

O 89: Oxide and Insulator Surfaces: Adsorption III

Time: Thursday 10:30–12:45

Location: TRE Phy

O 89.1 Thu 10:30 TRE Phy

Adsorption of Water on (Ca,Sr)₃Ru₂O₇ surfaces — ●WERNFRIED MAYR-SCHMÖLZER, DANIEL HALWIDL, FLORIAN MITTENDORFER, ULRIKE DIEBOLD, JOSEF REDINGER, and MICHAEL SCHMID — Institute of Applied Physics, TU Vienna

Perovskite oxides are promising materials for a wide range of applications as diverse as sensors, fuel cells and catalysts. Surprisingly an atomic scale knowledge of their surface chemistry is still rather poor. Here we present a combined DFT, STM and XPS study of the first monolayer H₂O formation on the (001) surfaces of three Ruddeldsen-Popper type compounds, Sr₃Ru₂O₇, Ca doped Sr₃Ru₂O₇ and Ca₃Ru₂O₇. All cleave nicely, yielding flat rocksalt-like SrO-, (Sr,Ca)O- and CaO-type terminated surfaces. Adsorbed H₂O monomers dissociate on all surfaces by transferring an H to an apical O while the remaining OH resides at a nearby Sr-Sr, Ca-Sr, or Ca-Ca bridge, respectively. On the SrO-type surface dimers of dissociated H₂O are formed, which at higher coverage combine to chains and cages[1]. The CaO-type surface is much more reactive ($\Delta E_{Ads}^{H_2O} \approx 0.4\text{eV}$) and also shows chains of dissociated H₂O, but due to the different rotation and tilting of the RuO octahedra they only occur along the [010] direction. On the Ca doped SrO-type surface the dissociated H₂O molecule is preferably located at the dopant site and reactivity is increased by 0.1eV compared to the pure SrO-type surface. Additionally the dopant impedes dimer formation.

[1]D. Halwidl et. al., Nature Materials, 15(4), 450-455.

O 89.2 Thu 10:45 TRE Phy

Consecutive Charging of a Molecule-on-Insulator Ensemble Using Single Electron Tunnelling Methods — ●PHILIPP RAHE¹, RYAN P. STEELE², and CLAYTON C. WILLIAMS³ — ¹Fachbereich Physik, Universität Osnabrück, Osnabrück, Germany — ²Department of Chemistry, The University of Utah, Salt Lake City, USA — ³Department of Physics and Astronomy, The University of Utah, Salt Lake City, USA

Redox-active molecules are attractive materials for memory elements in future electronic devices [1]. Early success [2] in fabricating molecular memory cells notwithstanding, combining and interconnecting the functionality of single molecules into devices while electrically insulating them from the environment still remains a challenge [3].

Here, we follow the bottom-up strategy to fabricate a ferrocene-on-insulator system where the molecules self-assemble into islands stable at room-temperature. The charge state of this ferrocene-on-calcite(10 $\bar{1}$ 4) system can locally be modified at room temperature [4], where single electron tunnelling methods reveal the charging step. Kelvin probe force microscopy confirms a trapping of the charge within the island structure, and we introduce a model to explain the KPFM contrast [5]. Interestingly, our data gives evidence for charge stability even for multiple charges.

[1] J.S. Lindsey and D.F. Bocian, Acc. Chem. Res. 44, 638 (2011); [2] Z. Liu et al., Science 302, 1543 (2003); [3] J.R. Heath, Annu. Rev. Mater. Res. 39, 1 (2009); [4] P. Rahe et al., Nano Letters 16, 911 (2016); [5] J.L. Neff and P. Rahe, Phys. Rev. B 91, 085424 (2015).

O 89.3 Thu 11:00 TRE Phy

Electron Transfer between Anatase TiO₂ (101) and an Adsorbed O₂ Molecule: Direct Observation by nc-AFM — ●MARTIN SETVIN, JAN HULVA, GARETH PARKINSON, MICHAEL SCHMID, and ULRIKE DIEBOLD — TU Wien

The electron transfer between the substrate and an adsorbed molecule is a key process in catalysis, photocatalysis, electrochemistry or redox chemistry. We use a low temperature q-Plus STM/AFM to study the electron transfer between the anatase TiO₂ (101) surface and a single adsorbed O₂ molecule. We can directly distinguish neutral physisorbed O₂ molecules in the triplet state from negatively charged (O₂)⁻ radicals, based on their different chemical reactivity towards the tip apex. Neutral O₂ molecules are inert, while the (O₂)⁻ radicals readily form a chemical bond with the tip. By biasing the tip, we can charge and discharge the molecules at will and we show that the identical processes occur during UV illumination of the sample. Using the Kelvin-probe force spectroscopy, we investigate in detail the process of charge transfer between the substrate and the adsorbed molecule. The experiments point towards a key importance of the physisorbed O₂

state and its electron affinity. The AFM data are supported by area-averaged spectroscopic techniques such as temperature programmed desorption or photoelectron spectroscopy.

