

## O 51: Metal Substrates: Adsorption III

Time: Thursday 11:15–12:45

Location: H39

O 51.1 Thu 11:15 H39

**Sub-surface oxygen in Pd(100): Density-functional theory calculations** — ●JÖRG MEYER and KARSTEN REUTER — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin, Germany

We use density-functional theory to investigate a possible incorporation of oxygen into the Pd(100) surface at low coverages. As a first step, we compare the stability of oxygen atoms in high-symmetry sites between the first and second substrate layer with that of oxygen adsorbed on the surface. In agreement with similar results for other (100) and (111) late transition metal surfaces, sub-surface oxygen is found to be significantly less favorable. Calculated barriers show furthermore, that even if populated, sub-surface oxygen will rapidly pop up to the surface at room temperature. We discuss a possible stabilization in the sub-surface sites through nearby on-surface O atoms, and perform molecular dynamics simulations to study the accessibility of sub-surface sites in molecular beam experiments.

O 51.2 Thu 11:30 H39

**The Pd(110)-(3x2)-O surface phase investigated by STM and DFT** — ●MARKO KRALJ<sup>1,3</sup>, TOBIAS PERTRAM<sup>1</sup>, NICOLA SERIANI<sup>2</sup>, ALEKSANDER KRUPSKI<sup>1</sup>, CONRAD BECKER<sup>1</sup>, GEORG KRESSE<sup>2</sup>, and KLAUS WANDEL<sup>1</sup> — <sup>1</sup>Institute of Physical Chemistry, University of Bonn — <sup>2</sup>Institute for Material Physics, University of Vienna — <sup>3</sup>Institute of Physics, Zagreb

The catalytic activity of palladium has intrigued researchers to study the interaction of gases with its surfaces for many decades. The complexity of the O-Pd(110) interaction manifests itself in a number of observed surface phases, which depend on oxygen exposures and various surface temperatures. According to LEED measurements six different structures have been reported and surface oxide formation is accompanied by a missing-row restructuring. This type of reconstruction is generally observed with bare and adsorbate covered (110) surfaces of similar metals and is believed to be the most stable reconstruction because it is accompanied by the formation of (111) micro-facets.

Most data about the system have been published in relation to the c(2x4) phase which is easy to prepare and it seems to dominate the phase diagram. Consequently, not much is known about other oxygen overlayer structures. In this study we have used STM in combination with DFT in order to further explore the O/Pd(110) phase diagram. In particular, we have concentrated on the Pd(110)-(3x2)-O surface oxide which corresponds to a low oxygen coverage. Measured and calculated data are in very good agreement and indicate that oxygen atoms are adsorbed in three-fold hollows of the reconstructed surface.

O 51.3 Thu 11:45 H39

**In-situ x-ray investigation on the oxidation of platinum (111) surfaces** — ●CLAUS ELLINGER, NIKOLAI KASPER, ANDREAS STIERLE, and HELMUT DOSCH — Max-Planck-Institut für Metallforschung,

We determined the oxide structure on the Pt(111) surface using surface x-ray diffraction. Platinum is one of the most important catalysts for the oxidation of carbonmonoxide and hydrocarbons and is also used as protecting coating material in highly reactive environments. For the understanding of these technological processes a detailed knowledge of Pt oxidation is essential. A important role in the high reactivity of Pt surfaces is attributed to existence of oxide structure phases. At 250 °C and an O<sub>2</sub> pressure of 500 mbar we observe the formation of an oxide similar to  $\alpha$ -PtO<sub>2</sub>. The determined structure is described by a thin bulk oxide like film consisting of two layers of oxidized platinum. We find that the hexagonal unit cell of the oxide and the Pt(111) are aligned parallel which is in contrast to recent DFT calculations [1]. In addition, specular in-situ reflectivity measurements were carried out during the oxidation of a 100 Å thin Pt(111) film on a sapphire substrate. We demonstrate that an oxide is formed on the platinum film at 300 °C and oxygen pressures from 100 mbar to 500 mbar. Furthermore a material loss during the reaction with oxygen was observed as macroscopic holes appeared locally in the Pt film at an O<sub>2</sub> pressure of 150 mbar and a temperature of 450 °C.

[1] W.X. Li and B. Hammer, *Chem Phys Lett* **409**, 1-7 (2005).

