

O 72: Oxide and Insulator Surfaces: Adsorption I

Time: Wednesday 10:30–12:45

Location: WIL C107

O 72.1 Wed 10:30 WIL C107

Detection of Protons on Atomically Defined Cobalt Oxide Thin Films on Ir(100). An Infrared Reflection Absorption Spectroscopy Study of D2O and Deuterated Benzoic Acid on Co3O4(111), CoO(111), CoO(100) on Ir(100) — •MATTHIAS SCHWARZ, SUSANNE MOHR, CHANTAL HOHNER, KRISTIN WERNER, TAO XU, and JÖRG LIBUDA — Lehrstuhl für Physikalische Chemie II Friedrich-Alexander-Universität Erlangen-Nürnberg

We applied infrared reflection adsorption spectroscopy (IRAS) in a comparative surface science model study under ultra-high vacuum (UHV) conditions to investigate the interaction of D2O and deuterated benzoic acid (D-BA) with well-ordered Co3O4(111), CoO(111) and CoO(100) thin films on Ir(100). For both, water and D-BA, nature and thermal stability of the formed surface species are strongly depend on the surface structure. On Co3O4(111), water forms partially dissociated clusters with strongly temperature dependent size and structure. On the oxygen-terminated CoO(111) surface, water can dissociate and bind to defect sites only. On CoO(100) only coordination of molecular water at 200 K is observed. For higher temperatures no protons were found. D-BA forms benzoates on all three surfaces and we could identify the surface OD groups formed in this process. On Co3O4(111) and CoO(111) the protons and the benzoates show a broad distribution of chemical states. In sharp contrast, a well-defined coadsorbate layer consisting of carboxylates and protons is found on CoO(100).

O 72.2 Wed 10:45 WIL C107

Hungry Porphyrins: Protonation and Self-Metalation of Tetraphenylporphyrin on TiO2(110) - 1 × 1 — •JULIA KÖBL¹, TAO WANG², CICI WANG², MARTIN DROST¹, FAN TU¹, QIAN XU², HUANXIN JU², DANIEL WECHSLER¹, MATTHIAS FRANKE¹, HAIBIN PAN², HUBERTUS MARBACH¹, HANS-PETER STEINRÜCK¹, JUNFA ZHU², and OLE LYTKEN¹ — ¹Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 — ²National Synchrotron Radiation Laboratory, 42 S Hezuohua Road, Hefei, 230029, China

In order to obtain a detailed understanding of organic electronic devices such as dye-sensitized solar cells, one has to characterize the interactions of organic molecules with oxide substrates at the atomic level. Thus, we have studied the adsorption and self-metalation of tetraphenylporphyrin (2HTPP) on TiO2(110) - 1 × 1 with X-ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). Upon adsorption at room temperature, the first monolayer of 2HTPP is protonated, forming porphyrin diacid (4HTPP²⁺). As the surface is heated to 400 K, all unprotonated 2HTPP molecules in the second layer metalate, forming titanyl tetraphenylporphyrin (TiOTPP), but the protonated molecules in the first layer stay intact. As the surface is heated further to 550 K even the protonated 4HTPP²⁺ molecules metalate and only TiOTPP remain on the surface^a. Supported by the DFG through FOR 1878 (funCOS), the Chinese Scholarship Council and BayCHINA.

^aKöbl et al., Chemistry Select, 2016, 1, 6103 - 6105.

O 72.3 Wed 11:00 WIL C107

Insights into the adsorption of SO2 on the rutile (110) surface from first principles — •THOMAS TEUSCH and THORSTEN KLÜNER — Carl-von-Ossietzky-Universität, Oldenburg, Germany

Titanium dioxide is well known for its photocatalytic activity. One example for an industrial applied reaction is the synthesis of sulfonic acids [1].

In order to simulate this reaction systematically with state-of-the-art calculations, the interaction between SO2 and the rutile surface needs to be investigated in detail.

Therefore, we modelled the rutile (110) surface with respect to the surface energy and investigated preferred adsorption sites of SO2 in the ground and excited state.

In this work we present first results of the adsorbate-rutile interaction within density functional theory (DFT) using the CRYSTAL14 [2] program package.

