

O 43: Oxides and Insulators: Adsorption I

Time: Tuesday 14:00–16:00

Location: H6

O 43.1 Tue 14:00 H6

Dissociated but not separated: Adsorption of water at the SrO surface of ruthenates — ●FLORIAN MITTENDORFER¹, DANIEL HALWIDL¹, BERNHARD STÖGER¹, WERNFRIED MAYR-SCHMÖLZER¹, JIRI PAVELEC¹, DAVID FOBES², JIN PENG², ZHIQIANG MAO², GARETH PARKINSON¹, MICHAEL SCHMID¹, JOSEF REDINGER¹, and ULRIKE DIEBOLD¹ — ¹Inst. of Applied Physics, TU Wien, Vienna, Austria — ²Dept. of Physics, Tulane University, New Orleans, USA.

Despite their great promise in applications ranging from solid oxide fuel cells to catalysts, molecular level knowledge about the surface chemistry of perovskite oxides is surprisingly poor. To gain more insight, we follow the formation of the first monolayer of H₂O at the (001) surfaces of Sr_{n+1}Ru_nO_{3n+1} (n=1,2) using low-temperature STM, XPS, and DFT. These layered perovskites cleave between neighbouring SrO planes, yielding almost ideal, rocksalt-like surfaces. An adsorbed monomer dissociates and forms a pair of hydroxide ions. The OH stemming from the original molecule stays trapped at Sr-Sr bridge positions, circling the surface OH with a measured activation energy of 187 ± 10 meV confirming almost perfectly the calculated DFT value of 171 meV [1]. At higher coverage, dimers of dissociated H₂O assemble into one-dimensional chains and form a percolating network where H₂O adsorbs molecularly in the gaps. Our work clearly shows that caution is needed when applying surface chemistry concepts derived for binary rocksalt oxides to perovskites.

[1] D. Halwidl et. al., Nature Materials, doi: 10.1038/nmat4512, 2015.

O 43.2 Tue 14:15 H6

Adsorption of water on the (001) surface of Fe₃O₄ studied by surface x-ray diffraction — ●BJÖRN ARNDT^{1,2}, HESHMAT NOEI¹, ROLAND BLIEM³, OSCAR GAMBA³, GARETH PARKINSON³, ULRIKE DIEBOLD³, and ANDREAS STIERLE^{1,2} — ¹Deutsches Elektron-Synchrotron (Desy), D-22607 Hamburg, Germany — ²Fachbereich Physik, Universität Hamburg, D-20355 Hamburg, Germany — ³Institute of Applied Physics, Vienna University of Technology, 1060 Vienna, Austria

Magnetite (Fe₃O₄) exhibits interesting properties which makes it attractive for applications e.g. in catalysis, where it is used to catalyze the water-gas shift reaction. The (001) surface of magnetite shows a (sqrt(2)x sqrt(2))R45° surface reconstruction in UHV [1], which gets lifted upon adsorption of water vapor at room temperature. Previous studies of the adsorption of water at different coverages on this surface were done by XPS measurements [2], without linking it to the surface structure. To probe the unreconstructed surface structure, we therefore performed surface x-ray diffraction at the ESRF ID03 beamline under flow conditions at a photon energy of 11 keV and at the MPG diffraction beamline at ANKA under static conditions at 10 keV and water vapor pressures in the mbar regime at room temperature. We were able to follow the lifting of the surface reconstruction and observed changes in the morphology of the surface. Crystal truncation rod data give insight into the surface structure. 1. Bliem et al., Science, 346, 1215-1218 (2014) 2. Kendelewicz, T. et al., J. Phys. Chem. C 117, 2719-2733 (2013)

O 43.3 Tue 14:30 H6

Ab-initio simulations of water splitting on hematite — ●NICOLA SERIANI — The Abdus Salam ICTP, Trieste, Italy

Hematite has recently raised considerable interest as a possible photocatalyst for water oxidation. Despite the on-going research efforts, its efficiency is still unsatisfactory. To understand the behaviour of hematite in a realistic environment, we have performed first-principles simulations based on density functional theory. By taking into account the presence of water and oxygen under illumination, we show that the thermodynamically stable surface termination under reaction conditions is oxygen rich. On this termination, water oxidation proceeds by nucleophilic attack with an overpotential of 0.84 V. Then, we have considered the possible effect of surface modifications such as impurities and ultrathin films on the properties of the surface. Nitrogen doping lowers the overpotential, while detrimental surface states disappear in presence of ultrathin films of gallium oxide or aluminium oxide. I am going to compare calculations with available experiments, and to discuss open questions and future developments in this field.

O 43.4 Tue 14:45 H6

Derivation and Validation of a Classical Potential for Surfaces of Ionic Crystals — ●SARA PANAHIAN JAND and PAYAM KAGHAZCHI — Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany

In this work, we present a method to parametrize Coulomb+Buckingham (C-B) pairwise potentials that can be used to study the atomic structure and stability of surfaces of ionic crystals. Our training sets are based on density functional theory (DFT) calculations. In the parametrization procedure, ionic charges are calculated using electrostatic energies and then Buckingham parameters are fitted to reproduce energy changes versus atomic displacements and unit cell size in bulk. Although depending on the starting points different sets of parameters are obtained, only one set of them can qualitatively reproduce (DFT-calculated) atomic structure and stability of low-index surfaces of ionic crystals. We found that the constructed potentials can calculate relaxations and relative stabilities of higher-index surfaces in good agreement with experiments and DFT [1]. Most of electrode and (solid) electrolyte materials in Li-based batteries have ionic crystals. Therefore, the method discussed in the present work [2] can be applied to construct reliable classical potentials for these materials to study electrode/electrolyte interfaces in Li-based batteries.

