O 74: Metal Substrates: Adsorption of O and/or H

Time: Thursday 15:00–17:15 Location: MA 141

O 74.1 Thu 15:00 MA 141

Structure determination for the W(100)-(2×2)-O surface phase — •Wolfgang Meyer, Kerstin Biedermann, Lutz Hammer, and Klaus Heinz — Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7, D-91058 Erlangen

For oxygen adsorbed on the W(100) surface and annealed at a temperature of 1000°C a (2×2) reconstruction is observed for which an O coverage larger than 1.0 ML has been reported [1]. Although the existence of this surface phase has been known for long, its structure is still unknown. We investigated this W(100)-(2×2)-O phase by means of quantitative LEED. The analysis reveals that the surface comprises two coexisting domains with p(2×2) and p(2×1) order, respectively. The p(2×1) structure is the already known missing row reconstruction with 1 ML oxygen atoms residing in the three-fold sites along the tungsten chains [2]. The p(2×2) domain consists of a single W atom per (2×2) unit cell decorated by four O atoms. Another oxygen atom is located on top of the 3^{rd} layer tungsten atoms, resulting in a total oxygen coverage of 1.25 ML for this domain. The surface is covered with the two domains at a fraction of 60 % for the (2×2) order and 40 % for the (2×1) order. The W(100)-(2×2)-O surface phase can be considered as a precursor for the (2×1) missing row structure which is fully developed for higher annealing temperatures.

[1] E. Bauer et al., Surf. Sci. **58** (1976) 517

[2] H. Yamazaki et al., Surf. Sci. **477** (2001) 174

O 74.2 Thu 15:15 MA 141

Oxidation of Fe_3Al followed by surface X-ray diffraction — •Claus Ellinger, Vedran Vonk, Navid Khorshidi, Andreas Stierle, and Helmut Dosch — Max-Planck-Institut für Metallforschung,

The interaction between oxygen and alloy surfaces plays a key role in many processes, such as thin film growth, corrosion and catalysis. Due to preferential surface segregation in binary alloys, one of the constituents will react with oxygen to form a thin oxide layer. These oxide layers are used as templates for model catalysts, tunneling barriers in electronic devices, or corrosion-resistant devices. To study the structural composition of the alloy surfaces at realistic conditions and to follow their oxidation process, surface sensitive x-ray diffraction (SXRD) provides a non-destructive in-situ technique. In this talk, the oxidation of Fe_3Al(110) will be discussed and compared to NiAl(110). Using AES, LEED and SXRD, we find a chemically well ordered surface of a clean Fe_3Al crystal. After exposure to a small amount of oxygen this ordering of the substrate completely disappears in the near surface region and a smooth thin Al_2O_3 layer is formed. While the fundamental, disordered A2 phase of Fe_3Al still exists in the surface region after the oxidation, the two ordered phases of the alloy are only found in the bulk. We therefore conclude that the substrate-oxide interface is still sharp and well-defined, while there is an oxygen induced shift of the stoichiometry within the surface towards the A2 phase.

O 74.3 Thu 15:30 MA 141

Oxidation of palladium surfaces and nanoparticles — •Nicola Seriani[1], Florian Mittendorfer[1], Georg Kresse[1], Jan Klikovits[2], Evelyn Napetschnig[2], Michael Schmid[2], Peter Varga[2], Rasmus Westerstrom[3], and Edvin Lundgren[3] — [1]University of Vienna, Austria — [2]TU Vienna, Austria — [3]Lund University, Sweden

Palladium finds wide application as oxidation catalyst, where a fundamental role is played by the interaction of its surfaces with oxygen. We have investigated formation of adsorption structures and surface oxides on selected Pd surfaces at atomistic level by density functional theory and first-principles thermodynamics as complement to experimental investigations. Surface oxide monolayers with stoichiometry close to that of bulk PdO have been observed and characterized and conditions for their thermodynamic stability have been predicted. Surface free energies of formation are then used in a Wulff construction to predict the shape of nanoscopic particles of palladium in dependence of temperature and oxygen pressure.

O 74.4 Thu 15:45 MA 141

Hot adatom motion tackled from first-principles — •Jörg Meyer and Karsten Reuter — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin (Germany)

The initial stages of the oxidation of metal surfaces are still far from being understood - despite their essential importance for example in the field of oxidation catalysis. In view of the exothermicity of the dissociative adsorption of O_2 at most metal surfaces, one fundamental question concerns the energy dissipation into the substrate, which, if sufficiently slow, could give rise to a transient mobility of the adsorbed, but not yet equilibrated oxygen atoms. In order to address this issue by first-principles theory we separate the molecular encounter with the surface into two stages: At large distances from the surface, substrate mobility can still be neglected and we focus our density-functional theory calculations on the six-dimensional potential-energy surface (PES) representing the molecular degrees of freedom. Performing extensive molecular dynamics (MD) runs on this suitably interpolated PES we evaluate the steering of thermal molecules into specific entrance channels. The corresponding molecular orientations and positions at intermediate heights above the surface form then statistically relevant starting geometries for first-principles MD trajectories of the remaining dissociation path that consider a full substrate mobility in large surface unit-cells. Applying this scheme to the O_2 dissociation over Pd(100), we will critically discuss a possible transient mobility especially in view of the restrictions on phononic dissipation inside the employed supercell geometry.