[1] Parrino, F., Ramakrishnan, A., Kisch, H. *Angew. Chem.* 2008, 47, 7107 - 7109

[2] Dovesi, R., Saunders, V. R., Roetti, C., Orlando, R., Zicovich-Wilson, C. M., Pascale, F., Civalieri, B., Doll, K., Harrison, N. M., Bush, I. J., D'Arco, Ph., Llunell, M., Causà, M., Noël, Y. *Crystal14*, University of Torino, 2014

O 72.4 Wed 11:15 WIL C107

Diffusion barriers block defect occupation on reduced CeO2(111) — P. G. LUSTEMBERG¹, Y. PAN², R. PÉREZ³, M. V. GANDUGLIA-PIROVANO³, and •N. NILIUS⁴ — ¹Instituto de Física Rosario, 2000 Rosario, Argentina — ²Institute of Physics, Chinese Academy of Sciences, 100190 Beijing, China — ³Instituto de Catálisis y Petroleoquímica, 28049 Madrid, Spain — ⁴Institute of Physics, Carl von Ossietzky University, 26111 Oldenburg, Germany

Surface defects are believed to control the adsorption behavior of reducible oxides. We challenge this perception on the basis of a combined STM/DFT study that explores the mechanisms of Au adsorption on reduced CeO2(111). While theory predicts a clear binding preference to O-vacancies, Au atoms were found to populate mostly regular surface sites. Even at elevated temperature, no defect decoration is observed and gold rather aggregates at oxide step edges. Our findings are explained with the polaronic nature of the Au-ceria system, which results in a strongly diabatic diffusion of adatoms. The associated barriers are higher than in the adiabatic regime, in particular if the hopping step couples to an electron transfer between Ce3+ ions in the oxide and ad-gold. As population of O vacancies always requires such a charge exchange, adatom diffusion into the defect is kinetically hindered. Our study thus demonstrates that polaronic effects strongly govern the adsorption behavior, hence the chemistry of reducible oxides.

O 72.5 Wed 11:30 WIL C107

STM study of water adsorption on crystalline Cu2O films — •CHRISTOPH MÖLLER and NIKLAS NILIUS — Institute of Physics, Carl von Ossietzky University, 26111 Oldenburg, Germany

A direct band gap of 2.1 eV makes cuprous oxide a promising material for the photocatalytic splitting of water. To explore elementary processes associated with this reaction, we have prepared Cu2O(111) thin films on an Au(111) support and investigated them by low-temperature STM. Water exposure below 100 K gives rise to a weakly-bound, physisorbed state of water that cannot be imaged with STM. After annealing to 200 K, a chemisorbed state is reached and small, magic H2O clusters as well as extended, flat islands appear on the surface at dosages below and above 0.1 ML, respectively. Although water islands seem to be amorphous at first glance, protrusions resolved in the STM exhibit a smeared, hexagonal pair-correlation function. Its periodicity of 6 Å matches the Cu2O(111) lattice parameter, suggesting that the molecules populate characteristic sites on the oxide surface, e.g. low-coordinated Cu ions. Further insight into water binding comes from TDS measurements performed on the same system.

O 72.6 Wed 11:45 WIL C107

In-situ Spectro-electrochemical Infrared Investigations at Atomically-Defined Pt/Co3O4(111) Model Catalysts — •FIRAS FAISAL, OLAF BRUMMEL, MANON BERTRAM, CORINNA STUMM, and JÖRG LIBUDA — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

We prepared in ultra-high-vacuum (UHV) highly ordered thin films of Co3O4(111) on Ir(100) and deposited Pt nanoparticles to obtain model catalysts for electrochemical investigations. The model systems were directly transferred from UHV into the spectro-electrochemical cell and back without contact to ambient conditions. As a probe reaction we used the electrooxidation of CO, monitored by electrochemical infrared-reflection absorption spectroscopy (EC-IRRAS) in thin film configuration. All samples were characterized by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) before and after the electrochemical treatment. We identified a pH and potential window in which the Co3O4(111) film is perfectly stable in the electrochemical environment. This allowed us to explore potential-dependent differences in the CO site occupation on the UHV-prepared supported

model catalyst in comparison to a Pt(111) reference sample prepared by flame annealing. Specifically, we observed strong suppression of bridging CO on Pt facets and identify additional strongly bound CO at low coordinated Pt atoms which persists at the electrode up to high electrode potentials.