[1] S. Panahian Jand and P. Kaghazchi, J. Phys.: Condens. Matter, 26, 262001 (2014)

[2] S. Panahian Jand and P. Kaghazchi, submitted

O 43.5 Tue 15:00 H6

UHV-IR spectroscopy study of carbon monoxide adsorption on ceria single crystal surfaces — ●CHENGWU YANG, ALEXEI NEFEDOV, YUEMIN WANG, and CHROSTOF WÖLL — Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

Ceria, one of the most easily reducible metal oxides, exhibits extraordinary reactivities in diverse catalytic processes. The importance of this material has triggered numerous experimental and theoretical studies, in particular aiming at elucidating the properties of oxygen vacancies. The studies on bulk single crystal surfaces, however, are still scarce.

On a novel apparatus combining a state-of-the-art FT-IR spectrometer with a dedicated UHV-chamber, we used carbon monoxide (CO) to probe regular sites and oxygen vacancies at surfaces of bulk CeO₂(111), CeO₂(110), and CeO₂(100) single crystals. It was found that the vibrational frequency of C-O stretching mode strongly depends on facet orientations as well as the reduction of ceria surfaces. The assignment of the CO stretch frequency as determined by IR-spectroscopy was supported by ab-initio electronic structure calculations using density functional theory. The obtained results clearly indicate that the application of CO adsorption as a IR-probe is quite suitable for the determination of facet orientations as well as for probing surface oxygen vacancies and allows us to clarify the ambiguous assignments derived from previous powder and thin film data.

O 43.6 Tue 15:15 H6

An ab initio study of adsorption and defect formation energies at the surface of Ni-doped MgO – a catalyst for the Sabatier process — ●ALIAKSEI MAZHEIKA, SERGEY LEVCHENKO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Berlin, Deutschland

We present an *ab initio* study of Ni_{Mg} defects in Ni-doped MgO - a promising material for the catalytic conversion of methane and CO₂. First, a fraction of exact exchange α in the hybrid DFT functional HSE06 is identified such that HSE(α) closely reproduces CCSD(T) formation energies of Ni_{Mg} in MgO bulk, as well as the adsorption energies of CO and H₂ at the surface defects, calculated with embedded cluster models. HSE($\alpha = 0.3$) is found to reproduce all the CCSD(T) results with deviations of at most 0.1 eV. Using this functional and periodic models, we calculate the formation energy dependence on the position of Ni_{Mg} (in the bulk, subsurface, at the (001) terrace, monolayer step and corner), and the influence of the defects on the adsorption energies of CO₂, CH₄, CO, and H₂. The presence of Ni_{Mg} at the surface is found to have a minor effect on the adsorption energies of CH₄ and CO₂, independent of the coordination of the adsorption site, whereas it increases the adsorption energy of CO and particularly H₂. The adsorption energy of CO₂ calculated with HSE($\alpha = 0.3$) plus the

ab initio many-body van der Waals correction [1] is about 0.4 eV larger than the PBE adsorption energy. - [1] A. Tkatchenko et al. PRL. 108, 236402 (2012)

O 43.7 Tue 15:30 H6

Adsorption and reactivity of phthalic acid on MgO(100) thin films — •QURATULAIN TARIQ, MATTHIAS FRANKE, DANIEL WECHSLER, MICHAEL RÖCKERT, LIANG ZHANG, HANS-PETER STEINRÜCK, and OLE LYTKEN — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, 91058 Erlangen, Egerlandstraße 3, Germany

The adsorption of functional organic species on oxide surfaces has importance in many areas of research, for example, in molecular electronics, photovoltaics and biomedical implants. In this work, we report on the adsorption of phthalic acid, a simple dicarboxylic acid, on MgO(100) thin films on Ag(100), as a model for the anchoring of large, functional organic entities such as porphyrins or fullerenes. Using high-resolution synchrotron radiation photoelectron spectroscopy (SRPES), near-edge X-ray absorption fine structure (NEXAFS) and temperature-programmed desorption (TPD), we find that the phthalic acid dissociates below 150 K to phthalic anhydride and carboxylate. Phthalic anhydride desorbs at around 240 K. Carboxylate binds to MgO as bis-bidentate species and stable up to 500 K, after which it decomposes, through desorption of CO₂. This project is supported by the DFG through FOR 1878 (funCOS).

O 43.8 Tue 15:45 H6

Electrospray deposition of organic molecules in UHV on bulk insulator surfaces — •ANTOINE HINAUT, RÉMY PAWLAK, THILO GLATZEL, and ERNST MEYER — Department of Physic, University of Basel Klingelbergstrasse 82, CH-4056 Basel, Switzerland

Adsorption of molecules, isolated or as assemblies, on surfaces under ultra high vacuum (UHV) conditions is an important field in nanoscience and lead to many applications such as photovoltaic, molecular electronic or surface functionalization. To study larger and more complex molecules in such conditions, suitable for such devices an alternative method to thermal evaporation is to use Electrospray ionisation system. In that way, the deposition of molecules contained in solution on atomically-clean surfaces is not limited to their size or their reactivity.

In our measurement we imaged, by bimodal non-contact atomic force microscopy (ncAFM), adsorbed molecules that were deposited on the bulk insulator surface KBr(001) via electrospray deposition. The molecule is a triply fused diporphyrin, which includes two zinc atoms and two di-cyanophenyl groups for a better anchoring on the KBr(001) surface. For large coverage we found charging of the surface due to the deposition. Comparison of the surface before and after the charge compensation will be presented. For lower coverage no charging effects were observed and single molecules have been imaged.