

O 81: Oxide and Insulator Surfaces: Adsorption II

Time: Wednesday 16:00–18:30

Location: WIL C107

O 81.1 Wed 16:00 WIL C107

Adsorption Sites of Individual Metal Atoms on MgO Thin Films Determined by Means of STM — ●EDGAR FERNANDES, FABIO DONATI, FRANÇOIS PATTHEY, and HARALD BRUNE — Institute of Physics (IPHY), Ecole Polytechnique Fédérale de Lausanne (EPFL), Station 3, CH-1015 Lausanne, Switzerland

Single Atoms on ultrathin insulating layers grown on metal surfaces have shown magnetic bistability up to 40 K [F. Donati & *al.*, *Science* **352**, 318 (2016)] and catalytic activity [B. Qiao & *al.*, *Nat. Chem.* **3**, 634 (2011)]. These spectacular properties are determined by the adsorption site that influences the charge state, crystal field, diffusion barrier, and magnetic ground state.

Here, we present a novel experimental method to determine the adsorption site of adatoms on thin MgO(100) layers on Ag(100) with the scanning tunnelling microscope. We determine the lattice constant and orientation of the atomic lattice from atomic resolution images recorded on pristine MgO and identify the sub-lattice imaged as protrusions by means of doping with Ca atoms that substitute and thereby mark the Mg atoms. Ho atoms adsorb on O and bridge sites, with their respective abundance depending on MgO thickness. Co and Fe atoms are on O sites while Au atoms are on bridge sites in contrast to former work [M. Sterrer & *al.*, *Phys. Rev. Lett.* **98**, 206103 (2007)].

O 81.2 Wed 16:15 WIL C107

Photochemical switching of azobenzene derivatives on an insulating surface — ●SIMON JAEKEL¹, ANTJE RICHTER², ROBERT LINDNER², ANGELIKA KÜHNLE², STEFAN HECHT³, and LEONHARD GRILL¹ — ¹Department of Physical Chemistry, University of Graz, Austria — ²Institute for Physical Chemistry, Johannes-Gutenberg University Mainz, Germany — ³Department of Chemistry, Humboldt-University Berlin, Germany

Studying single molecular switches is of interest for a better understanding of fundamental physical and chemical processes, but also in view of their possible use in molecular nanotechnology [1].

A prototypical conformational switch is azobenzene, which changes between trans and cis isomers at the central N=N bond upon an external stimulus, showing efficient photochemical activation. In the past years, various studies have shown that adsorption on metal substrates strongly influences the switching properties [2,3], especially for activation by light [4].

We present non-contact atomic force microscopy (nc-AFM) results on the switching of individual azobenzene molecules on a calcite surface where the molecules retain their photochemical activity.

[1] C. Joachim *et al.*, *Nature* **506**, 651 (2000); [2] Choi *et al.*, *Phys. Rev. Lett.* **96**, 156106 (2006); [3] Dri *et al.*, *Nature Nanotechnology* **3**, 649 (2008); [4] Comstock *et al.*, *Phys. Rev. Lett.* **99**, 038301 (2007)

O 81.3 Wed 16:30 WIL C107

DFT Study of Water Adsorption on Cation Doped (001)-MgO Surfaces — ●THOMAS RUH¹, CHRISTIAN KNOLL², DANNY MÜLLER², PETER WEINBERGER², and PETER BLAHA¹ — ¹Institute of Materials Chemistry, TU Wien — ²Institute of Applied Synthetic Chemistry, TU Wien

Combined hydration/dehydration processes of oxide/hydroxide systems can be used for storage of industrial excess heat. An example is the system CaO/Ca(OH)₂ [1]. The exothermal reaction of CaO and water (to release stored energy) is fast and complete at ambient temperature; however, the reverse reaction to recover CaO requires high temperatures. For several applications a system operable at lower temperatures would be desirable.

