

## O 86: Oxides and Insulators: Adsorption

Time: Friday 9:30–11:15

Location: MA 141

O 86.1 Fri 9:30 MA 141

**Water Adsorption on Fe<sub>3</sub>O<sub>4</sub>(001): A First Principles Study** — •NARASIMHAM MULAKALURI<sup>1</sup>, ROSSITZA PENTCHEVA<sup>1</sup>, WOLFGANG MORITZ<sup>1</sup>, and MATTHIAS SCHEFFLER<sup>2</sup> — <sup>1</sup>Section Crystallography, Dept. for Earth and Environmental Sciences, University of Munich — <sup>2</sup>Fritz-Haber-Institut der MPG, Berlin

The mode of adsorption of water (dissociative versus molecular) as well as its effect on the structural and electronic properties of the Fe<sub>3</sub>O<sub>4</sub>(001) surface is studied using density functional theory (DFT) calculations with the FP-LAPW method in the WIENK2k implementation. We vary the concentration of water and hydroxyl groups starting from a single water molecule per ( $\sqrt{2} \times \sqrt{2}$ )R45° unit cell and compare the surface stability of the different terminations as a function of the O<sub>2</sub> and H<sub>2</sub>O partial pressure within the framework of *ab-initio* thermodynamics. Over a substantial range above the oxygen and water poor conditions, a clean Jahn-Teller distorted bulk termination is most favorable (*modified* B-layer) [1]. With increasing water pressure a water monomer, parallel to the surface, and finally a fully hydroxylated B-layer is stabilized. The calculations give indications of a lifting of the ( $\sqrt{2} \times \sqrt{2}$ )R45°-reconstruction upon hydroxylation, consistent with low energy electron diffraction (LEED) measurements.

[1] R. Pentcheva et al., Phys. Rev. Lett. 94,126101 (2005).

O 86.2 Fri 9:45 MA 141

**Water adsorption at low-indices (001) and (100) V2O5 surfaces. Cluster DFT studies.** — PAWEŁ HEJDUK and •MALGORZATA WITKO — Institute of Catalysis and Surface Chemistry, PAS, Krakow, Poland

Vanadia-based materials are well known as the catalysts for numerous number of different chemical processes, as a consequence of an existence of non-equivalent active centers, both O and V types, localized on various faces of the catalyst crystal. Dependently on the preparation technique the V2O5 crystals can expose different surfaces, where the low-indices faces like (010), (001) and (100) are the most common. The (010) face is built of fully saturated V and O sites, whereas both (001) and (100) surfaces of unsaturated V and O surface atoms. Thus, the faces built of unsaturated character should behave differently in catalytic reactions compared to the (010) surface and an adsorption of small molecules should be enhanced.

In the present study water adsorption at the unsaturated surfaces is examined using cluster DFT approach. In addition a comparison with respect to saturated (010) surface is done. Results of calculations show that water molecule stabilizes at unsaturated surfaces due to the interaction of lone electron pair from O (from water) and unoccupied 3d states of vanadium. Upon adsorption, with low dissociation energy, water can dissociate and two hydroxyl groups are formed V(surface)-OH and O(surface)-H. It is in contrast to the (010) surface where water molecule undergo stabilization but only due to weak hydrogen bonding and its dissociation does not occur.

O 86.3 Fri 10:00 MA 141

**Electronic properties of the active sites present at the (011)MoO2 surface. Periodic and cluster DFT quantum chemical studies.** — •RENATA TOKARZ-SOBIERAJ<sup>1</sup>, MALGORZATA WITKO<sup>1</sup>, and ROBERT GRZYBOS<sup>2</sup> — <sup>1</sup>Institute of Catalysis and Surface Chemistry PAS, Niezapominajek 8, 30-239 Krakow, Poland — <sup>2</sup>Faculty of Physics and Center for Computational Materials Science, Universitaet Wien, Sensengasse 8, A-1090 Wien, Austria

DFT method is applied to describe electronic structure of catalytically important (011) surface of molybdenum dioxide. MoO2 exists in literature mainly as a product of MoO3 reduction; however the problem of its role in catalytic process is still unsolved. In present paper attention is focused on the properties of surface active sites, both Mo and O, which are present at the selected (011) surface. In addition, comparison of (011)MoO2 and (100)MoO3 surfaces is carried out due to a fact that both surfaces contain not only the differently coordinated O sites but also the bare Mo centers. The electronic structure of studied systems is calculated using both periodic (VASP code) and cluster (StoBe code) approaches with gradient corrected functional. Local properties of different surface sites that are exposed at both surfaces are examined by means of charge densities, bond orders indices and molecular orbital diagrams whereas the global properties of both surfaces are discussed

by density of states. The differences (existence of pairs of metallic sites on (011)MoO2 surface) and similarities (electronic states of bare Mo ions in both surfaces) in electronic properties of active sites are investigated taking adsorption of hydrogen and oxygen as examples.

