

O 9: Oxides and Insulators: Adsorption I

Time: Monday 11:15–12:45

Location: H42

O 9.1 Mon 11:15 H42

Interrogating the strength of the bond between salt and water: a combined DFT and MP2 study — ●BO LI, ANGELOS MICHAELIDES, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft Faradayweg 4-6, D-14195 Berlin, Germany

The interaction of water with salt (NaCl) is of widespread importance and of considerable general interest. Although numerous theoretical studies have been reported [1], none has provided a convincingly reliable estimate of the strength of the bond between water and a flat NaCl surface, such as NaCl(001). Moreover, the computed adsorption energies predicted by DFT vary from 0.2-0.7 eV/H₂O depending on the choice of exchange-correlation functional [2]. Here, we address this issue through an extensive series of periodic Hartree-Fock and post-Hartree Fock [Møller-Plesset perturbation (MP2) and coupled cluster (CCSD(T))] calculations. Periodic Hartree-Fock calculations have been performed for H₂O molecules adsorbed on NaCl slabs, and by evaluating the local dependence of the correlation contribution to the adsorption energy with respect to cluster size, we obtain accurate MP2 and CCSD(T) estimates of the H₂O adsorption energy on NaCl(001). Our computed adsorption energy, which is around 0.6 eV/H₂O, comes close to the experimental value [3] and is at the upper end of the range predicted by DFT.

[1] A. Verdager, G. M. Sacha, H. Bluhm, and M. Salmeron, Chem. Rev. 106, 1478 (2006). [2] B. Li, A. Michaelides, and M. Scheffler, in preparation. [3] L. W. Bruch, A. Glebov, J. P. Toennies, and H. Weiss, J. Chem. Phys. 103, 5109 (1995).

O 9.2 Mon 11:30 H42

Force controlled lateral manipulation of water adsorbed on CaF₂(111) — ●SABINE HIRTH, FRANK OSTENDORF, and MICHAEL REICHLING — Universität Osnabrück, Fachbereich Physik, Barbarastrasse 7, 49076 Osnabrück

We demonstrate for the first time the force controlled manipulation of a molecular adsorbate on an insulating substrate. We show that physisorbed water can be manipulated along three principal symmetry directions of CaF₂(111). Imaging and manipulation of water molecules is accomplished by scanning the surface at different tip-surface-distances. During manipulation steps, the movement of the molecules results in characteristic chain-like features along the slow scanning direction having a periodicity of the CaF₂ surface lattice. The form of the profiles can be assigned to a pushing type interaction. The movement of the molecule from one position to another is instantaneous on the time scale of the measurement leading to a jump of the defect position within certain scan lines. Complicated scanning profile forms result from the manipulation of defect groups. We describe the manipulation protocol in detail, explain the manipulation mechanism and discuss possible improvements for the manipulation.

O 9.3 Mon 11:45 H42

High resolution imaging of stable and mobile water related defects on fluoride (111) surfaces — ●FRANK OSTENDORF, SABINE HIRTH, LUTZ TRÖGER, and MICHAEL REICHLING — Fachbereich Physik, Barbarastrasse 7, 49076 Osnabrück

Fluoride (111) surfaces are chemically rather inert and surface degradation due to the interaction with the residual gas of a UHV system is a slow process. Atomic surface features occurring during this process and during a controlled exposure to water were investigated with highest resolution dynamic force microscopy and are analysed in detail. Two distinct types of defect features arise, namely stable defects that can be associated with specific ionic positions on the surface and mobile defects for which we have recently shown that they can be manipulated on the surface [1]. We discuss the kinetics of defect formation and phenomena of defect clustering on the basis of experiments involving a systematic variation of gas exposure parameters. From the experimental evidence we, furthermore, draw conclusions about the identity of the defects being either molecular water adsorbed onto the surface or dissociated water with hydroxyl groups embedded into the surface.

[1] Hirth S, Ostendorf F and Reichling M Nanotechnology 17 (2006)

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O 9.4 Mon 12:00 H42

Hydrogen storage by adsorption on microporous materials — ●KATJA HÖNES, BARBARA PANELLA, and MICHAEL HIRSCHER — Max Planck Institut für Metallforschung, Heisenbergstr. 3, 70569 Stuttgart

Different microporous materials have been investigated for their capability to store hydrogen by physisorption. The amount of adsorbed hydrogen for three metal organic frameworks (IRMOF 8, MIL 101 and MOF 74) and the zeolite NaX has been measured volumetrically by a Sieverts' apparatus at 77K and at room temperature. Additionally, thermal desorption spectroscopy measurements between 22K and 370K have been carried out in order to distinguish different adsorption sites. The highest hydrogen uptake at 77K was measured for MIL 101 (4.25 wt%), which possesses the highest specific surface area of all materials investigated. According to their lower specific surface area IRMOF 8 adsorbed 3.4wt%, MOF 74 2.3 wt% and NaX 1.3 wt% at 77K.

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O 9.5 Mon 12:15 H42

Ammonia adsorption on V₂O₅ - DFT cluster model studies — ●MALGORZATA WITKO and PAWEŁ HEJDUK — Institute of Catalysis and Surface Chemistry, PAS, ul. Niezapominajek 8, 30 239 Krakow, Poland

Catalysts based upon vanadia are used in many processes belonging to very different types of chemical reactions, among them to the selective catalytic reduction of NO_x by NH₃. Although the last mentioned reaction is of a great technological importance its mechanism is still under debate. In order to understand the details of the process the adsorption on ammonia on hydroxyl groups existing on different low-indices (010), (100) and (001)V₂O₅ surfaces will be discussed based upon cluster model DFT calculations within GGA-RPBE functional. The results of the performed calculations indicate spontaneous stabilization of NH₃ at any surface hydroxyl groups with the adsorption energy in the range of 0.8 to 1.3 eV. Ammonia becomes adsorbed in various geometries and the reaction proceeds according to different mechanism depending on the type of oxygen forming OH group and on the type of surface. In all cases the significant role of hydrogen bonds of different strengths is found.

O 9.6 Mon 12:30 H42

Influence of Mo coordination on oxygen activation in hetero and homogeneous molybdena catalysts. DFT cluster model studies. — ●RENATA TOKARZ-SOBIERAJ and MALGORZATA WITKO — Institute of Catalysis and Surface Chemistry, PAS, ul. Niezapominajek 8, 30 239 Krakow, Poland

Activation of the molecular oxygen may be caused by bonding it to the transition metal center in metal complex (homogeneous process) or to the metal center present at the solid surface (heterogeneous reaction). The electronic properties of the bonded molecular oxygen, and what follows, its reactivity depend on the character of bonding defined by the type of metal and its surrounding ligand(s) or surface atom(s). The aim of present studies is to examine O₂ activation process in molybdenum porphyrin (homogeneous systems) and molybdenum trioxide (heterogeneous catalysts) using quantum chemical DFT methods within GGA-RPBE functional. The preference to form superoxo or peroxy structure for each of the systems and their possible further transformed forms that are hydroperoxo or oxo species is considered. It is found that in any system the direct consequence of O₂ binding to the molybdenum ions is its activation expressed by the elongation and weakening of the O-O bond. The adsorption of the H atom on the O₂ species leads to the further weakening of the O-O bond. The second H atom undergoes adsorption and water species is formed. The later may desorb leading to the oxygen atom doubly bonded to the molybdenum ion. As the result the high valent oxo porphyrin complex or molybdenyl bond at the oxide surface is formed.