

O 65: Oxides and Insulators

Time: Wednesday 18:15–21:00

Location: Poster A

O 65.1 Wed 18:15 Poster A

Adsorption behaviour of 2H-Tetraphenylporphyrin on rutile TiO₂(110): a room temperature STM investigation — ●MARTIN DROST, FAN TU, FLORIAN VOLLNHALS, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058

The controlled fabrication of well-defined nanostructures can be addressed by the self-assembly of functional molecules on surfaces. In this regard, we investigate the adsorption behavior of 2H-tetraphenylporphyrin (2HTPP) as a prototype functional molecule on rutile TiO₂(110) with scanning tunneling microscopy (STM) mainly at room temperature. A coverage dependent study reveals that at low coverages the 2HTPPs are mainly observed as isolated individual molecules in registry with the Ti-rows of the substrate. With increasing coverage, more and more loosely ordered molecular domains are found. Interestingly, upon moderate heating a significant restructuring of the adsorption system is observed, which yield to the formation of well-ordered supramolecular assemblies of the porphyrins. The specific contributions of molecule-substrate and molecule-molecule interactions will be discussed.

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O 65.2 Wed 18:15 Poster A

The Role of H-Termination on the ZnO (10 $\bar{1}$ 0) Surface — ●MARIA E. STOURNARA¹, OLIVER T. HOFFMAN^{1,2}, PATRICK RINKE^{1,3}, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Institut für Festkörperphysik, Technische Universität Graz, Graz, Austria — ³COMP/Department of Applied Physics, Aalto University School of Science, Aalto, Finland

The optical and electronic properties of H-terminated ZnO surfaces play a significant role for the electronic and excitonic states in hybrid inorganic/organic semiconductor technologies. As the intrinsic presence of H affects the properties of the ZnO surface even at infinitesimally low concentrations, a careful evaluation of the stable H-surface configurations is necessary to understand the effect of H adsorption on the surface electronic structure. To elucidate the role of the latter we perform density-functional theory PBE-vdW^{MBD} calculations for various H-concentrations. We find that H adsorption results in a complex behavior with a competition between hydrogen adsorption on surface O and surface Zn atoms, even at low H concentrations. This is responsible for a diverse surface electronic structure, where OH-bonding leads to a metallic behavior, whereas a semiconducting state is restored for adsorption on Zn-sites. Our results indicate that the former is favored at infinitesimally low coverage, whereas the latter is displayed for half-monolayer concentrations where H is adsorbed on neighboring Zn- and O- sites, forming ZnO-"stripes". In light of this, we evaluate intermixed site-motifs via a lattice gas hamiltonian (LGH) to describe H adsorption for a wide range of concentrations.

O 65.3 Wed 18:15 Poster A

adsorption of PTCDA on KCl and NaCl(100) surfaces — HAZEM ALDAHAK, ●WOLF GERO SCHMIDT, and EVA RAULS — Universität Paderborn, Warburger Str. 100, 33098 Paderborn

The adsorption of PTCDA (C₂₄H₈O₆) on metal substrates has for a long time been used as model system for understanding molecular self-assembly. Ionic crystals as substrate provide the additional possibility to study the molecular properties with little perturbation by substrate screening or strong substrate-adsorbate bonds [1]. Here, we present density-functional theory calculations on the adsorption and adsorbate-substrate interaction between PTCDA and planar and as well as stepped NaCl as well as KCl surfaces. The adsorption is dominated by van-der-Waals and electrostatic forces. This lead to a site-specific adsorption of the molecule on the surface, possibly resulting in commensurate long-range ordered structures [2]. The influence of the substrate and bonding mechanism on the molecular electronic structure as well as the molecular vibrations is investigated in detail and compared with the experimental data available [3-5]. Our calculations for different kinds of step-edge defects show the importance of these surface defects for initiating the adsorption of organic molecules on

ionic surfaces.

[1] V. W. Henrich, P.A Cox, The surface of metal Oxides, vol.1, Cambridge University Press, 1996 [2] H. Aldahhak et al, Surf. Sci. 617, 242-248, 2013. [3] Que et al., J. Phys. Chem. C (in Press). [4] H Karacuban et al. Nanotechnology, 22 (29), 295305, 2011. [5] A. Paulheim et al., Phys. Chem. Chem. Phys.15 (2013) 4906.

O 65.4 Wed 18:15 Poster A

Improving ceramic-polymer interface stability: Ab-initio study of benzoic acid on TiO₂ — ●WOLFGANG HECKEL, AXEL DREYER, GEROLD A. SCHNEIDER, and STEFAN MÜLLER — Hamburg University of Technology, Institute of Advanced Ceramics, Denickestr. 15, D-21073 Hamburg

In order to prepare functional hybrid composites with desired mechanical properties, the control of the interface stability is crucial. For a strong binding, carboxylic acids (CA) as a linker between ceramics and polymer are often used and extensively studied in the past.