O 89.4 Thu 11:15 TRE Phy

Methanol adsorption and reaction on a CuWO₄ monolayer on Cu(110) — ●MATTHIAS A. BLATNIK, CARL DRECHSEL, NASSAR DOUDIN, FALKO P. NETZER, and SVETLOZAR SURNEV — Surface and Interface Physics, Institute of Physics, University of Graz, Universitätsplatz 5, 8010 Graz, Austria

Here we investigate the chemical reactivity of CuWO₄ nanolayers on Cu(110), with a coverage between 0 and 1 ML, towards adsorption and reaction of methanol (CH₃OH) using a combination of high-resolution XPS and STM. Methanol has been dosed at 110 K, at which temperature it adsorbs molecularly as a multilayer. On heating to 160 K the methanol multilayer transforms into a methanol monolayer, methoxy (CH₃O) and some formaldehyde (CH₂O) intermediates. After heating to 260 K the methanol monolayer has fully converted into methoxy and some hydrocarbon (CH_x) adsorbates, which remain stable up to 310 K. After heating to 450 K methoxy has been desorbed from most of the CuWO₄ surface, except on those with coverages between 0.65 ML and 0.8 ML. The latter CuWO₄ surfaces show the largest methoxy yield and degree of reduction. This is a strong indication that the oxidation reaction is promoted at the periphery of the oxide islands, which expose a large number of active under-coordinated reaction sites. This is indeed confirmed by the STM measurements, which show that the methanol oxidation reaction is initiated at the boundaries between the Cu-O and CuWO₄ islands. Finally, flashing above 500 K results in the complete methoxy removal from the CuWO₄ surfaces

O 89.5 Thu 11:30 TRE Phy

Adsorption properties and reactivity of single Rh atoms on Fe₃O₄ (001) — ●JAN HULVA¹, ROLAND BLIEM¹, ZDENĚK JAKUM¹, ADAM ZÁVODNÝ¹, MICHAEL SCHMID¹, ULRIKE DIEBOLD¹, PETER BLAHA², and GARETH S. PARKINSON¹ — ¹Institute of Applied Physics, TU Wien, Wiedner Hauptstrasse 8-10, 1040 Vienna, Austria — ²Institute of Materials Chemistry, TU Wien, Getreidemarkt 9, 1060, Vienna, Austria

Single atom catalysis operates in the smallest particle size limit of supported metal catalyst. Although it has been shown that this approach is promising for the synthesis of highly active catalysts containing only small amount of expensive metal [1], the concept still remains controversial. It has been shown that Fe₃O₄ (001) surface is able to stabilize single metal atoms up to relatively high temperatures [2] due to its surface reconstruction [3]. This makes it an ideal candidate for a model system for fundamental studies of the single atom catalysis.

STM shows that Rh adatoms can be adsorbed at the magnetite surface in several different configurations. This can be linked to different chemical states of Rh seen by XPS. As predicted by DFT, CO bounds strongly to Rh adatoms and dimers giving an origin to two desorption peaks in TPD at 460K and 530K. Strong interaction of CO and Rh also leads to CO₂ formation by Mars-van Krevelen mechanism at these temperatures.

[1] Qiao B., Nature Chemistry, 3, (2011): 634-641. [2] Novotný Z., et al., Phys.Rev.Lett.108(2012): 216103 [3] Bliem R., et al. Science 346 (2014): 1215-1218.

O 89.6 Thu 11:45 TRE Phy

Imaging and manipulation of dissociated water on In₂O₃(111) — ●MARGARETA WAGNER¹, MARTIN SETVIN¹, STEFFEN SEILER², LYNN A. BOATNER³, MICHAEL SCHMID¹, BERND MEYER², and ULRIKE DIEBOLD¹ — ¹Institut für Angewandte Physik, TU Wien, Österreich — ²Computer Chemistry Center, FAU Erlangen-Nürnberg, Deutschland — ³Materials Science and Technology Division, ORNL, Tennessee, USA

Indium oxide is one of the most important transparent conductive oxides (TCOs), and commonly used as a contact and sensor material.

