O 104: Oxides and Insulators: Adsorption I

Time: Thursday 16:45–18:15 Location: MA 041

O 104.1 Thu 16:45 MA 041

Bulk Defect Dependent Adsorption of Acetone on Rutile TiO_2(110) — •Jessica Kräuter and Katharina Al-Shamery — Carl von Ossietzky University of Oldenburg, Institute of Chemistry, D-29129 Oldenburg

In chemical industry acetone is produced by the cumene process using peroxides. As alternative to get rid of the explosive peroxides a heterogeneous catalyzed process on TiO_2 is considered. As first step the adsorption of acetone on rutile TiO_2(110) was studied. Recently, an influence of the temperature dependent mobility of bulk defects on the reductive coupling of benzaldehyde was concluded from own work.[1] In previous coverage dependent studies on acetone and coadsorbed molecular oxygen the occurrence of a diolate species has been identified with surface science methods on a medium reduced rutile single crystal at liquid nitrogen temperatures.[2,3] Here we present the influence of bulk defects from studies on temperature dependent adsorption of acetone coadsorbed with molecular oxygen and oxygen adatoms. On a more strongly reduced rutile(110) single crystal a diolate species can be observed even without oxygen coadsorption. Furthermore, in TPRS an additional surface species appeared from 235 to 274 K when coadsorbing acetone with oxygen which has not been reported before. A possible β hydroxy ketone formation was identified by polarization dependent IRRAS measurement. [1] P. M. Clawin, C. M. Friend, K. Al-Shamery, A European Journal, 2014, 90, 7665. [2] M. A. Henderson, J. Phys. Chem. B, 2008, 108, 18932. [3] N. G. Petrik, M. A. Henderson, G. A. Kimmel, J. Phys. Chem. C., 2015, 119, 12273.

O 104.2 Thu 17:00 MA 041

Covalent Anchoring and Interfacial Reactions of Adsorbed Porphyrins on TiO_2(110) — •Daniel Wechsler[1], Cynthia Fernández[2], Hans-Peter Steinrück[1], Ole Lytken[1], and Federico Williams[2] — [1]Chair of Physical Chemistry II, University Erlangen-Nürnberg, 91058 Erlangen, Egerlandstraße 3, Germany — [2]Department of Inorganic, Analytical and Physical Chemistry, University of Buenos Aires, Buenos Aires C1428EHA, Argentina

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. We have studied the adsorption and covalent anchoring of 5-monocarboxyphenyl-10,15,20-triphenylporphyrin (MCTPP) on TiO_2(110) with X-ray Photoelectron Spectroscopy. At elevated temperatures, the free-base porphyrin molecules metalate on the surface, forming what we expect to be titanyl (Ti=O) porphyrin. The reaction is strongly coverage-dependent with lower coverages metalating at lower temperatures, possible caused by flat-lying molecules at low coverages being in closer proximity to the surface. We also find the metalation of porphyrins exposed to Zn^{2+} ions in solution to depend on the porphyrin coverage on the TiO_2(110) surface, but the effect is less pronounced.

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O 104.3 Thu 17:15 MA 041

Hydroxy Species on TiO_2-Rutile(110): *ab initio* Adsorption Studies — •Niklas Thoben and Thorsten Klüner — Carl von Ossietzky Universität, Oldenburg, Germany

Since the deposits of fossil fuels are limited and therefore will run out in the future, the search for renewable energies and fuels is an important topic of today's researching activities. A promising candidate is molecular hydrogen produced by photocatalytic water splitting, which can be used in fuel cells to generate CO_2-free power [1]. To find new photocatalysts and make them more efficient an exact understanding of the elementary steps of the water splitting mechanism is needed.

In this contribution, we address the adsorption of hydroxy species on the titania-rutile(110) surface, which is found to be a suitable photocatalyst [2]. The investigated hydroxy species play an essential role in proposed reaction mechanisms [3]. In the calculations done with the MOLCAS program package we use an embedded cluster approach to describe the rutile(110) surface and the CASSCF/CASPT2 methodology for a faithful description of the electronic configuration of the system.

