Thursday Morning, November 2, 2017

Surface Science Division
Room: 25 - Session SS+EM+HC+MI-ThM

Oxides: Structures and Reactions

Moderators: Valeria Lauter, Oak Ridge National Laboratory, Charles Sykes, Tufts University

8:00am SS+EM+HC+MI-ThM1 Influence of Iron Doping on Cobalt Oxide Bilayers on Au(111): Toward a Model of Synergistic Catalytic Effect in Oxygen Evolution Reaction, *Jonathan Rodriguez-Fernandez, Z. Sun, J. Fester, J.V. Lauritsen*, Aarhus University, Denmark

Iron doped cobalt oxides have been shown enhanced activity for promoting the oxygen evolution reaction (OER) compared with unary iron oxides and cobalt oxides, respectively[1]. However, the nature of such synergistic catalytic effect and in particular the way of iron species incorporate with cobalt oxides are only understood on a superficial level, which presents a significant obstacle to further exploration on rational design of efficient OER catalysts. Noble metal supported transition metal oxides have been previously applied as model catalysts, which enables the powerful surface science techniques, and successfully reveal the catalytic active sites and help researchers understand the catalytic process further[2].

Here, aiming to study the origin of the synergistic catalytic effect, we dope iron into well-characterized cobalt oxide bilayer nanoislands supported on a single crystal Au(111) substrate[3]. Atomic-resolved scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) are used to compare the growth of cobalt oxide and cobalt-iron oxide bilayers. We perform a comprehensive analysis of the iron doping induced influence on the atomic structure of the nanoislands and oxidation states of both the dopant and host species.

We find that doped iron species integrate into the cobalt oxide nanoislands and are mostly under oxidative condition. The Co atoms surrounding the doped Fe appear brighter and form 6-fold flower-like features under STM due to the local modification of electronic structure, which indicates changed chemical activities of these atoms. Similar situation happens on O atoms near doped Fe and form 3-fold triangle-like features. XPS spectra imply that Co keeps 2+ oxidation state whereas Fe shows 3+ oxidation state, which is not the same with the oxidation state of 2+ in the iron oxide nanoislands, indicating that iron species in the cobalt-iron oxides have stronger oxidizing ability. Further water exposure experiments demonstrate that hydroxyl groups usually appear next to the doped iron sites while almost randomly distributed on the basal plane of pure cobalt oxide nanoislands, suggesting that iron species in the cobalt-iron oxide play an important role in promoting the catalytic activity.

References

1. Burke, Michaela S., et al., Journal of the American Chemical Society 137.10 (2015): 3638-3648.

2. Fester, J., et al., Nature Communications 8 (2017): 14169.

3. Walton, Alex S., et al., ACS Nano 9.3 (2015): 2445-2453.

8:20am SS+EM+HC+MI-ThM2 An Ordered Mixed Oxide Monolayer formed by Iron Segregation on Rutile-TiO$_2$(011), *Sandamali Halpegamage*, University of South Florida, *L. Bignardi, P. Lacovig,* Elettra-Sincrotrone Trieste, Italy, *A. Kramer*, University of South Florida, *Z. Wen, X. Gong,* East China University of Science and Technology, PR China, *S. Lizzit,* Elettra-Sincrotrone Trieste, Italy, *M. Batzill*, University of South Florida

Ternary oxide monolayers supported on or intermixed with a second oxide surface have attracted great interest in designing new materials with unique chemical functional properties including selective heterogeneous catalysts and nanocatalysts. Due to the complexity of the structure and composition, it is challenging to discover and characterize such phases. Here we synthesized an ordered mixed oxide monolayer of FeTi$_2$O$_5$ on rutile-TiO$_2$(011) via two different experimental pathways; firstly, by annealing the clean TiO$_2$(011) in 1×10^{-7} mbar of O$_2$ at ~450 ^{0}C and secondly, by physical vapor depositing Fe on clean TiO$_2$(011) in 1×10^{-7} mbar of O$_2$ at ~450 ^{0}C.In both procedures the Fe atoms intermixe with Ti atoms in the surface layer of the substrate and form an ordered mixed-oxide monolayer with FeTi$_2$O$_5$ composition. High resolution and fast X-ray photoemission spectroscopy (XPS) reveals that Fe and Ti are in 2+ and 4+ charge states respectively. The structure of this mixed oxide monolayer was predicted by a combination of atomically-resolved STM (Scanning Tunneling Microscopy) and DFT-based calculations and further confirmed by synchrotron based angle scanned x-ray photoelectron diffraction (XPD) studies. Multiple electron scattering simulations implemented in the Electron Diffraction in Atomic Clusters (EDAC) package