A potential candidate is the system MgO/Mg(OH)₂. However, the reaction of the oxide with water is slow and incomplete at room temperature. Many studies of the adsorption behaviour of water on MgO surfaces suggest that the reaction is kinetically hindered. Hu *et al* [2], for instance, found in a DFT study, that adsorbed water does not dissociate on MgO surfaces, whereas on CaO surfaces hydroxyls are formed.

In the present work we investigate the effects of cation doping of the (001)-surface of MgO with different cations on the formation and subsequent stability of hydroxyls.

[1] S. Jujimoto *et al.*, *Energ. Convers. Manage.*, 2002, **43**, 947-960
[2] X.L. Hu *et al.*, *Phys. Chem. Chem. Phys.*, 2011, **13**, 12447-12453

[3] <http://www.wien2k.at>

O 81.4 Wed 16:45 WIL C107

Adsorption of Organic Molecules on Magnetite Single Crystal Surfaces — ●MARCUS CREUTZBURG^{1,2}, HESHMAT NOEI¹, and ANDREAS STIERLE^{1,2} — ¹Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, Hamburg, Germany — ²Fachbereich Physik, Universität Hamburg, Jungiusstraße 9, Hamburg, Germany

Magnetite (Fe₃O₄) is a very important and diverse transition metal oxide with applications in catalysis, data storage and biomedical imaging. In a recent study magnetite nanoparticles linked by oleic acid molecules show exceptional isotropic mechanical properties [1]. To give further insight on how these nanoparticles interact with organic molecules it is crucial to study flat single crystal and vicinal Fe₃O₄ surfaces. In this contribution, we present initial results on the adsorption of water and organic molecules like formic acid and oleic acid on the magnetite (111) and on the vicinal (112) surface under UHV conditions obtained by vibrational spectroscopy and X-ray photoemission spectroscopy. We show low energy electron diffraction patterns of the vicinal (112) which allows us to conclude that this surface is indeed stable and presents regularly ordered terraces and steps.

[1] A. Dreyer *et al.*, *Nature Materials* **15**, 522-528 (2016)

O 81.5 Wed 17:00 WIL C107

Temperature-dependent reactions of Phthalic Acid on Co₃O₄(111) — ●DANIEL WECHSLER, MATTHIAS FRANKE, QURATULAIN TARIQ, HANS-PETER STEINRÜCK, and OLE LYTKEN — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, 91058 Erlangen, Egerlandstraße 3, Germany

Understanding the bonding between organic molecules and metal-oxide surfaces plays an important role in many nanotechnology devices. Functional groups, like -COOH, can act as linkers to attach molecules to surfaces in a controlled manner.

Using synchrotron-radiation X-ray photoelectron spectroscopy and temperature programmed desorption we have followed the adsorption and reactions of phthalic acid, a model system with two carboxylic acid linker groups, with Co₃O₄(111) as a function of coverage and temperature. Upon annealing from 105 to 800 K, three different temperature regions have been identified. They were assigned to intact phthalic acid, a carboxylate species forming at 350 K and finally thermal composition beginning at 750 K. Near-edge X-ray absorption fine structure measurements confirm an upright-standing adsorption geometry of the carboxylate species.

The project is supported by the DFG through FOR 1878 (funCOS).

O 81.6 Wed 17:15 WIL C107

Theoretical Description of the Adsorption of Water and Ethanol on Pt₄/Pt(111) and Pt₄/CeO₂(111) Substrates — ●YOHANNA SEMINOVSKI¹, POLINA TERESHCHUK¹, ADAM KIEJNA², and JUAREZ L. F. DA SILVA¹ — ¹São Carlos Institute of Chemistry, University of São Paulo, São Carlos, SP, Brazil — ²Institute of Experimental Physics, University of Wrocław, Wrocław, Poland