Our results of a thermogravimetric analysis give rise to the assumption, that CA with an aromatic side chain can still improve the binding energy compared to CA with simple aliphatic ones. We present a corresponding DFT analysis of benzoic acid on both, anatase and rutile TiO₂ surfaces. To describe properly the attractive interaction of adsorbing molecules among each other, our results show clearly the requirement of applying an exchange correlation functional with van der Waals correction. On all surfaces, the resulting binding energies increase up to about 0.2 eV per molecule compared to CA with aliphatic side chains.

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O 65.5 Wed 18:15 Poster A

Fine structure in infrared spectra of high quality CO₂ ultrathin films on the NaCl(100) surface — ●JOCHEN VOGT — Chemisches Institut der Uni Magdeburg, Magdeburg, Germany

The splitting of the ν_3 asymmetric stretch mode into a longitudinal optical (LO) and a transverse optical mode (TO) is a well known feature of CO₂ ice thin films [1]. In new experiments, high quality ultrathin films were grown by exposure of a saturated monolayer CO₂-p(2x1)/NaCl(100) to additional CO₂ at 40 K. Films prepared in this way appear to be highly ordered over a wide spatial range and show additional fine structure between the TO and LO modes. A mode at 2348.9 cm⁻¹ is observed in p- and s-polarized spectra and does not shift with increasing film thickness. According to a simulation of the film spectra based on vibrational exciton theory, this mode can be assigned to a collective vibrational excitation of molecules near the interface with the substrate. Additional peaks e. g. at 2359.1 cm⁻¹ and 2363.8 cm⁻¹ show up and disappear again during film growth. These modes can be assigned to resonant excitation of domains with unique film thickness. [1] O. Berg, R. Disselkamp, G. E. Ewing, Surf. Sci. 277 (1992), 8.

O 65.6 Wed 18:15 Poster A

Adsorption of H₂O at Cleaved Sr_{n+1}Ru_nO_{3n+1} and Ca₃Ru₂O₇ (001) Surfaces — ●DANIEL HALWIDL¹, BERNHARD STÖGER¹, FLORIAN MITTENDORFER¹, WERNFRIED MAYR-SCHMÖLZER¹, ZHIMING WANG¹, DAVID FOBES², JIN PENG², ZHIQIANG MAO², MICHAEL SCHMID¹, JOSEF REDINGER¹, and ULRIKE DIEBOLD¹ — ¹Institute of Applied Physics and Center for Computational Materials Science, Vienna University of Technology, Vienna, Austria — ²Department 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 scanning tunneling microscopy and DFT to investigate the adsorption of H₂O on Sr_{n+1}Ru_nO_{3n+1} (n=1,2) and Ca₃Ru₂O₇. Dosing water at 105 K on the clean surfaces leads to dissociation of the molecule forming an (OH)_{ads} group and an O_{surf}H group. While no long-range diffusion was observed at 78 K on neither Sr_{n+1}Ru_nO_{3n+1} or Ca₃Ru₂O₇, we observe a locally restricted movement of the (OH)_{ads} around the O_{surf}H on Sr_{n+1}Ru_nO_{3n+1}. Annealing to room temperature leads to diffusion, enabling interactions and the formation of 1D chains. Adsorbed water forms various superstructures with long-range

order depending on the coverage, dosing temperature and annealing time. 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 65.7 Wed 18:15 Poster A

Methanol Adsorption on CeO₂(111) Single Crystal Surface — CHENGWU YANG, FABIAN BEBENSEE, ●ALEXEI NEFEDOV, and CHRISTOF WOELL — Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

Due to the oxygen mobility and the reducibility of cerium ions, ceria and related materials have extensive catalytic applications [1]. Studying the interaction of methanol with ceria surfaces taking the so-called surface science approach is of crucial importance to gain a fundamental understanding of the oxidation of alcohols to aldehydes [2]. Here, we used a novel apparatus [3] combining a state-of-the-art FT-IR spectrometer with a dedicated UHV-chamber to monitor the adsorption of methanol on CeO₂(111) surfaces. The system allows acquiring spectra in both reflection at grazing incidence on single crystals and in transmission geometry on polycrystalline powders. From the comparison to data obtained on well-defined single crystals, a precise interpretation of the complicated infrared spectra for adsorbates on powders can be reached. Methanol adsorbs dissociatively at 120 K at defective CeO₂(111) surfaces to yield a surface methoxy species. The IR spectra of this methoxy species, in particular the C-O stretch frequency, provide information about their coordination to the oxide surface and the presence of surface oxygen vacancies.