were performed for comparing experimental XPD patterns with structural models. Judged by the reliability factor (R$_p$), the experimentally determined XPD patterns are in good agreement with the simulated XPD patterns. The study has been extended to a few of the other transition metals namely, V, Cr, and Ni. Due to the similarities in the bulk oxide structures of these transition metals they all are capable of forming similar intermixed monolayer oxide surfaces with the composition MTi$_2$O$_5$ (M=V,Ni,Cr). For all these monolayers, the valance band maximum (VBM) is above the VBM for TiO$_2$, suggesting that these monolayers may trap holes at the surface efficiently and thus may modify the photocatalytic activity of TiO$_2$.

8:40am SS+EM+HC+MI-ThM3 Growth and Chemistry of rutile IrO$_2$ Surfaces, *Jason Weaver*, Z. Liang, T. Li, R. Rai, University of Florida, Gainesville, *M. Kim, A. Asthagiri*, The Ohio State University **INVITED**

Interest in the surface chemistry of late transition-metal oxides has been stimulated by observations that the formation of metal oxide layers tends to dramatically alter the catalytic performance of transition metals in applications of oxidation catalysis. In this talk, I will discuss our recent investigations of the growth and chemical properties of rutile IrO$_2$ surfaces. I will discuss our studies of the oxidation of metallic Ir surfaces by O-atom beams as well as O$_2$ at pressures above 1 Torr. We find that stoichiometrically-terminated IrO$_2$(110) layers could only be formed by oxidizing Ir(111) and Ir(100) at sufficiently high temperature and O$_2$ pressure. I will discuss the binding characteristics of small molecules, and our recent discovery of highly facile CH$_4$ activation on the IrO$_2$(110) surface at temperatures as low as 150 K.

9:20am SS+EM+HC+MI-ThM5 Formation and Manipulation of Water Clusters on Bilayer ZnO Surface, *Junseok Lee, D.C. Sorescu, X. Deng*, National Energy Technology Laboratory

Adsorption of water on the nanostructured metal oxide surfaces has implications in catalysis and serves as a prototypical system in studying water-oxide interfaces. By using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, the clustering behavior of water on the bilayer ZnO surface grown on Au(111) has been studied at low coverage regime. Diffusion and clustering of water molecules at specific sites in the Moire pattern are observed after initial adsorption of water on bilayer ZnO at T = 77 K. Heating the surface to T < ~240 K reveals that the adsorbed water molecules form triangular shape clusters with two specific orientations in the STM images. The DFT calculations along with the experimental findings suggest that the clusters are comprised of mixed water and hydroxyl groups with a binding energy of 21 kcal/mol. The two types of clusters can be converted to each other by the injection of electron from the STM tip. The inelastic electron scattering process is considered to be responsible for the conversion of the clusters via O-H stretch vibration mode excitation.

9:40am SS+EM+HC+MI-ThM6 Formation of Metastable Water Chains on Anatase TiO$_2$(101), *Arjun Dahal*, Z. Dohnálek, Pacific Northwest National Laboratory

The interaction of water with metal oxide surfaces is of great importance in many diverse areas such as catalysis, electrochemistry, corrosion, atmospheric science, geology, astrophysics, and others. Anatase TiO$_2$ surface is particularly relevant because it is the most active polymorph of TiO$_2$ and its commercially employed nanomaterials grow preferentially as anatase. In this study, we employ scanning tunneling microscopy (STM) to study the adsorption of water on a model stoichiometric anatase TiO$_2$(101) surface. Well-defined anatase TiO$_2$(101) surface has saw-tooth-like morphology exposing alternating rows of two-fold-coordinated oxygen atoms (O$_{2c}$) and five-fold-coordinated Ti atoms (Ti$_{5c}$) along the [010] direction. Our STM data show that at 80 K isolated water monomers bind molecularly to the Ti$_{5c}$ sites. The onset of diffusion is found at ~190 K where water monomers diffuse both along and across the Ti$_{5c}$ rows. The analysis shows that the along-the-row diffusion is energetically favored by only 0.03 eV. Surprisingly, we find that at 80 K water molecules start to form linear chains along the Ti$_{5c}$ rows as the coverage is increased. This indicates the presence of transient mobility of water molecules suggesting that the adsorption occurs via a precursor state. When the water chains are annealed at 190 K, they fall apart to monomers that reside on the next-nearest-neighbor Ti$_{5c}$ sites. These results demonstrate that the water chains are metastable in nature. This is at odds with many other oxide surfaces where hydrogen-bonded water clusters are energetically preferred over the isolated monomers.

