

O 58: Oxide and Insulator Surfaces II

Time: Wednesday 16:00–19:00

Location: PHY C 213

O 58.1 Wed 16:00 PHY C 213

Oxygen activation on Mo-doped CaO films — YI CUI¹, ●NIKLAS NILIUS^{1,2}, and HANS-JOACHIM FREUND¹ — ¹Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin, Germany — ²Carl von Ossietzky Universität, Institut für Physik, D-26111 Oldenburg, Germany

Already trace amounts of aliovalent dopants can be sufficient to change the physical and chemical properties of oxide materials. Using low temperature STM, we have shown that Mo ions in a crystalline CaO film of 8 eV band gap act as charge donors and may provide up to three extra electrons to suitable adsorbates. The relevant species for charge exchange are Mo²⁺ ions sitting in Ca substitutional sites in near surface layers of the oxide. (1) Their charge state is probed and manipulated with the STM tip. The results were found to be in agreement with DFT calculations of the Mo 4d states split in the crystal field of the CaO lattice. Charge transfer from the Mo donors is identified both into metallic (Au) and molecular adsorbates (O₂) bound to the surface. (2) In the latter case, formation of superoxo-species is revealed, characterized by a large affinity for dissociation. Additional means to modify electronic and optical properties of oxides via doping are envisioned.

1. Cui, Nilus, Freund, Prada, Giordano, Pacchioni, *Phys. Rev. B* 88 (2013) 205421.

2. Cui, Nilus, Shao, Baldowski, Sauer, Freund, *Angew. Chem. Int. Ed.* 52 (2013) 11385.

O 58.2 Wed 16:15 PHY C 213

High chemical activity of a perovskite surface: Reaction of CO with Sr₃Ru₂O₇ — ●BERNHARD STÖGER¹, MARCEL HIECKEL¹, FLORIAN MITTENDORFER¹, ZHIMING WANG¹, MICHAEL SCHMID¹, DAVID FOBES³, JIN PENG³, RAIMUND PODLOUCKY², ZHIQIANG MAO³, JOSEF REDINGER¹, and ULRIKE DIEBOLD¹ — ¹Institute of Applied Physics, Vienna University of Technology, Vienna, Austria — ²Institute for Physical Chemistry, University of Vienna, Vienna, Austria — ³Department of Physics and Engineering Physics, Tulane University, New Orleans, LA, USA

We focus our studies on Sr₃Ru₂O₇, which is the two-layer member of the ruthenate Ruddlesden-Popper series Sr_{n+1}Ru_nO_{3n+1}. In-situ cleaving of high-quality single crystals opens up the possibility to investigate a very well defined Sr-O surface layer by low-temperature Scanning Tunneling Microscopy. Exposing Sr₃Ru₂O₇ to CO at 78 K shows that CO adsorbs at regular surface sites above an apical surface O atom with a binding energy, E_{ads} , of 0.6 eV. Above 100 K this physisorbed CO reacts by pushing out the surface O atom, forming a bent CO₂ molecule with its C atom bound to the Ru underneath. The resulting species is best described as chemisorbed metal carboxylate (Ru-COO). The low activation energy (0.29 eV) of the process and the high binding energy ($E_{\text{ads}} = 2.17$ eV) of the resulting adsorbate confirm a strong reaction between CO and regular surface sites of Sr₃Ru₂O₇.

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O 58.3 Wed 16:30 PHY C 213

Adsorption of water on rutile (110) – Ground and excited states — ●JAN MITSCHKER and THORSTEN KLÜNER — Theoretical Chemistry, Carl von Ossietzky Universität Oldenburg, PO Box 2503, 26111 Oldenburg

The interaction of water with TiO₂ is of great importance for a variety of technical applications like self-cleaning surfaces. Water splitting on these surfaces may become a new route to hydrogen used as a fuel in the future. Despite this promising ability of TiO₂, a fundamental understanding of the interaction of water with rutile, especially after an electronic excitation with light is still missing.

Here, we present results for the water/TiO₂ system. We use the embedded cluster approach in order to calculate potential energy surfaces for this system. The rutile surface is modelled by a Ti₉O₁₈Mg₇¹⁴⁺ cluster embedded in about 4500 point charges to account for the long-ranging Coulomb interaction. This model has been used for the CO photodesorption successfully. [1] The potential energy surfaces are calculated on a post Hartree-Fock level of theory. This is important for dissociation and excitation energies. We intend to perform a quantum dynamical treatment of the dissociation process within the framework

of a stochastic wave-packet model.