[1] C. Acar, I. Dincer, G.F. Naterer, *Int. J. Energy. Res.* **2016**, 40, 1449-1473.

[2] A. Fujushima, K. Honda, *Nature* **1972**, 238, 37-38.

[3] V. Diesen, M. Jonsson, *J. Phys. Chem. C* **2014**, 118, 10083-10087.

O 104.4 Thu 17:30 MA 041

***Ab initio* Cluster Calculations on the Adsorption and Electronic Excitation of SO_2 on TiO_2-Rutile(110)** — •Luca Gerhards and Thorsten Klüner — Carl von Ossietzky Universität, Oldenburg, Germany

The production of sulfonic acids as precursors for several products such as detergents or pharmaceutical drugs is a vital process for today's society. An efficient way to synthesize these compounds can be conducted by the sulfoxidation of alkenes. The photocatalytic heterogeneous sulfoxidation on titanium dioxides seems to be a promising new and more energy efficient alternative to the industrially applied homogeneous reaction. Experimental investigations on the mechanism revealed that the adsorption of SO_2 and the excitation with visible light lead to a formation of a charge-transfer complex on the surface which seems to catalyze the subsequent chain reaction.[1] These results stand in contrast to the homogenous mechanism and need a deeper investigation. In this contribution, we examine the adsorption and electronic excitation of SO_2 on the ideal TiO_2-rutile(110) surface from a quantum chemical perspective. For this purpose, an embedded cluster model was constructed in order to faithfully describe the substrate-adsorbate interaction. Along these lines, post-HF and multireference methods like MP2 or CASSCF/NEVPT2 as implemented in the program package ORCA were used to calculate electronic excitations of the adsorbate.

[1] F. Parrino, A. Ramakrishnan, H. Kisch, *Angew. Chem. Int. Ed.*, **47**(37), p. 7107-7109, 2008.

O 104.5 Thu 17:45 MA 041

Adsorption of Water and Organic Molecules on Magnetite (111) — •Marcus Creutzburg[1,2], Heshmat Noei[1], Björn Arndt[1,2], Elin Grånäs[1], Gregor Feldbauer[3], Kai Sellschopp[3], and Andreas Stierle[1,2] — [1]Deutsches Elektronen-Synchrotron (DESY) — [2]University of Hamburg — [3]Institute of Advanced Ceramics, Hamburg University of Technology

Magnetite (Fe_3O_4) is an important transition metal oxide with diverse 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 get insight into the interaction of these nanoparticles with organic molecules it is crucial to study flat single crystal surfaces. In this contribution, we present results on the adsorption of water and organic molecules like formic acid and oleic acid on the magnetite (111) surface under UHV conditions obtained by infrared reflection absorption spectroscopy and X-ray photoelectron spectroscopy. These findings are complemented by scanning tunneling microscopy results and surface X-ray diffraction measurements.

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

O 104.6 Thu 18:00 MA 041

Binding of Isophorone to single Au atoms on MgO(001) and Au(111) — •Niklas Nilius[1], Thomas Meyer[1], Christian Stiehler[1], Karoliina Honkala[2], and Hannu Häkkinen[2] — [1]Institute of Physics, Carl von Ossietzky University, D-26111 Oldenburg, Germany — [2]Departments of Physics and Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, FI-40014 Finland

Formation of various metal/organic complexes comprising isophorone (C9H14O) and Au ad-atoms and clusters has been observed on MgO thin films by STM. The aggregates are hold together by electrostatic forces between the hydroxyl groups of the enol-isophorone and negative excess charges residing on the ad-gold. The energetically favorable keto-tautomer, on the other hand, is unreactive towards gold. DFT calculations find a tautomerization barrier between the keto- and enol-form of 0.76 eV on the MgO surface. On Au(111), no tautomerization takes places and isophorone physisorbs in the form of magic clusters containing four, six or nine molecules. Our study demonstrates how tautomerization of an unreactive ketone can be triggered by the presence of low-coordinated and charged metal ad-atoms on an oxide surface.