

O 24 Adsorption III

Time: Tuesday 15:45–18:30

Room: TRE Phys

O 24.1 Tue 15:45 TRE Phys

Adsorption of Molecular Oxygen on Metal Surfaces — ●CHRISTIAN MOSCH and AXEL GROSS — University of Ulm, Albert-Einstein-Allee 11, D-89069 Ulm

The dissociation barrier of O₂ on the aluminum (111) surface has been of large interest in the past years since the theoretical description within density functional theory (DFT) using the generalized gradient approximation (GGA) failed to reproduce the barrier that is found in experiments. Recently a dynamical description of this process assuming that the oxygen molecule does not adiabatically switch to a singlet state near the surface but stays in its gas phase triplet state has provided an explanation for this problem [1].

We investigate the problem from another point of view. We systematically study the adsorption process of O₂ on Al (111) in detail using both a planewave based slab approach within the GGA approximation as well as a gaussian based cluster method going beyond the local DFT approximations, thus elucidating the dependence of the theoretical results on the treatment of the electronic correlation. In addition, we will also address the adsorption of O₂ on Pt/Ru overlayer structures.

[1] J. Behler, B. Delley, S. Lorenz, K. Reuter, and M. Scheffler, Dissociation of O₂ at Al(111): The role of spin selection rules. *Phys. Rev. Lett.* **94**, 036104 (2005)

O 24.2 Tue 16:00 TRE Phys

The ordering behavior of oxygen at Pd(100) studied with a first-principles lattice-gas Hamiltonian approach — ●YONGSHENG ZHANG, JUTTA ROGAL, and KARSTEN REUTER — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin, Germany

We study the mesoscopic ordering behavior of oxygen on Pd(100) from first-principles by parametrizing a lattice-gas Hamiltonian (LGH) with density-functional theory data. Using this LGH we carry out mesoscopic Monte Carlo simulations in order to obtain the surface phase diagram for sub-monolayer coverages or as a function of the oxygen pressure. The calculated lateral interactions between oxygen atoms adsorbed in fourfold hollow sites are dominated by a first-nearest neighbor repulsion. Together with a smaller second nearest-neighbor repulsion and a third nearest-neighbor attraction, this stabilizes both experimentally known ordered structures, namely a $p(2 \times 2)$ and a $c(2 \times 2)$ phase. The critical temperatures for the order-disorder transition are found to be in good agreement with experimental values from low-energy electron diffraction measurements [1]. The population of bridge sites at higher coverages is critically discussed.

[1] S.-L. Chang and P.A. Thiel, *J. Chem. Phys.* **88**, 2071 (1988).

O 24.3 Tue 16:15 TRE Phys

A first-principles statistical mechanics investigation of the stability of a thin surface oxide in reactive environments — ●JUTTA ROGAL, KARSTEN REUTER, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin, Germany

Sufficiently oxygen-rich environmental conditions lead to the formation of oxides at metal surfaces. This could for example happen under the oxygen-rich conditions of high-pressure oxidation catalysis, and oxide films forming in the reactive environment could then actuate the catalytic behavior that is traditionally ascribed to the pristine transition metal substrate. At more noble metals with their rather unstable bulk oxides, the focus is here primarily on the relevance of so-called “surface oxides”, i.e. nanometer thin oxide films.

Using the CO oxidation over Pd(100) as example, we investigate the composition and stability of this model catalyst in the reactive environment with a first-principles statistical mechanics approach. In a first step we consider the surface in *constrained* thermodynamic equilibrium with an O₂ and CO gas phase. Under ambient gas phase conditions representative of technological CO oxidation catalysis the known $(\sqrt{5} \times \sqrt{5})R27^\circ$ surface oxide structure on Pd(100) is then indeed the most stable structure. In a second refined step we explicitly consider the effect of the reaction kinetics on the stability of this surface oxide through first-principles kinetic Monte Carlo simulations. Our simulations indicate that the stability of this surface oxide depends intricately on the ratio of reactant partial pressures in the environment.

O 24.4 Tue 16:30 TRE Phys

High-Pressure Oxidation of Pd(111) Single Crystal Surface: In-situ X-ray Diffraction studies — ●NIKOLAI KASPER, A. STIERLE, P. NOLTE, and H. DOSCH — Max - Planck-Institut für Metallforschung, Heisenbergstr. 3, D 70569 Stuttgart, Germany

The interaction of molecular oxygen with a Pd(111) single crystal surface has been studied in a wide temperature and pressure range (30 - 800 °C and 10⁻¹⁰ mbar - 1 bar, respectively). The stability regions of the surface oxide Pd₅O₄ and the bulk PdO have been obtained. Independent on the oxygen partial pressure, only chemisorbed oxygen layers form below 300 °C. The Pd₅O₄ surface oxide exhibits rather narrow stability (p, T) region - it can be formed only at temperatures 300 ° ≤ T ≤ 650 °C. Increasing pressure induces the transformation of the surface oxide into the PdO bulk oxide. The formation of unstable Pd₅O₄ structure has been observed during the decomposition of bulk oxide. The chemisorbed oxygen layers transform directly into the bulk PdO at the temperatures above 650 °C. From comparison of the stability diagram with the results of DFT-calculations one can easily see the effect of kinetic hindrance in formation of both surface and bulk oxides at low temperatures (300 ° ≤ T < 450 °C), similar to the case of Pd(100) oxidation [1]. The crystal structure of Pd₅O₄ obtained from crystal truncation rod measurements agrees with the literature data [2].