In this contribution, we present results for the potential energy surfaces of the electronic ground and a selected excited state.

[1] M. Mehring, T. Klüner, *Chem. Phys. Lett.* 2011, 513, 212.

O 58.4 Wed 16:45 PHY C 213

Three-dimensional study of the photodesorption of CO on rutile(110) — ●HENDRIK SPIEKER and THORSTEN KLÜNER — Theoretical Chemistry, Carl von Ossietzky Universität Oldenburg, PO Box 2503, 26111 Oldenburg

Due to its high photocatalytic activity, titanium dioxide is already of interest for a manifold of applications. However, the fundamental mechanisms of the underlying surface photochemistry are not yet completely understood. In this study, the desorption of CO on rutile(100) is studied in terms of a model system. Making use of an embedded cluster approach to simulate the rutile(110)-surface, BSSE-corrected three-dimensional potential energy surfaces for the ground state and relevant excited states of the CO molecule are calculated on a post Hartree-Fock level of theory. The latter serve as potentials for three-dimensional quantum dynamical studies, which unveil a quantum state resolved and up to this point completely unknown desorption mechanism for the CO molecule in consequence of a vertical laser excitation.

O 58.5 Wed 17:00 PHY C 213

LEED-I(V) structure analysis of the physisorption system CO p(2×1)/NaCl(100) — ●JOCHEN VOGT and BIRGIT VOGT — Chemisches Institut der Uni Magdeburg, Magdeburg, Germany

The system CO/NaCl(100) is one of the model systems of physisorption. Although intensively studied both experimentally and theoretically (see e. g. [1-3]), an experimental structure analysis of its low temperature p(2×1) phase has been missing so far. Using the MCP-LEED technique, we have recorded diffraction peak intensities of the saturated p(2×1) phase as a function of electron energy at a temperature of 21 K. The data were the basis of a full dynamical LEED-I(V) analysis. Our structure model, involving two inequivalent molecules related by the observed glide-plane symmetry, contains only 5 molecular structure parameters, and the rumpling of the substrate surface. According to our results, the carbon end of CO is located 2.58±0.08Å over Na⁺, laterally shifted 0.4±0.1Å towards the neighbor chlorine. The molecular tilt angle is 28±5 degrees with respect to the surface normal, in satisfactory agreement with infrared spectroscopic results [2]. In a structure model with oxygen pointing towards the surface, the Pendry R-factor worsens from 0.22 to 0.25. [1] D. Schmicker, J. P. Toennies, R. Vollmer, H. Weiss, *J. Chem. Phys.* 95 (1991), 9412 [2] J. Heidberg, E. Kampshoff, M. Suhren, *J. Chem. Phys.* 95 (1991), 9408 [3] M.-N. Carre et al., *Surf. Sci.* 347 (1996), 128

O 58.6 Wed 17:15 PHY C 213

IRRAS on Metal Oxide Single Crystals: First Experiments on ZnO(10-10) — MARIA BUCHHOLZ, ●FABIAN BEBENSEE, PETER G. WEIDLER, ALEXEI NEFEDOV, and CHRISTOF WÖLL — Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany

Due to the low reflectivity in the infrared regime of oxides, Infrared Reflection Absorption Spectroscopy (IRRAS) studies on molecules adsorbed on metal oxide single crystals have remained elusive until recently. Furthermore, the fact that the classic surface selection rule for IRRAS does not apply on dielectrics renders the data analysis in such experiments rather difficult. Here, we present the first experiments on adsorption of molecules on zinc oxide (ZnO) single crystals. We demonstrate the great potential this technique offers for the study of such adsorbate systems emerging from consideration of all three components of the incident polarized light separately [1]. We find that carbon dioxide adsorption results in a tridentate (surface) carbonate [2] oriented along the [0001] direction. Comparing these data recorded on single crystalline ZnO to nanoparticles provides useful insights into the role of defects for the surface chemistry of powder particles.

