

O 26: Oxides and Insulator Surfaces: Adsorption

Time: Monday 18:15–20:30

Location: Poster E

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Vibrational Spectroscopic Studies of Formaldehyde Adsorption on Rutile TiO₂(110) — ●XIAOJUAN YU¹, CHENGWU YANG¹, FABIAN BEBENSEE¹, ALEXEI NEFEDOV¹, ZHENRONG ZHANG², QINGFENG GE³, ZDENEK DOHNÁLEK⁴, YUEMIN WANG¹, and CHRISTOF WÖLL¹ — ¹Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344 Karlsruhe, Germany — ²Department of Physics, Baylor University, Waco, Texas 76798, USA — ³Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901, USA — ⁴Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, Richland, Washington 99352, USA

TiO₂ is one of the most important metal oxides used in catalysis and photocatalysis. The interaction of TiO₂ with aldehydes is of particular interest due to its promising applications in ethanol fuel cells, hydrogen production, biomass and in the control of air pollution. Here, the adsorption of formaldehyde (CH₂O) on the rutile TiO₂(110) surface was studied by infrared reflection-absorption spectroscopy (IRRAS). The IR data reveal the presence of different species depending on the temperature and coverage. The CH₂O monomer is identified after submonolayer adsorption at 70 K, in which CH₂O is weakly bound to the surface Ti_{5c} sites. Further adsorption at 70 K leads to the formation of multilayer CH₂O, which desorbs completely upon heating to 120 K. Simultaneously, paraformaldehyde is formed at Ti_{5c} sites along [001] direction and becomes the dominant surface species. In addition, dioxymethylene is detected as a minority one formed via reaction of CH₂O with neighboring O_{br} along [1-10] direction.

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Dimerization of benzoic acid on TiO₂ surfaces—an ab-initio study — ●WOLFGANG HECKEL, TIM WÜRGER, and STEFAN MÜLLER — Hamburg University of Technology, Institute of Advanced Ceramics

At the hybrid organic–metal-oxide interface intermolecular forces may contribute to improving mechanical stability. For instance linker molecules possessing an aromatic side chain interact with each other via van-der-Waals interaction.

In this regard, the adsorption of benzoic acids on TiO₂ (110) rutile serves as a prototype system. A very regular 2 × 2 overlayer due to dimerization via the phenyl groups has recently been reported [1].

Here, we present a density functional theory analysis of the dimerization of benzoic acids on both, anatase and rutile TiO₂ surfaces. To properly describe the attractive interaction of adsorbing molecules among each other, we applied an exchange correlation functional with van-der-Waals correction. For all surface orientations, the preferred dimer formation mode (hydrogen-to- π -orbital or tilted and twisted π -to- π) as well as the amount of energy gain resulting from dimerization will be discussed.

[1] Grinter et al., J. Phys. Chem. Lett. **5**, 4265 (2014).

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O 26.3 Mon 18:15 Poster E

Coverage-dependent behaviour of water on hematite(0001) from first principles — ●ROMAN OVCHARENKO and ELENA VOLOSHINA — Humboldt-Universität zu Berlin, Berlin, Germany

It is well established that the water adsorption behaviour at high coverage regime may differ drastically from its adsorption at low coverage. The hydrogen bond network between polar water molecules and their residues tends to stabilize the water layer structure on top of a surface preventing following dissociation. Thus, the qualitative changes from the dissociative adsorption to the molecular one were found to take place on top of the aluminium oxide (0001) surface, which is isomorphic to hematite, at coverage more than 1 ML. For magnetite(001) such mixed dissociative-molecular adsorption was established already for the second water molecule in the 2x2 unit cell. Partially inheriting the properties of both aforementioned metal oxides, the hematite surface may affect the upper water layers forcing them to demonstrate adsorption behaviour different to the one on aluminium oxide or magnetite.

Here we present the theoretical study of the water adsorption on top of the hematite(0001) single-iron termination within the PBE+U+D level of accuracy to account for both the Fe 3d strongly correlated electrons as well as the weak dispersion interactions between water fragments on top of the surface.

