

O 8: Oxides and insulators: Adsorption I

Time: Monday 11:15–13:00

Location: WIL C307

O 8.1 Mon 11:15 WIL C307

Ab initio calculations on the interaction of CO with C₆₀ — ●JAN MITSCHKER and THORSTEN KLÜNER — Carl von Ossietzky Universität Oldenburg, PO Box 2503, 26111 Oldenburg, Germany

The outstanding properties of C₆₀-Fullerenes aroused high interest ever since this class of molecules has been discovered. In spite of the large number of atoms they are only composed of one element and are a new modification of carbon. They form *molecular* systems but are of well-defined shape and large size.

Our group is interested in elementary processes on surfaces, especially the dynamics of excited states. So far adsorption and photodesorption of small molecules on metal-oxide surfaces have been investigated. Photodesorption can be considered as a prototyp of non-adiabatic surface reactions.

In this study we use first-principle methods to characterize the interaction of CO with a *single* C₆₀-molecule. In contrast to metal-oxides C₆₀ is a completely covalent system. Therefore, the interaction is very weak, making correlation methods and BSSE-correction necessary. Experimentally an adsorption energy of 8 kJ/mol has been estimated.[1] On MP2-level using a cc-pVTZ basis set an energy of 8.5 kJ/mol for the adsorption on top of a hexagon was found. Due to the large basis set (1860 basis functions) excited state calculations necessary for the theoretical modelling of photodesorption are very demanding. In order to encounter this challenge, we propose different computational strategies and report first results.

[1] M. Folman et al., *Langmuir* 13 (1997) 1118–1122.

O 8.2 Mon 11:30 WIL C307

DFT study of the Interaction of Hydrogen with ZnO(10 $\bar{1}$ 0) Surfaces — ●JAKUB GOCLON and BERND MEYER — Interdisciplinary Center for Molecular Materials ICMM and Computer-Chemistry-Center CCC, University of Erlangen-Nürnberg, Germany

Understanding the interaction of hydrogen with ZnO is of fundamental interest in view of its widespread use in heterogeneous catalysis for hydrogenation and dehydrogenation reactions. Using DFT calculations in combination with a thermodynamic analysis we have calculated the relative stability of various structural models of the mixed-terminated nonpolar ZnO(10 $\bar{1}$ 0) surface as a function of hydrogen and water chemical potentials. The coverage dependence of heterolytic hydrogen adsorption on O and Zn sites as well as surface hydroxylation via homolytic hydrogen and dissociative water adsorption were taken into account. From the adsorption energies a phase diagram of the lowest energy adsorbate structures in thermodynamic equilibrium with hydrogen and water reservoirs is constructed. It is found that at low hydrogen coverage only OH groups are formed, leading to a reduction of ZnO. However, as soon as a critical degree of reduction is reached, heterolytic hydrogen adsorption becomes more favorable, and at very hydrogen rich conditions a structure in which all surface O and Zn atoms are saturated with hydrogen is the most stable one. On the other hand, in water rich conditions a surface structure with a full zinc hydroxide layer is predicted to be the lowest energy structure.

O 8.3 Mon 11:45 WIL C307

Laser induced desorption of CO from rutile(110) — ●MATTHIAS MEHRING and THORSTEN KLÜNER — Theoretische Chemie, Carl von Ossietzky Universität Oldenburg, PO Box 2503, 26111 Oldenburg

Titania plays an important role in materials science. It serves as heterogeneous catalyst, photocatalyst, white pigment or corrosion protective coating. Photodesorption can be described as a prototype of a huge group of non-adiabatic surface reactions like simple rotational and vibrational excitations of small molecules or photodiffusion. These reactions serve as a basis for photon driven molecular switches or molecular rotors. The present study provides an insight into the adsorption and desorption processes of carbon monoxide on a rutile surface. Using the embedded cluster approach, we employed a relaxed Ti₉O₁₈Mg₇¹⁴⁺ cluster surrounded by 4421 point charges. Within this model we are able to calculate multi-dimensional PESs of both electronic ground state and necessary $5\sigma \rightarrow 2\pi^*$ electronically excited state(s) on MP2 and CASPT2 level, respectively. Quantum dynamical studies using the *ab initio* PES allow a detailed microscopic understanding of processes involved in the laserinduced desorption process. First 2D quantum dynamical studies regarding desorption coordinate Z and polar an-

gle θ show interesting results with respect to the polar angle and the eigenstate of adsorbed CO molecule.