[1] M. Buchholz, P. G. Weidler, F. Bebensee and C. Wöll, *Physical Chemistry Chemical Physics*, 2013, DOI:10.1039/C1033CP54643H.

[2] Y. Wang, R. Kováčik, B. Meyer, K. Kotsis, D. Stodt et al., *Angewandte Chemie International Edition*, 2007, 46, 5624-5627.

O 58.7 Wed 17:30 PHY C 213

Stability and Metastability of Clusters in a Reactive Atmosphere: Theoretical Evidence for Unexpected Stoichiometries of Mg_MO_x — ●SASWATA BHATTACHARYA, SERGEY V. LEVCHENKO, LUCA M. GHIRINGHELLI, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

We study the (meta)stability of metal-oxide clusters in a reactive atmosphere at thermodynamic equilibrium, using free metal (Mg) clusters in an oxygen atmosphere as a model system. The low energy minimum structures of a large set of Mg_MO_x clusters are generated via a massively parallel cascade genetic algorithm. The term “cascade” means a multi-step procedure with increasing accuracy and each next level uses information obtained at the immediate lower level. It starts with a (reactive) force field and goes up to density-functional theory (DFT) with hybrid functionals. The stable compositions are identified using *ab initio* atomistic thermodynamics. We find^[1] that highly oxidised states are more stable at thermodynamic equilibrium when $M \leq 5$, while for bigger sizes ($6 \leq M \leq 15$) there is a competition between stoichiometric ($x = M$) and non-stoichiometric ($x > M$) clusters. The highly oxidised clusters ($x > M$) exhibit peculiar magnetic behaviour, suggesting the possibility of tuning magnetic properties by changing environmental (T, p_{O_2}) conditions. Our studies are validated with the highest level currently achievable within DFT, i.e.; the renormalized second-order perturbation theory (rPT2).

[1] S. Bhattacharya, S. V. Levchenko, L. M. Ghiringhelli, M. Scheffler, *Phys. Rev. Lett.* **111**, 135501 (2013)

O 58.8 Wed 17:45 PHY C 213

Fe adsorption on the hematite (0001) and magnetite (111) surface — TOMASZ PABISIAK and ●ADAM KIEJNA — Institute of Experimental Physics, University of Wrocław, Wrocław, Poland

A detailed *ab initio* investigation of the structural, electronic and magnetic properties of Fe-atom adsorption on the hematite (0001) and magnetite (111) surfaces is presented. Spin-polarized density functional theory calculations are applied accounting for strong electron correlation effects by including a Hubbard-type on-site Coulomb repulsion (the DFT+U approach). For each oxide surface, the adsorption on two terminations has been studied: one terminated with iron and the other with oxygen. The binding sites and coordination geometry of Fe adatoms are identified. Different adatom coverages were considered. The Fe atoms bind strongly to the iron-oxide surfaces and induce large changes in their near surface geometry, and the electronic and magnetic properties. The binding of Fe is distinctly stronger at the O- than at the Fe-terminated surfaces of both oxides. The resulting adsorption energetics, structure and bonding are discussed based on the calculated local density of states and electron charge transfer. Comparison with the results for Au and Pd atoms adsorption [1,2] at these surfaces is also made.

This work was supported by the National Science Center (NCN), Poland (Grant No. 2012/07/B/ST3/03009).

[1] A. Kiejna, T. Ossowski, T. Pabisiak, *Phys. Rev. B* **85**, 125414 (2012). [2] A. Kiejna, T. Pabisiak, *J. Phys. Condens. Matt.* **24**, 095003 (2012).

O 58.9 Wed 18:00 PHY C 213

Tuning the electronic structure of Fe_3O_4 by adsorbates: A DFT+U investigation — ●NARASIMHAM MULAKALURI¹ and ROSSITZA PENTCHEVA² — ¹Fraunhofer Institute for Mechanics of Materials, Freiburg, Germany — ²Dept. for Earth and Environmental Sciences, University of Munich, Germany