O 51.4 Thu 12:00 H39

**Subsurface oxygen in Ni on ( $\sqrt{2}\times\sqrt{2}$ ) R45° O/Cu(001)** — ●HOLGER MEYERHEIM<sup>1</sup>, DIRK SANDER<sup>1</sup>, RADIAN POPESCU<sup>1</sup>, WEI

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Growth, morphology and magnetic properties of Ni deposited on Cu(001) are distinctly influenced by preadsorption of oxygen. The pre-oxidized Cu(001) surface exhibits a ( $\sqrt{2}\times\sqrt{2}$ ) R45° reconstruction characterized by a "missing row" geometry. Subsequent Ni-adsorption changes the reconstruction to c(2x2) and previous studies indicated that oxygen acts as a surfactant always floating on the surface. The spin re-orientation transition (SRT) from in-plane to out of plane is shifted from ten monolayers (ML) in the case of the non-oxidized Cu substrate to five ML (1 ML=  $1.53\times 10^{15}$  atoms/cm<sup>2</sup>). We present an in-depth surface x-ray diffraction analysis of the interface structure of Ni grown on the reconstructed ( $\sqrt{2}\times\sqrt{2}$ ) R45° O/Cu(001) surface in the coverage range between 1.25 and 5.00 monolayers (ML). In contrast to common belief that oxygen atoms always float on the surface, we find a significant fraction (up to  $\approx 0.17$  ML) of oxygen located in octahedral interstitial sites below the surface. Surface stress measurements in combination with density functional calculations support this finding. The implications for the understanding of the oxygen induced SRT in the Ni/O/Cu(001) system are discussed.

O 51.5 Thu 12:15 H39

**Hindered Spin-Transitions in the Dissociative Adsorption of O<sub>2</sub> on Al(111)** — ●CHRISTIAN CARBOGNO<sup>1</sup>, JÖRG BEHLER<sup>2</sup>, AXEL GROSS<sup>1</sup>, and KARSTEN REUTER<sup>3</sup> — <sup>1</sup>Inst. of Theoretical Chemistry, University of Ulm, Germany — <sup>2</sup>Dept. of Chemistry and Applied Biosciences, ETH Zürich, Switzerland — <sup>3</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The low sticking probability for thermal O<sub>2</sub> molecules at Al(111) has recently been related to spin selection rules, which hinder a spin transition from the initial O<sub>2</sub> gas-phase triplet state to the singlet state of the adsorbed O atoms [1]. A constrained density-functional theory (DFT) approach was employed to compute the potential energy surfaces (PESs) of O<sub>2</sub> in different spin-configurations, and the lowered sticking probability was calculated when restricting the O<sub>2</sub> molecule to motion on the spin-triplet PES only. Here, we extend these studies by considering the dissociation dynamics on multiple spin PESs, allowing transitions between them within the quantum-classical fewest-switch algorithm as recently implemented [2], and calculating the non-adiabatic coupling between the PESs with various quantum chemical methods. The established framework enables us to study the adsorption process in detail, both as a function of the incident kinetic energy and incidence angle. Obtaining good agreement with experiment, we critically discuss the effects of the approximate non-adiabatic couplings and the uncertainties underlying the DFT PESs.

[1] J. Behler *et al.*, *Phys. Rev. Lett.* **94**, 036104 (2005).

[2] C. Bach *et al.*, *Israel J. Chem.* **45**, 46 (2005).

O 51.6 Thu 12:30 H39

**The influence of surface oxides on the hydrogen absorption behaviour of metal hydride alloys** — ●MARK SCHÜLKE<sup>1</sup>, HUBERT PAULUS<sup>2</sup>, MARTIN LAMMERS<sup>2</sup>, GABOR KISS<sup>3</sup>, and KARL-HEINZ MÜLLER<sup>1,2</sup> — <sup>1</sup>University of Applied Sciences of South Westphalia, Luebecker Ring 2, 59494 Soest, Germany — <sup>2</sup>Institute for Technology and Knowledge Transfer (TWS), Luebecker Ring 2, 59494 Soest, Germany — <sup>3</sup>Technical University of Budapest, Institute of physics, Chair of atom physics, H-1111 Budapest, Budafoki ut 8, Hungary

Metal hydride alloys are one promising alternative for hydrogen storage. However the influence of their surface on the hydrogen absorption process is not yet understood in detail. Oxygen adsorption from the gas phase as well as oxygen segregation and the segregation of alloy components play an important role in the hydrogen absorption process. The presented investigations are part of a series of experiments dealing with these subjects.

The presented experiments deal with the influence of adsorbed oxygen on the surface composition and the absorption behaviour of a AB<sub>2</sub> Laves phase alloy, namely Ti<sub>0.95</sub>Zr<sub>0.05</sub>Mn<sub>1.53</sub>V<sub>0.47</sub>Fe<sub>0.08</sub>Al<sub>0.02</sub>. In order to examine this, the samples were exposed to different doses of oxygen (e.g. 100 L, 1000 L) and analyzed by XPS and SNMS. It is shown that all main alloy components (Ti, Mn, V) are oxidized to

certain oxidation states. Also a Mn enrichment at the surface can be observed (oxygen-induced segregation). The influence of these ef-

fects on the hydrogen absorption behaviour (capacity, dynamics) is discussed, too.