ using oxygen plasma-assisted molecular beam epitaxy (OPA-MBE) and were shown to exhibit the (1x1) rutile structure using reflection high energy electron diffraction (RHEED), low energy electron diffraction (LEED) while X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) showed that monolayer films contained V^{5+} while V^{4+} predominated in the bulk of multilayer films. Two reaction channels at 400 K and above 500 K were detected for submonolayer coverages for 1-propanol oxidation to form propionaldehyde. The reaction channel at 400 K persists through multilayer films and thus is designated to the deprotonation of alkoxide intermediates attached to V^{5+} surface cations; meanwhile, a comparison of the vanadia coverage and the branching ratio between these two reaction channels suggests that the reaction above 500 K might involve alkoxides atop both V^{5+} and Ti^{4+}. It is also found that the activation energy of the lower temperature channel is stable on the submonolayer film, independent of reduction and reoxidaton, while the activation energy starts to increase for the higher temperature channel upon reduction. The same lower temperature reaction channel at 400 K exists throughout multilayer films where the titania support is absent, indicating that multilayer epitaxial films retain reactivity, in contrast to prior studies where disordered vanadia films were reported to be unreactive. Comparing the branching ratio of aldehyde desorption vs. alcohol desorption on films from submonolayer to multilayer, the fraction of the alcohol that dehydrogenates is higher for the submonolayer films. Together the results indicate that the TiO_2 support increases the reactivity of vanadia by structural promotion and by aiding the initial deprotonation of adsorbed alcohols.

4:40pm **SS+NC-MoA9 The Chemistry of Volatile Organic Compounds on $TiO_2(110)$ and the Influence of Defects and Coadsorbed Species**, ***L. Benz***, *J. Haubrich, R.G. Quiller, C.M. Friend*, Harvard University

Surprisingly high reactivity has been observed over the most stable (110) surface of TiO_2 in the reactions of volatile organic compounds, in particular, in molecules containing O moieties. Ultra-high vacuum techniques such as temperature programmed reaction spectroscopy and scanning tunneling microscopy were employed in researching the fundamental underpinnings of this reactivity, including the dependence of reactivity on the presence of intrinsic surface defects. Specifically, carbon-carbon bond formation was observed, and the effect of environmentally relevant species such as water and oxygen on these reactions was examined. These reactions are of general interest in both environmental and catalytic processes.

5:00pm **SS+NC-MoA10 Tetraoxygen on Reduced TiO$_2$(110): Oxygen Adsorption and Reactions with Oxygen Vacancies**, *G.A. Kimmel*, ***N.G. Petrik***, Pacific Northwest National Laboratory

The interaction of oxygen with TiO$_2$ is critical for a variety of applications including the photooxidation of organic materials, purification of water and air, and (potentially) photocatalytic water splitting. In this paper, oxygen adsorption on reduced TiO$_2$(110) is investigated using temperature programmed desorption and electron-stimulated desorption.[1] At low temperatures, two O$_2$ molecules can be chemisorbed in each oxygen vacancy. These molecules do not desorb upon annealing to 700 K. Instead for $200 \text{ K} < T < 400 \text{ K}$, the two O$_2$ convert to another species which has four oxygen atoms, i.e. tetraoxygen, that decomposes at higher temperatures. In contrast when only 1 O$_2$ is adsorbed in an oxygen vacancy, the molecule dissociates upon annealing above ~150 K to heal the vacancy in agreement with previous results. These experimental results, which provide a new model for the interaction of oxygen with TiO$_2$(110), are consistent with the recent prediction that O_4^{2-} is the most stable form of oxygen in bridging oxygen vacancies.[2]

[1] G.A. Kimmel and N.G. Petrik, PRL 100, 196102 (2008).

[2] D. Pillay, Y. Wang, and G. S. Hwang, J. Am. Chem. Soc. 128, 14000 (2006).

5:20pm **SS+NC-MoA11 Decomposition of Dimethyl Methylphosphonate on Ceria Thin Films**, ***D.A. Chen***, *J.S. Ratliff*, University of South Carolina, *D.R. Mullins, S.D. Senanayake*, Oak Ridge National Laboratory, *X. Hu*, University of South Carolina

The decomposition of dimethyl methylphosphonate (DMMP) on ceria thin films has been investigated by temperature programmed desorption and high resolution X-ray photoelectron spectroscopy. Ordered ceria films with different levels of oxidation were grown on Ru(0001), and DMMP was used as a simulant molecule for understanding the chemistry of the organophosphorus nerve agents. Methanol and formaldehyde were the major gaseous products detected from initial DMMP decomposition on the fully oxidized ceria thin films, and PO$_x$ as well as a small amount of atomic carbon or CH$_x$ remained on the surface after heating to 800 K. On reduced ceria, CO and hydrogen were the main desorption products with methanol and formaldehyde as minor products. DMMP chemistry on ceria was unusual because activity increased with each adsorption-reaction cycle even though phosphorus did not desorb from the surface. This increase in activity appears to be caused by the reduction of cerium oxide by DMMP itself; one possible mechanism for the redox reaction involves the formation of cerium phosphate. The chemistry of DMMP on ceria is compared with that on single-crystal TiO$_2$(110) surfaces. Gaseous methyl and methane were the primary products from DMMP decomposition on titania. In contrast to the ceria surfaces, titania was poisoned by the byproducts of DMMP reaction and exhibited less sustained activity for DMMP decomposition after multiple adsorption-reaction cycles.

Authors Index

Bold page numbers indicate the presenter