O 8.4 Mon 12:00 WIL C307

Silica-modified titania photocatalysts: a computational investigation — ●NICOLA SERIANI¹, CARLOS PINILLA¹, and SANDRO SCANDOLO^{1,2} — ¹The Abdus Salam International Centre for Theoretical Physics — ²INFN-DEMOCRITOS National Simulation Center

Titanium dioxide is the catalyst of choice in solar-to-fuel applications. Silica can be used to enhance its catalytic activity, but its effect is not fully understood. Through a combination of classical and quantum simulations we build realistic models of titania/silica mixed oxides, interfaces and ultrathin films. The electronic structure of the oxide is heavily modified by the interaction with silica. Band bending is observed in a neighborhood of the interface, which might be responsible for the modified photocatalytic properties of titania-silica materials. This work is part of the FP7 project ADGLASS.

O 8.5 Mon 12:15 WIL C307

Interaction of H₂O and D₂O with NaCl(100) — ●STEPHAN HÄRTEL, JOCHEN VOGT, and HELMUT WEISS — Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, 39106 Magdeburg

Interactions of water with the surfaces of solids play an important role in a variety of fields such as catalysis, corrosion, and atmospheric physics. Numerous studies have been carried out so far dealing with the adsorption of water on the NaCl(100) surface. However, the structure of the water molecules on this surface is still under discussion. There are evidences for a c(4×2) superstructure as well as a (1×1) structure [1,2]. In the present work H₂O and D₂O were used as adsorbates on NaCl(100). In order to study the influence of water adsorption on the surface defect concentration, the latter was probed with CO₂ before and after the water experiments by means of Fourier transform infrared (FTIR) spectroscopy. The water-NaCl(100) adsorbate was prepared at crystal temperatures of 140 K. In low-energy electron diffraction (LEED) experiments the c(4×2) superstructure as well as the (1×1) structure could be observed. LEED I(V) curves in an energy range between 70 and 300 eV were recorded. First results of the LEED I(V) analysis will be presented. In additional experiments the adsorption of H₂O on a CO₂-precovered surface was examined. H₂O replaces the CO₂ quickly which indicates a growth of the H₂O mainly on the terraces.

[1] J. P. Toennies et al., *J. Chem. Phys.*, **120**, 24 (2004)

[2] P. Cabrera-Sanfeliix et al., *J. Chem. Phys.*, **126**, 214707 (2007)

O 8.6 Mon 12:30 WIL C307

Sorption of Arsenic Complexes at FeOOH Surfaces from First Principles — ●KATRIN OTTE, WOLFGANG W. SCHMAHL, and ROSSITZA PENTCHEVA — Section Crystallography, Dept. of Earth and Environmental Sciences, University of Munich

Iron oxyhydroxides (FeOOH) possess high surface areas and are of relevance for various processes in nature and technology as cycling and retention of contaminants, e.g. for water treatment purposes. [1] Using density functional theory (DFT), we investigate the adsorption affinities of the FeOOH polymorphs goethite (α), akaganeite (β), and lepidocrocite (γ) to heavy metal complexes. The knowledge of the clean surfaces goethite(101), akaganeite(100), and lepidocrocite(010) is a starting point to address those. The GGA+ U calculations reveal that the termination impacts the oxidation state of the topmost iron, providing a possibility to tune the catalytic activity. The energetics and bonding mechanisms of contaminants in different adsorption geometries on the surfaces are analyzed.

Funding by the BMBF programme Geotechnologies and Elitenetzwerk Bayern is acknowledged.

[1] R. M. Cornell and U. Schwertmann, *The Iron Oxides* (Wiley, Weinheim, 2001).

O 8.7 Mon 12:45 WIL C307

DFT studies of reaction mechanisms of methane combustion on PdO(100) — ●AREZOO DIANAT¹, MANFRED BOBETH², and LUCIO COLOMBI CIACCHI¹ — ¹Faculty of Production Engineering, University of Bremen, 28359 Bremen, Germany — ²Institute for Materials

Science, Dresden University of Technology, 01062 Dresden, Germany
Palladium oxides are renowned for their high activity in the catalytic combustion of methane. We have investigated the complex reaction mechanisms of methane combustion on the PdO(100) surface within the framework of density functional theory. From an analysis of the calculated driving forces and activation energies for the dissociative adsorption of methane and the successive dehydrogenation of adsorbed hydrocarbons, we conclude that the experimentally observed conversion rates at temperatures of about 600 K cannot be explained in terms of direct dehydrogenation processes.

Investigations of alternative reaction routes reveal that the reaction of oxygen molecules from the gas phase with hydrogen previously adsorbed on the catalyst surface can efficiently produce water. According to combined ab initio molecular dynamics and static total energy calculations, the combustion reaction proceeds through the spontaneous formation of H₂O₂ followed by its dissociation and water formation with an activation energy of about 0.7 eV. Following an analogous mechanism, oxygen molecules from the gas phase can also react with adsorbed CH₃ groups to produce CH₂O as an intermediate reaction product.