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In-situ studies on the growth and functionalization of MgO/Ag(100) — ●SABRINA PECHMANN¹, GINA PESCHEL², HAGEN KLEMM², THOMAS SCHMIDT², and RAINER FINK¹ — ¹Physical Chemistry, FAU Erlangen-Nuremberg, Erlangen, Germany — ²Chemical Physics, Fritz-Haber-Institute of the Max Planck Society, Berlin, Germany

Metal oxide thin films on metal supports are important for various technological applications like catalysis or the fabrication of electronic devices [1]. Surface modification and functionalization plays an important role to tune the oxide surface properties. We investigated the in-situ growth and structural properties of epitaxial MgO thin films on Ag(100) using surface-sensitive LEEM and XPEEM. MgO on Ag(100) serves as an attractive model system as the lattice mismatch between both bulk structures is only 3.1%, allowing epitaxial growth with just a small number of grain boundaries [2]. MgO is sensitive to both, electron and x-ray illumination. We could follow the structural modifications. While electrons induce a long-range ordered superstructure different from the pristine material, x-ray illumination induces the formation of square-like nanostructures. We attribute the long-range order to H₂O or OH adsorption, which has been further investigated by temperature-programmed desorption (TPD). The adsorption of medium-sized organic molecules on thus modified surfaces will be compared to the non-reconstructed surfaces. This work is funded by the DFG within the funCOS research unit (FOR 1878) [1]Kramer, J. et al., Surf. Sci. 517, 87-97, 2002 [2]Valeri, S. et al., Surf. Sci. 507-510, 311-317, 2002

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Self-assembly of polycyclic aromatic hydrocarbons on bulk MgO(001) — ●TIM SANDER¹, MAXIMILIAN AMMON¹, NATALIE HAMMER², MILAN KIVALA², and SABINE MAIER¹ — ¹Department of Physics, FAU Erlangen-Nürnberg, Germany — ²Department of Chemistry and Pharmacy, FAU Erlangen-Nürnberg, Germany

MgO is a wide band gap insulator and a prototype oxide material with interesting catalytic properties. First, we report on the surface preparation and characterization of clean MgO(001) surfaces based on atomically resolved non-contact atomic force microscopy (nc-AFM) measurements. The MgO surfaces were cleaved in ultra-high vacuum using a home-built cleaving device and annealed prior to imaging to compensate surface charges. Second, we discuss the self-assembly of halogen-substituted bridged triphenylamine derivatives on MgO(001). Molecularly resolved nc-AFM images were performed to analyze the adsorption geometry and sites of the molecules.

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LEED-FTIR-DFT investigation of a twodimensional mixed phase CO₂-C₂H₂ adsorbed on the KCl(100) surface — ●JOCHEN VOGT — Uni Magdeburg, Magdeburg, Germany

Results from aerosol chemistry point towards the existence of a mixed phase CO₂-C₂H₂ (1:1) that is metastable with respect to bulk CO₂ and bulk C₂H₂ under cryogenic conditions [1,2]. On the KCl(100) surface, CO₂ and C₂H₂ are known to form well-ordered 2D layers with $(6\sqrt{2} \times \sqrt{2})R45^\circ$ and $(\sqrt{2} \times \sqrt{2})R45^\circ$ symmetry, respectively. In coadsorption experiments a KCl(100) surface was precovered with CO₂ at 80 K and then exposed to acetylene and CO₂ at partial pressures of 10⁻⁸ mbar. LEED patterns and infrared spectra indicate the displacement of the high-order CO₂ layer and the formation of acetylene islands under these conditions. However, previously unobserved IR bands at 2368.6 cm⁻¹ (CO₂) and 3192.3 cm⁻¹ (C₂H₂) both with dipole moments perpendicular to the surface are a strong indication for the formation of a mixed phase. Results of plane wave DFT calculations are presented which show that the total energy of a CO₂-C₂H₂ (1×1)/KCl(100) structure with perpendicularly oriented acetylene on top of Cl⁻ and CO₂ on top of K⁺ is only 1.8 kJ mol⁻¹ higher compared to total energies of the separated phases. In addition, phonon calculations based on this structure model can reproduce the observed blue shift (CO₂) and red shift (C₂H₂). [1] T. E. Gough, T. E. Rowat, J. Chem. Phys. **109** (1998), 6809 [2] T. C. Preston, R. Signorell, J. Chem. Phys. **136** (2012), 94510