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[1] E. Lundgren *et al.*, *Phys. Rev. Lett.*, **88**, 246103 (2002)

[2] E. Lundgren *et al.*, *Phys. Rev. Lett.*, **92**, 046101 (2004)

O 24.5 Tue 16:45 TRE Phys

Origin of anomalous surface lattice expansion in Pd(001) — ●HOLGER L. MEYERHEIM¹, S. H. KIM¹, J. H. SEO², J.-S. KIM³, J. BARTHEL¹, and J. KIRSCHNER¹ — ¹MPI f. Mikrostrukturphysik, 06120 Halle — ²Dept. of Ophthalmic Optics, Chodang Univ. (Korea) — ³Dept. of Physics, Sook-Myung Women's Univ. (Korea)

We present a systematic study of the hydrogen induced anomalous expansion of the top layer spacing, $d_{\{12\}}$, using low-energy electron diffraction and surface x-ray scattering. After exposure of 6 Langmuirs of hydrogen at 150 K sample temperature, the hydrogen atoms occupy the surface hollow sites and a lattice expansion of $\Delta d_{\{12\}} = +4.7\%$ is determined in agreement with theoretical predictions (5.2%). Heating the sample above the hydrogen desorption temperature ($T_{\{D\}} \approx 340$ K), leads to an almost complete relaxation of $d_{\{12\}}$ to the bulk value of 1.945 Å. Similarly, no expansion is observed for clean Pd(001) prepared by rapid cooling after thermal treatment to remove hydrogen. Hydrogen re-adsorption from the residual gas atmosphere and possibly hydrogen agglomeration in the near surface region leads to an expansion of $d_{\{12\}}$ in the 2-3% range as observed in previous experiments. On the basis of our results, surface magnetism as a mechanism to trigger lattice expansion in Pd(001) needs not to be invoked.

O 24.6 Tue 17:00 TRE Phys

Hydrogen adsorption dynamics on clean and precovered Pd(100) surfaces from first principles — ●AXEL GROSS — Department of Theoretical Chemistry, University of Ulm, 89069 Ulm/Germany

Ab initio molecular dynamics simulations based on density functional theory (DFT) calculations have been performed to study the adsorption of H₂ on clean and hydrogen-covered Pd(100) surfaces. In the simulations, the surface atoms have been treated dynamically thus allowing a realistic description of the energy transfer from the impinging molecules to the substrate. On the clean surface, the sticking probability is hardly influenced by the recoil of the metal substrate atoms because of the large mass mismatch. However, if the H₂ molecules impinge on a hydrogen-covered surfaces with coverages $\Theta_H \leq 0.5$, the recoil of the preadsorbed hydrogen atoms causes a significant enhancement of the sticking probability. This leads to a H₂ sticking probability which is much larger than what one would expect from a simple site-blocking picture. For higher coverages, the repulsive interaction between the hydrogen atoms has to be taken into account which partially counterbalances the promoting effect of the recoil.

O 24.7 Tue 17:15 TRE Phys

SFG and TDS studies of CO adsorption on Pd nanoparticles supported by Nb2O5 and Fe3O4 thin films — ●FRANK HÖBEL, ATULA BANDARA, GÜNTHER RUPPRECHTER, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

CO adsorption on Nb2O5- and Fe3O4-supported Pd nanoparticles was studied by sum frequency generation (SFG) vibrational spectroscopy from ultrahigh vacuum (UHV) to 100 mbar, and by thermal desorption spectroscopy (TDS) under UHV. Differences between the Pd-Nb2O5/Cu3Au(100) and Pd-Fe3O4/Pt(111) model catalysts will be discussed. Heating the Pd-Nb2O5 system to 300 K resulted in an irreversible decrease in CO chemisorption associated with a phase shift in the SFG spectra. This indicates a modification of the electronic structure of the particles and a formation of mixed Pd-NbOx sites. Pd-Fe3O4 model catalyst, on the other hand, were rather stable up to ~600 K. For 10 nm Pd particles no pronounced changes were observed by SFG and TDS spectra, both methods revealing well-ordered particle facets. However, smaller Pd particles (~6 nm) showed different CO bands in SFG, pointing to rougher surfaces, and also phase changes occurred during annealing. Possible surface modifications during annealing (TDS) will be discussed

O 24.8 Tue 17:30 TRE Phys

STM/STS investigations of Cu-phthalocyanine molecules on Al2O3/Ni3Al(111) — ●A. KRUPSKI^{1,2}, M. MOORS¹, S. DEGEN¹, M. KRALJ¹, C. BECKER¹, and K. WANDEL¹ — ¹Institute of Physical and Theoretical Chemistry, University of Bonn, Germany. — ²Institute of Experimental Physics, University of Wrocław, Poland.