11:00am SS+EM+HC+MI-ThM10 The Structure of Fe$_2$O$_3$(012) and its Reactivity to Water, *Gareth Parkinson*, F. Kraushofer, Z. Jakub, M. Bichler, J. Hulva, M. Schmid, U. Diebold, P. Blaha, TU Wien, Austria

Hematite (α-Fe$_2$O$_3$) is a promising material for technological applications due to its abundance, low cost and chemical stability. Its 2.2 eV bandgap makes

it potentially ideal as a photoanode for photoelectrochemical water splitting, [1] but performance is hampered by slow reaction kinetics and the need for a significant overpotential. Little is known about the atomic-scale structure of hematite surfaces, and even less about how this relates to photocatalytic activity.

To date, most surface science studies of α-Fe_2O_3 have focused on the (001) facet, but preparing a stoichiometric surface under UHV conditions has proven problematic. Some authors have investigated the equally relevant (012) surface, [2][3][4] and reported that a (1x1) and a reduced (2x1) termination can be reversibly prepared. Several models have been proposed for the (2x1) reconstruction, but as yet no scanning probe data exists to support or refute them.

Here we present a multi-technique study of the (1x1) and (2x1) surfaces of α-Fe_2O_3 (012), as well as their interaction with water. The data acquired for the (1x1) termination support a bulk termination model, as predicted by previous publications, but STM and nc-AFM images of the (2x1) reconstruction are inconsistent with previously proposed models. [3] We propose a new model based on ordered oxygen vacancies, the plausibility of which is confirmed by density functional theory (DFT) results. TPD and XPS data reveal that the (1x1) surface adsorbs water in a mixed-mode fashion, whereas the interaction with the (2x1) surface is entirely dissociative. We propose models for the structure of the adsorbed overlayers based on scanning probe microscopy data.

References

[1] Parkinson, G. S. *Surface Science Reports* **71**, 272-365 (2016).

[2] Henderson, M. A., Joyce, S. A. & Rustad, J. R. *Surface Science* **417**, 66-81 (1998).

[3] Henderson, M. A. *Surface science* **515**, 253-262 (2002).

[4] Gautier-Soyer, M., Pollak, M., Henriot, M. & Guittet, M. *Surface science* **352**, 112-116 (1996).

11:20am **SS+EM+HC+MI-ThM11 Interaction of Water with anatase TiO₂(001)-1x4**, *Igor Beinik*, *K.C. Adamsen, S. Koust, J.V. Lauritsen, S. Wendt*, Aarhus University, Denmark

The interaction of water with titanium dioxide (TiO_2) is pivotal for many practical applications of this material in heterogeneous catalysis because water is almost always present either as a reactant or a product in many catalytic reactions. In our model study, we focus on the anatase polymorph of TiO_2 that has demonstrated a higher catalytic activity in water splitting than rutile and is generally considered as a more technologically relevant polymorph. The nanocrystals of anatase that are present in powder catalysts normally expose a high fraction of low surface energy (101) facets and a significantly smaller fraction of high energy, but supposedly more reactive (001) facets. The (001) facet is intrinsically unstable and reconstructs upon annealing in vacuum forming 1x4 reconstructed terraces, where rows of bridging oxygen atoms in [100] and [010] directions are replaced by TiO_3 units [1]. This kind of reconstruction has been found both on the (001) facets of anatase single crystals and nanoparticles [2], however the interaction of water with this surface has been significantly less investigated.

In the present work, we study the adsorption and dissociation of water on the anatase (001) 1x4 reconstructed surface by means of STM, TPD, and synchrotron core-level and valence band PES under UHV conditions. Our results show that water dissociates to some extent even at 120 K and that low water exposures (up to 3 L) at this temperature results in a mixture of molecularly and dissociatively adsorbed molecules. A systematic analysis of the data obtained using all three techniques leads us to a conclusion that the A-TiO2(001)-1x4 surface is rather reactive - in agreement with an earlier study [3] we find that water dissociates at the ridges of the 1x4 reconstruction. Moreover, the 1x4 reconstruction remains stable upon water exposures at least up to ~45 L (at 120 K). However, after desorption of a multilayer ice film, the ridges themselves contain a high number of defects, which remain stable up to 800 K. The nature of these defects will be discussed.

References:

1. Lazzeri, M. & Selloni, A. Phys. Rev. Lett. **87**, 266105 (2001).

2. Yuan, W. et al. Nano Letters **16**, 132–137 (2016).

3. Blomquist, J., et al. J Phys Chem C **112**, 16616–16621 (2008).

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