Pt-ceria, which has been proposed as catalyst for H₂ production in ethanol steam reforming reaction process, show formation of partially reduced Ce cations because of charge transfer from Pt transition metal towards oxide surface.[1] However, the role of the independent active adsorption sites on TM_n/CeO₂(111) substrates is not well understood yet. For instance, it is not known if the cationic Pt sites coexistent with the newly formed Ce³⁺ influence the adsorption properties of molecule on the substrates. In this work,[2] we applied DFT+U to study the active sites and the role of partial cationic charge of the Pt atoms on the adsorption properties of water and ethanol (probe molecules) on four selected substrates, Pt(111), Pt₄/Pt(111), CeO₂(111), and Pt₄/CeO₂(111). Results show each molecule preferentially located in the cationic sites of the base of the tetrahedron Pt₄ cluster, while in the anionic, lower-coordinated Pt atom sites located on the cluster-top or in the surface Ce and O sites the molecule adsorption is less favored. The Ce³⁺ atoms aren't found to be directly involved in the adsorption process of molecules, however these are important in the stabilization of the substrate.[1]P. Tereshchuk *et al.*, *PCCP* **17**, 13520 (2015) [2]Y. Seminovski *et al.*, *JCP* **145**, 124709 (2016)

O 81.7 Wed 17:30 WIL C107

High-resolution photoemission and X-ray absorption spectroscopy of a functionalized porphyrin adsorbed on MgO(100) — •QURATULAIN TARIQ, MATTHIAS FRANKE, DANIEL WECHSLER, HANS-PETER STEINRÜCK, and OLE LYTKEN — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, 91058 Erlangen, Egerlandstraße 3, Germany

Ultra-thin layers of functional organic molecules on oxide surfaces have a huge scientific and technological potential in molecular electronics. Porphyrins, in particular, represent an interesting class of compounds that can be modified synthetically by variation of the metal center, by attaching different substituents to the macrocycle, or by introduction of specific linker groups for the attachment on surfaces. In present work, a cobalt porphyrin bearing carboxylic groups, 5,10,15,20-tetrakis (4-carboxyphenyl) porphyrin (CoTCPP), was anchored on MgO(100)/Ag(100) thin films, at room temperature. High-resolution synchrotron radiation photoelectron spectroscopy (SRPES) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy are used to characterize the system, as a function of coverage and temperature. SRPES analysis for different coverages reveals that CoTCPP binds to the surface via formation of bidentate carboxylate. From NEXAFS spectroscopy, it is found that for sub-monolayer coverage, CoTCPP adsorbs almost parallel to the oxide substrate, whereas for monolayer and higher coverages, CoTCPP adsorbs at an angle from the surface plane (with a possible tilt angle of $< 45^\circ$ relative to the surface normal). This project is supported by the DFG through FOR 1878 (funCOS).

O 81.8 Wed 17:45 WIL C107

Adsorption of Oxygen on Ca₃Ru₂O₇(001) — •DANIEL HALWIDL¹, WERNFRIED MAYR-SCHMÖLZER^{1,2}, FLORIAN MITTENDORFER^{1,2}, DAVID FOBES³, JIN PENG³, ZHIQIANG MAO³, MICHAEL SCHMID¹, JOSEF REDINGER^{1,2}, and ULRIKE DIEBOLD¹ — ¹Institute of Applied Physics, TU Wien, Wiedner Hauptstraße 8-10, A-1040 Vienna, Austria — ²Center for Computational Materials Science, TU Wien, Wiedner Hauptstraße 8-10, A-1040 Vienna, Austria — ³Department of Physics and Engineering Physics, Tulane University, New Orleans, LA, USA

Complex ternary perovskite oxides are increasingly used in solid oxide fuel cells and catalysis [1]. Therefore it is highly desirable to obtain a better understanding of their surface chemical properties. We use low-temperature STM, nc-AFM, XPS and DFT to investigate the adsorption of oxygen on the layered perovskite Ca₃Ru₂O₇.