LT-STM and STS have been used to investigate the growth of Cu-phthalocyanine ($C_{32}H_{16}N_8Cu$) molecules on an ultrathin Al_2O_3 oxide film grown on the $Ni_3Al(111)$ surface [1] as a function of coverage and annealing temperature. For sub- and monolayer coverage and a deposition temperature of 140 K two different planar molecular adsorption configurations rotated by 30° with respect to each other were observed with sub molecular resolution in the STM images. For θ_{CuPc} about 1 ML, before completion of the first layer, the growth of a second layer was already observed. The measured distance of 0.35 nm between 1st and 2nd layer corresponds to the distance between layers in the a modification of crystalline CuPc. By the use of STS the lowest unoccupied molecular orbital (LUMO) of the adsorbed CuPc molecules has been identified at an energy of 1.2 eV. The lateral distribution of the electronic states of the CuPc has been analysed and mapped by STS. The $C_{32}H_{16}N_8Cu$ molecules grown at 140 are thermal stable up to 350 K against shape changes upon prolonged annealing to temperatures up to 350 K. A template effect of the underlying oxide film on the CuPc growth, as has been observed for metals like Pd [2], has not been found.

[1] S. Degen et al., Surf. Sci. Lett. 576 (2005) L57.

[2] S. Degen et al., Faraday Discuss. 125 (2003) 343.

O 24.9 Tue 17:45 TRE Phys

Self-Organization of Au Atoms on a polar FeO film — ●EMILE D. L. RIENKS, NIKLAS NILIUS, HANS-PETER RUST, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin

On polar oxide surfaces, the large surface dipole can have a significant effect on the adsorption characteristics. We have explored this effect using a mono-layer thick film of FeO grown on Pt(111). In this system a surface dipole is built up between the positive Fe and the negative O layers. A lattice mismatch between the FeO film and the Pt substrate gives rise to a Moiré pattern, in which Fe atoms alternately occupy on-top, fcc and hcp positions on the Pt lattice. Modulations of the surface dipole have been observed within the Moiré unit cell that can be traced back to the structural inhomogeneity of the film. Single Au atoms, deposited at 10 K, preferentially bind to the region of the Moiré cell with the largest surface dipole. This indicates a significant role of electrostatic interaction in the binding. In addition, the Au atoms display a remarkably small tendency to form clusters upon increasing the coverage. Instead, a hexagonal network of single atoms with a lattice constant of 2.5 nm is formed. Electrostatic repulsion between polarized or partially charged Au atoms can account for this phenomenon.

O 24.10 Tue 18:00 TRE Phys

Organic Molecule Intercalation in TaS_2 — ●SUJIT KUMAR DORA and OLAF MAGNUSSEN — Institut für Experimentelle und Angewandte Physik, Christian-Albrecht-Universität, Germany, Leibnizstr. 19, 24118 Kiel

Transition metal dichalcogenides are ideal host materials for the intercalation of organic molecules, resulting in large change of structural and electronic properties. In this study the atomic-scale mechanisms of the electrochemical intercalation/deintercalation of pyridine and octylamine (both 0.01 M solution pH 3) in $1T - TaS_2$ was investigated by in-situ electrochemical STM and cyclic voltammetry. Intercalation starts at potentials negative of $-0.45 V$ vs SCE. The STM observations show characteristic structural changes in the surface morphology during this process indicating an important role of surface defects, such as holes and steps. In particular, the formation of holes, step flow etching and the formation of small islands of submonolayer height were observed.

O 24.11 Tue 18:15 TRE Phys

Rb adsorption and intercalation on TaS_2 — ●PATRICK SCHMIDT, JÖRG KRÖGER, and RICHARD BERNDT — Institut für Experimentelle und Angewandte Physik, Universität Kiel, D-24098 Kiel, Germany

We report results of scanning tunnelling microscopy at room temperature (RT) and low temperature (LT, 9 K) of TaS_2 exposed to Rb. All samples are prepared by evaporating several monolayers of Rb at RT. STM topographs at RT show a $\sim 1 \text{ \AA}$ deformation of the first layer of TaS_2 on a $\sim 1000 \text{ \AA}$ lateral scale indicating Rb intercalation. Additionally the step height of TaS_2 -Rb is increased by 3 \AA compared to pristine TaS_2 . This value corresponds to the ionic radius of Rb. Finally, the hexagonal $\sqrt{13} \times \sqrt{13}$ charge density wave of TaS_2 changes to a rectangular phase. After evaporating ~ 4 monolayer (ML) of Rb we observe at LT Rb adatoms residing at maxima of the charge density wave. For higher exposure (~ 9 ML) the pattern changes to unordered arrangement of maxima with a typical nearest neighbour distance of 11 \AA .