- [1] A. Trovarelli, P. Fornasiero (Ed.), *Catalysis by Ceria and Related Materials* (2nd edition), Imperial College Press, London, 2013.
 [2] J. M. Vohs, *Chemical Reviews*, 2013, **113**, 4136.
 [3] C. Yang, et al., *Phys. Chem. Chem. Phys.* 2014, **16**, 24165.

O 65.8 Wed 18:15 Poster A

CO₂ adsorption on CeO₂(110) single crystal surface — CHENGWU YANG, ●ALEXEI NEFEDOV, JUN CHEN, FABIAN BEBENSEE, and CHRISTOF WOELL — Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

Interest in the adsorption of carbon dioxide on oxide surfaces arises not only from the need to mitigate emission of this greenhouse gas, but also its potential use as a feedstock for the chemical industry [1]. Ceria, one of the most reducible metal oxide, has proven to be a highly active catalyst for CO₂ reduction to methanol [2]. For a fundamental understanding of processes occurring on high surface-area CeO₂ catalysts under reaction conditions, adsorption studies on well-defined single crystal surfaces in ultrahigh vacuum (UHV), i.e. the surface-science approach, is indispensable [3, 4]. Here we report results on CO₂ adsorption onto pristine and defective CeO₂(110) single crystal surfaces characterized using x-ray photoelectron spectroscopy, UHV infrared spectroscopy, and near edge x-ray absorption fine structure spectroscopy. Our data indicate that CO₂ adsorbs predominantly as

a carbonate on this ceria surface.

- [1] M. Aresta (Ed.), *Carbon Dioxide as Chemical Feedstock*, Wiley-VCH, New York, 2010.
 [2] J. Graciani, et al., *Science*, 2014, **345**, 546.
 [3] H.-J. Freund, M. W. Roberts, *Surface Science Reports*, 1996, **25**, 225.
 [4] Uwe Burghaus, *Progress in Surface Science*, 2014, **89**, 161.

O 65.9 Wed 18:15 Poster A

DFT modeling of diatomic molecules physisorbed on the NaCl(100) surface — ●JOCHEN VOGT — Chemisches Institut der Uni Magdeburg, Magdeburg, Germany

Computational schemes to treat van der Waals interaction within density functional theory (DFT) are currently a field of vivid research and rapid development. Recent quantitative LEED studies have provided detailed experimental structure information on the low temperature geometries of CO, N₂, and O₂ adsorbed on the NaCl(100) surface [1-3]. For the modeling of these classical physisorption systems based on PBE functionals and pseudopotentials, different schemes to treat van der Waals interaction were used and compared with respect to binding energy, molecule-surface distance, and potential energy curves.

- [1] Jochen Vogt, Birgit Vogt, *J. Chem. Phys.* 2014, in press
 [2] Jochen Vogt, *J. Chem. Phys.* **137** (2012), 174705
 [3] Anne Möller, diploma thesis, Magdeburg 2012

O 65.10 Wed 18:15 Poster A

Using CO as a probe molecule for exploring rutile TiO₂ surface structures — ●HANNAH SCHLOTT¹, MARIA BUCHHOLZ², FABIAN BEBENSEE², CHRISTOF WÖLL², and BERND MEYER¹ — ¹Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg — ²Institut für Funktionelle Grenzflächen (IFG),Karlsruher Institut für Technologie (KIT)

Using density-functional theory (DFT) we investigated the adsorption of CO molecules on various structural models of the reconstructed rutile TiO₂(011) surface. While the adsorption of CO on rutile TiO₂(110), the most thoroughly studied oxide surface in surface science, is well understood [1,2], the situation is less clear for the reconstructed TiO₂(011) surface. Thermal treatment and infrared spectroscopy indicate a similar stability of the CO molecules as on TiO₂(110), albeit with the molecules lying flat on the surface. In the DFT calculations, however, we find for the recently proposed structural models of the reconstructed TiO₂(011) surface only adsorption sites either with horizontal CO orientation and lower binding energy or with similar binding energy as on TiO₂(110) and vertical CO orientation. Implications of this observation will be discussed.

- [1] P.M. Kowalski, B. Meyer, D. Marx, *Phys. Rev. B* **79**, 115410 (2009).
 [2] M. Kunat, F. Traeger, D. Silber, H. Qiu, Y. Wang, A.C. van Veen, Ch. Wöll, P.M. Kowalski, B. Meyer, C. Hättig, D. Marx, *J. Chem. Phys.* **130**, 144703 (2009).