Fe_3O_4 plays an important role in many technologically relevant catalytic reactions such as HT-WGS (high temperature water gas phase shift reaction). To tune the catalytic activity it is important to understand and selectively modify the surface electronic structure. Using density functional theory together with an on-site Coulomb repulsion term (GGA+U), we explore the progressive reduction of the $\text{Fe}_3\text{O}_4(001)$ surface by additional deposition of Fe [1] or hydrogen [2]. The thermodynamic stability of different terminations reveals that additional Fe atoms switch to surface octahedral sites instead of the bulk structure continuation at tetrahedral sites (A) on top of the B-termination (containing oxygen and octahedral iron). With increasing coverage an antiferromagnetic and strongly buckled FeO layer is formed on top of the $\text{Fe}_3\text{O}_4(001)$ surface. The deposition of Fe leads to a progressive reduction of Fe in the surface and subsurface layers to Fe^{2+} and thus allows control of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and the redox

activity at the $\text{Fe}_3\text{O}_4(001)$ surface. The enhancement of Fe^{2+} in the near surface region is also supported by XPS experiments [1]. Parallels to hydrogen and metal adsorption are also discussed.

[1] Z. Novotny, N. Mulakaluri *et al.*, *Phys. Rev. B* **87**, 195410 (2013).
[2] N. Mulakaluri, R. Pentcheva, *J. Phys. Chem. C* **116**, 16447 (2012).

O 58.10 Wed 18:15 PHY C 213

Thin iron oxides films as support for metal nano-particles: a LEEM/PEEM study — FRANCESCA GENUZIO, ALESSANDRO SALA, ●THOMAS SCHMIDT, and HANS-JOACHIM FREUND — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

The wide interest in characterizing Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$, the two most common and stable iron oxide phases, arises from the variety of their technological applications, ranging from magnetic devices to heterogeneous catalysis. Their crystal structure, stoichiometry as well as their surface properties can be tuned by special preparation procedures. Moreover, in thin film systems the interaction with the substrate can strongly influence the chemical and electric properties. As model systems for catalysis, these two oxides are successfully used as supports for noble metal nano-particles. In some particular cases, the strong interaction between the nano-particle and the support (SMSI) can induce their encapsulation, affecting the activity of the system, as observed for Pt nano-particles supported on a Fe_3O_4 film[1]. Here, we report on growth and stability of Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ thin films on a Pt(111) substrate, as well as their interaction with Pt nano-particles. The combined LEEM/LEED and XPEEM investigations were carried out with the SMART, the aberration-corrected and energy-filtered LEEM/PEEM installed at BESSY II in Berlin. [1] Z.-H. Qin, M. Lewandowski, Y.-N. Sun, S. Shaikhutdinov, and H.-J. Freund, *J. Phys. Chem. C* **112**, (2008), 10209-10213

O 58.11 Wed 18:30 PHY C 213

Improving ceramic-polymer interface stability: Ab-initio study of benzoic acid on TiO_2 — ●WOLFGANG HECKEL 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. Current thermal desorption measurements [1] 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 DFT analysis of benzoic acid on TiO_2 rutile 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. The resulting binding energies increase up to about 0.18 eV per molecule compared to CA with aliphatic side chains.

Supported by DFG, SFB 986, project A4.

[1] A. Dreyer and G. Schneider, unpublished

O 58.12 Wed 18:45 PHY C 213

Directed growth of functionalized triarylamines on $\text{KBr}(001)$ — CHRISTIAN STEINER¹, NATALIE HAMMER², UTE MEINHARDT², BETTINA GLIEMANN², MILAN KIVALA², and ●SABINE MAIER¹ — ¹Department of Physics, University of Erlangen-Nürnberg, Germany — ²Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Germany

The growth and imaging of well-ordered molecular self-assemblies is often challenging on bulk insulating surfaces owing to the low molecule-surface interaction. However, organic layers on insulating compared to metallic materials are more likely to be relevant for applications, e.g. in electronic devices such as organic field effect transistors. We investigated the self-assembly of triarylamine derivatives on an insulating $\text{KBr}(001)$ surface using non-contact atomic force microscopy in ultra high vacuum at low temperature. By carefully balancing the molecule-surface interaction and molecule-molecule interaction using similar triarylamine building blocks but changing the side groups we can direct their self-assembly on KBr from linear structures to flat well-ordered networks. We found that hydrogen-bonding moieties with carboxylic and diaminotriazine side groups prefer to self-assemble in well-ordered films while halogen atoms as side groups support the growth of $\pi - \pi$ stacked linear structures with the molecules standing nearly upright on the surface.