O 72.7 Wed 12:00 WIL C107

The effect of Ni substitutional defects on the structure and chemical properties of MgO surfaces — ●ALIAKSEI MAZHEIKA and SERGEY V. LEVCHENKO — Fritz-Haber-Institut der MPG

Ni-MgO solid solutions are promising materials for catalytic reduction of CO₂ and dry reforming of CH₄. To explain the catalytic activity, an *ab initio* study of Ni-substitutional defects in MgO (Ni_{Mg}) has been performed. At first, the validation of the theory level was done. We compared results of CCSD(T) embedded-cluster calculations of Ni_{Mg} formation energies and adsorption energies of CO, CO₂ and H₂ on them to the HSE(α) hybrid DFT functional with the fraction of the exact exchange α varied between 0 and 1 [1]. HSE(0.3) was found to be the best compromise in this study. Our periodic HSE(0.3) calculations show that Ni_{Mg} defects are most stable at corner sites, followed by steps, and are least stable at (001) terraces. Thus, Ni-doping stabilizes stepped MgO surfaces. The dissociative adsorption of H₂ on the terrace is found to be endothermic (+1.1 eV), whereas on (110) surface with Ni_{Mg} it is highly exothermic (−1.6 eV). Adsorbed CO₂ is also significantly stabilized (−0.6 vs. −2.2 eV). These findings explain recent microcalorimetry measurements of H₂ and CO₂ adsorption at doped Ni-MgO samples [2].—[1] A. Mazheika and S.V. Levchenko, DOI: 10.1021/acs.jpcc.6b09505; [2] A. Mazheika, M.-M. Millet, S. Wrabetz, A. Tarasov, E. Frei, S.V. Levchenko, A. Trunschke and R. Schlögl, manuscript in preparation.

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O 72.8 Wed 12:15 WIL C107

Enhanced photocatalytic activities of net-like hematite nanoparticle/graphene oxide composite and mechanism study — ●HUANMING ZHANG¹, MIN ZHOU¹, YANG XU¹, FANNA MENG², LIHONG QI², YUJIN CHEN², and YONG LEI¹ — ¹Institute für Physics & IMN MacroNano (ZIK), Technische Universität Ilmenau, Prof-Schmidt-Strasse 26, 98693 Ilmenau, Germany — ²Key Laboratory of In-Fiber Integrated Optics, Ministry of Education, College of Science, Harbin Engineering University, 150001 Harbin, China

In photocatalytic water oxidation, hematite possesses many attractive features, for instance favorable optical band gap (approximately 2.1 eV), chemical stability, natural abundance, nontoxicity and low cost. However, its surface reaction kinetics is sluggish. Herein, a facile strategy was developed to fabricate net-like hematite nanoparticle/graphene oxide (GO) composite (NHG), in which the degree of oxidization of GO could be controlled by simply changing annealing time, and GO replaces part of α -Fe₂O₃ as the reaction interface to speed up the oxygen evolution rate. NHG with GO of appropriate oxidization degree and content exhibited much higher photocatalytic activities than α -Fe₂O₃ nanorods and commercial α -Fe₂O₃. The strategy presented here could be expanded as a general method to synthesize other types of photocatalysts modified with GO for applications in photocatalysis.

O 72.9 Wed 12:30 WIL C107

Structure determination of the (7x√3)rect phase on Ag(111) — ●REGINA WYRWICH¹, TRAVIS JONES², WOLFGANG MORITZ¹, SEBASTIAN GÜNTHER³, MARTIN EHRENSPERGER¹, SEBASTIAN BÖCKLEIN¹, TEVFIK MENTEŞ⁴, ANDREA LOCATELLI⁴, MIGUEL NIÑO⁴, SIMONE PICCININ⁵, AXEL KNOP-GERICKE², ROBERT SCHLÖGL², and JOOST WINTTERLIN¹ — ¹Ludwig-Maximilians-Universität München, Germany — ²Fritz-Haber-Institut Berlin, Germany — ³Technische Universität München, Germany — ⁴Sincrotrone Trieste S.C.p.A., Italy — ⁵CNR-IOM Demicritos Trieste, Italy

The so-called ‘electrophilic oxygen’, characterized in XPS by an O 1s energy of 530.7 eV, is considered to be responsible for the Ag-catalyzed epoxidation of ethylene, a large-scale industrial process. The chemical nature of this oxygen species has remained unclear, but is certainly different from the known oxygen-induced reconstructions on the silver surface. A (7x√3)rect phase on Ag(111) incorporates this oxygen species, but all attempts to find a structure model have failed for a long time. Recent DFT calculations revealed that only covalently bound oxygen species exhibit O 1s energies in this region, which led to the consideration of oxygen bound to sulfur, a common contamination in ethylene. Based on a model proposed by DFT we have now solved the structure by a LEED I(V) analysis. The structure involves a reconstruction consisting of alternating rows of Ag triangles and SO₄ units along the √3 direction of Ag(111). The Ag atoms are found in three different geometries, on hcp, fcc, and bridge position. The findings shed new light on the already complex Ag/O system.