O 86.4 Fri 10:15 MA 141

**Wavefunction-based ab-initio results for the adsorption of CO on Ceria (110) surface** — CARSTEN MÜLLER<sup>1</sup>, BJÖRN HERSCHEND<sup>1</sup>, •BEATE PAULUS<sup>2</sup>, and KERSTI HERMANSSON<sup>1</sup> — <sup>1</sup>Department of Materials Chemistry, Uppsala University, Lägerhyddsvägen 1, 75121 Uppsala, Sweden — <sup>2</sup>Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

For the ab-initio description of the adsorption process on surfaces it is necessary to model all interactions on the same theoretical footing. The standard density functional methods have their difficulties with describing dispersion forces. But especially for the physisorption, where no covalent bonds are formed between the adsorbant and the surface these interactions are essential. They can only well described with wavefunction based correlation methods. With the method of increments [1] it is possible to apply these methods to extended systems. Here we want to present the first application to an adsorption process. As example we have chosen CO on ceria 110 surface. The idea is to partition the correlation part of the adsorption energy according to localized orbital groups of the adsorbant and the individual atoms in the surface. The main part of the binding are the correlation energies of the adsorbant with the different atoms of the surface. Therefore, with the method of increments it is not only possible to yield highly accurate results for the adsorption energy, but also gain information about the individual contributions to the adsorption.

[1] B. Paulus, Phys. Rep. 428, 1 (2006).

O 86.5 Fri 10:30 MA 141

**The thermal behavior of H in O-ZnO(000-1) subsurface: a HREELS study** — •HENGSHAN QIU, YUEMIN WANG, and CHRISTOF WÖLL — Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, 44780 Bochum, Germany

The presence of H adatoms has pronounced effects on the structure and chemical properties of metal oxide surfaces [1]. The structure and stabilization mechanisms of the polar O-terminated ZnO(000-1) surface are still under discussion [2]. In this work, the interaction of atomic hydrogen with the O-ZnO(000-1) surface was studied using high-resolution electron energy loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS) and low-energy electron diffraction (LEED). It is found that the clean, H-free O-ZnO surface exhibits a (1\*3) reconstruction with one third of the surface O atoms missing, in good agreement with the results obtained by He-atom scattering (HAS)[2]. Adsorption of atomic H (or H<sub>2</sub>O) at room temperature converts the (1\*3) reconstruction to (1\*1) with formation of OH species. In addition, The HREELS data reveal that exposing the clean O-ZnO surface to atomic hydrogen leads to a significant broadening of the incoherent elastic peak, indicating a surface metallization as determined on the ZnO(10-10) surface [3]. The metallization is induced by hydrogen adsorbed in subsurface. Upon heating these H atoms -instead of recombinative desorption- undergo migration into the bulk.

[1] Ch. Wöll, J. Phys. Condens. Matter. 16 (2004) 2981. [2] Ch.Wöll, Prog. Surf. Sci. 82 (2007) 55. [3] Y. Wang, et al., Phys. Rev. Lett. 95 (2005) 266104.

O 86.6 Fri 10:45 MA 141

**Single adatom adsorption on SiO2 thin films** — •STEFAN ULRICH, NIKLAS NILIUS, and HANS-JOACHIM FREUND — Fritz-Haber-Institut, Berlin, Germany

The contribution discusses the unusual adsorption characteristic of a thin SiO2 film grown on Mo(112), which strongly depends on the geometric size of the adsorbates. The SiO2 layer consists of a network of -Si-O- hexagons exposing nano-pores with 3-4 Angstrom diameter. As revealed from low-temperature STM measurements, Pd adatoms penetrate this opening with nearly no barrier and bind strongly to the Mo-SiO2 interface. Au atoms on the other hand are too big and adsorb only at line defects in the oxide surface, where larger pores are exposed. The electronic properties of the adatoms and their interaction with the SiO2 support are deduced from tunneling spectroscopy.

O 86.7 Fri 11:00 MA 141

**Self-Organization of MgPc Molecules on FeO Thin Films** —

•XIAO LIN and NIKLAS NILIUS — Fritz-Haber-Institut, Berlin, Germany

The spatial arrangement of Magnesium Phthalocyanine (MgPc) has been investigated on FeO films grown on Pt(111) with low-temperature STM and STS. The polar oxide film forms a coincidence lattice with

the Pt support and exhibits a surface dipole between the Fe(+) / O(-) layers that varies within the Moiré unit cell. The MgPc molecules preferentially adsorb on regions with large dipole strength. The rotational orientation of the molecules, on the other hand, is determined by their interaction with the atomic Fe-O lattice. The influence of the different binding configurations on the electronic structure of MgPc is revealed from spectroscopic investigations.