Here, the adsorption of water is investigated with low temperature STM/AFM, XPS and DFT. Above 100 K dissociative adsorption of water on In₂O₃(111) single crystals is observed. At room temperature the surface is saturated with three dissociated water molecules per unit cell, symmetrically arranged around the six-fold coordinated

In atoms. The fully hydroxylated surface shows a (1x1) structure with respect to the clean In₂O₃(111) surface. This leads to a well-ordered, hydroxylated surface where the three terminal OH groups plus the three protons (forming surface OH groups) are imaged together as one bright triangle in STM. The internal structure is revealed by AFM measurements, and manipulations with the STM tip, where surface OH groups can be individually removed.

O 89.7 Thu 12:00 TRE Phy

Water adsorption at the Zirconia Surface on Pt₃Zr — •PETER LACKNER¹, JAN HULVA¹, JOONG-IL J. CHOI^{1,2}, GARETH PARKINSON¹, ULRIKE DIEBOLD¹, and MICHAEL SCHMID¹ — ¹Institute of Applied Physics, TU Wien, Vienna, Austria — ²Institute for Basic Science, KAIST, Daejeon, Republic of Korea

Oxidation of Pt₃Zr(0001) single crystals leads to the formation of a ZrO₂(111) trilayer on top of a Pt layer [1]. In scanning tunneling microscopy (STM), the ZrO₂ layer shows a ($\sqrt{19}\times\sqrt{19}$)R23.4° superstructure with 12 Zr atoms in every unit cell. The Zr layer is strongly buckled and the ZrO₂ trilayer is distorted above substrate dislocation lines, thus creating different adsorption locations.

We have employed this ZrO₂/Pt₃Zr system as a model system for water adsorption studies on zirconia, combining temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and STM. In TPD, $\approx 90\%$ of the adsorbed D₂O contributes to the monolayer peak at 180 K ($E_{\text{ads}} = 0.5 - 0.6$ eV). According to XPS, these adsorbates are bound in molecular form. The remaining 10% are bound in the form of hydroxyls. They have higher binding energies, which leads to a tail in the TPD spectrum reaching up to 550 K.

Repeated TPD measurements lead to a decrease of the monolayer peak area and to an increase of the tail area. Thus, water changes the surface structure, creating adsorption sites with higher adsorption energies. This surface change was examined by low-temperature STM.

[1] Antlanger et al., Phys. Rev. B 86, 035451 (2012).

O 89.8 Thu 12:15 TRE Phy

Self-assembled π - π -stacked triphenylamine derivatives on bulk MgO(001) and KBr(001) — •TIM SANDER¹, MAXIMILIAN AMMON¹, NATALIE HAMMER², MARTIN GURRATH³, BERND MEYER³, MILAN KIVALA², and SABINE MAIER¹ — ¹Department of Physics, Friedrich-Alexander University Erlangen-Nürnberg, Erlangen, Germany — ²Chair of Organic Chemistry I, Department of Chemistry and Pharmacy, Friedrich-Alexander University Erlangen-Nürnberg, Erlan-

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Well-ordered molecular self-assemblies on insulating surfaces play a key role towards the controlled formation of organic nanostructures for potential applications in nanoelectronics. On bulk insulators, the subtle influence of the often weak and unspecific molecule-surface interaction on the self-assembly is of high interest.

Here, we discuss molecular self-assemblies of halogen-substituted carbonyl-bridged triphenylamine derivatives on bulk MgO(001) and KBr(001) by means of low temperature non-contact atomic force microscopy (nc-AFM) combined with density functional theory. We observe π - π -stacked structures with comparable adsorption energies on both surfaces. Molecularly resolved nc-AFM images indicate that the intermolecular distances in the triphenylamine structures are similar to the respective lattice spacing underneath. In addition, we find that the growth direction of the π - π -stacked chains is influenced by the choice of the substrate.

O 89.9 Thu 12:30 TRE Phy

Improving the photoelectrochemical performance of cobalt ferrite by transition metal substitution: A DFT+*U* study — •HAMIDREZA HAJIYANI and ROSSITZA PENTCHEVA — Fakultät für Physik and Center of Nanointegration (CENIDE), Universität Duisburg-Essen, 47057 Duisburg

Transition metal oxides are considered as promising materials for photo-anodes to convert solar energy into hydrogen fuel through water oxidation. Here we report density functional theory+*U* (DFT+*U*) calculations on the influence of transition metal mixing on the performance of cobalt ferrite (CoFe₂O₄) as anode material in the oxygen evolution reaction (OER). Our results on M_xCo_{1-x}Fe₂O₄ (111) surfaces illustrate that the overpotential during OER process can be reduced by partial substitution of Co sites with elements such as Ni. We find that this improvement is related to modification of the binding energy of the reaction intermediates during water oxidation. Analysis of spin density and electronic properties shows that substitution of nickel in cobalt ferrite varies the band gap, band edge positions and oxidation state of cations at the (111) surface.

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