Single oxygen molecules appear fuzzy in STM, but are resolved in nc-AFM at LHe and LN₂ temperature. At higher coverages the molecules form a (2 × 1) overlayer that covers almost the whole surface. Local contact potential difference (LCPD) measurements suggest that the oxygen molecules are charged, in agreement with DFT calculations predicting adsorption as superoxo species. Desorption of the O₂ occurs at approximately 220 K, again in agreement with the calculated adsorption energy of $E_{ads} = 0.7$ eV.

This work was supported by the Austrian Science Fund (FWF project F45) and the ERC Advanced Grant “OxideSurfaces”.

[1] M. A. Pena, and J. L. G. Fierro, Chem. Rev. 101, 1981 (2001)

O 81.9 Wed 18:00 WIL C107

Water adsorption on top of the hematite(0001) surface at medium and high coverage regimes — •ROMAN OVCHARENKO and ELENA VOLOSHINA — Institut für Chemie, Humboldt-Universität zu Berlin, Berlin, Germany

On the pristine hematite(0001) half-iron termination isolated water molecules form an dissociated structure with an OH group attached to a surface iron ion and a protonated surface oxygen ion [1]. At increasing water loading the water-water interaction starts to play a crucial role in the adsorption behaviour and energetics. Thus, according to our PBE+U+D2 calculations, for the 1/2 monolayer (ML) coverage fully dissociated and mixed adsorption structures are energetically degenerated. Nevertheless, both water molecules and OH-groups adsorb at different coordinatively unsaturated metal sites and do not tend to form a dimer structure as it was found for the magnetite(111) surface [2]. When increasing water loading further up to 3/4 ML, a tendency to form mixed adsorption structures become even more pronounced. This is different to water adsorption on top of the isomorphous corundum (0001) surface, where by increasing water loading each following molecule was found to dissociatively adsorb at new metal site up to the full monolayer. Thus, the hematite(0001) surface, partially inheriting the properties of both magnetite and aluminium oxide, demonstrates unique chemical reactivity towards water adsorption at medium and high coverage regimes. [1] R. Ovcharenko et al., Phys. Chem. Chem. Phys. 18, 25560 (2016) [2] X. Li et al., J. Phys. Chem. C 120, 1056 (2015)

O 81.10 Wed 18:15 WIL C107

Adsorption of Oxygen on Ruthenate Perovskite Surfaces — •FLORIAN MITTENDORFER, WERNFRIED MAYR-SCHMÖLZER, JOSEF REDINGER, DANIEL HALWIDL, and ULRIKE DIEBOLD — Institute of Applied Physics, TU Vienna

The surface chemistry of perovskite oxides plays a central role for promising applications, such as solid oxide fuel cells. In a recent study, we could demonstrate a high chemical activity of strontium ruthenate surfaces for the adsorption of CO [1] and H₂O[2]. In this presentation, I will discuss the adsorption of oxygen (O₂) on the (001) surface of the Ruddlesden-Popper perovskites Sr₃Ru₂O₇(SRO) and Ca₃Ru₂O₇(CRO) on the basis of density functional theory (DFT) calculations. Oxygen adsorbs as a charged molecular species on both surfaces, yet our results display pronounced differences between the two systems. In the low coverage case, the calculations predict a slight tilting of the O₂ molecule on the SRO (001) surface, and the surface is uniformly covered at higher coverages. In contrast, the additional tilting of the Ru octahedra at the bare CaO terminated CRO (001) surface leads to a striped pattern of wide and narrow rows. This pattern strongly influences the respective adsorption energies of the O₂ molecule, as the adsorption in the wide channels is significantly more stable than the adsorption in the narrow channels. Thus, in agreement with experiment, the saturation coverage is already reached at an oxygen coverage of 0.5 ML, where the occupation of symmetry-equivalent sites leads to the formation of a zig-zag arrangement of the O₂ molecules. [1] Phys. Rev. Lett 113, 116101 (2014) [2] Nature Materials 15, 450 (2016)