O 74.5 Thu 16:00 MA 141

Step decoration studied with first-principles statistical mechanics — •Yongsheng Zhang and Karsten Reuter — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin (Germany)

With respect to oxidation catalysis or oxide formation, surface defects like steps, kinks, or vacancies are widely believed to play a decisive role, e.g. in form of active sites or as nucleation centers. Despite this suggested importance, first-principles investigations qualifying this role for gas-phase conditions that are representative of these applications are scarce. This is mostly due to the limitations of electronic-structure calculations in tackling the large system sizes and huge configuration spaces involved. We overcome these limitations with a first-principles statistical mechanics approach coupling density-functional theory (DFT) calculations with grand-canonical Monte Carlo simulations, and apply it to obtain the phase diagram of on-surface O adsorption at a (111) step on a Pd(100) surface. The link between the electronic and mesoscopic techniques is achieved by a lattice-gas Hamiltonian expansion, in which we parameterize the lateral interactions affected by the step from DFT calculations at a Pd(117) vicinal surface, and all remaining lateral interactions from calculations at Pd(100). For a wide range of O gas-phase conditions we find the (111) step to be decorated by a characteristic zig-zag structure. Intriguingly, this structure prevails even up to the elevated temperatures characteristic for catalytic combustion reactions, where only small amounts of disordered oxygen remain at the Pd(100) surface.

O 74.6 Thu 16:15 MA 141

Hindered Spin-Transitions in the Dissociative Adsorption of O_2 on Al(111) — •Christian Carbogno[1], Jörg Behler[2], Axel Gross[1], and Karsten Reuter[3] — [1]Institut für Theoretische Chemie, Universität Ulm, Germany — [2]Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Germany — [3]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The low sticking probability for thermal O_2 molecules at Al(111) has recently been related to spin selection rules, which hinder transitions from the initial O_2 gas-phase triplet state to the singlet state of the adsorbed O atoms [1]. A constrained DFT approach was employed to compute potential energy surfaces (PESs) of O_2 in different spin-configurations from the surface, and the experimental sticking probability was qualitatively reproduced when restricting the O_2 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 Tully's fewest-switches algorithm as recently implemented [2]. The required non-adiabatic coupling elements have been derived in an *ab initio* fashion from the comparison between adiabatic and constrained-DFT PESs. Within this framework we obtain both good agreement with experiment for the fundamental features of the system as well as deeper insight into more peculiar characteristics of the dynamics. Based on our results, we propose experiments which can be used for the validation of our approach.

[1] J. Behler *et al.*, Phys. Rev. Lett. **94**, 036104 (2005).
[2] C. Bach *et al.*, Israel J. Chem. **45**, 46 (2005).

O 74.7 Thu 16:30 MA 141

Wechselwirkung von Wasserstoff mit einer Rhodium(210)-Oberfläche

— •Henan Li, Christian Pauls und Klaus Christmann — Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany

In Fortsetzung unserer Studien zur Wechselwirkung von Wasserstoff mit fcc(210)-Oberflächen haben wir die Adsorption von Wasserstoff auf Rh(210) im Bereich zwischen 70 und 700 K mittels LEED, Thermodesorption, H2-D2-Isotopenaustausch- und Austrittsarbeits-($\Delta\varphi$)-Messungen untersucht. Bei 70 K adsorbiert Wasserstoff in mindestens vier Bindungszuständen (β_3, β_2, β_1 und α), die sequentiell bevölkert werden. β_3 (T$_{des}$ = 300...360 K) und β_2 (200...250 K) desorbieren mit (leicht bedeckungsgradabhängigen) Energien von ca. 80 bzw. 63 kJ/Mol nach 2. Ordnung und zeigen eine Erhöhung der Austrittsarbeit um ca. 120 meV, während der β_1-Zustand (T_{des} = 150 K mit E_{des} = 35 kJ/Mol) ebenso wie der α-Zustand (T_{des} = 93 K mit E_{des} = 23 kJ/Mol) eine Desorptionsordnung von 1 aufweist und zudem mit einer deutlichen $\Delta\varphi$-Erniedrigung verknüpft ist ($\Delta\varphi_{\beta 1} \approx -80$ meV; $\Delta\varphi_\alpha \approx -300$ meV). Ähnlich wie bei Pd(210) und Ni(210) bildet keiner der Zustände eine LEED-Überstruktur. H2-D2-Isotopenaustausch weist die β-Zustände klar als atomare H-Zustände aus, während die reduzierte HD-Intensität des α-Zustandes sowie dessen starke Austrittsarbeitsabnahme - ähnlich wie bei Pd(210) - zumindest Anteile von *molekular chemisorbiertem* Wasserstoff nahelegen. Im Unterschied zu Pd(210) erhalten wir jedoch keine Hinweise auf Subsurface-Wasserstoff.

O 74.8 Thu 16:45 MA 141

Strain effects in the adsorption on early transition metals

— •Sebastian Schnur and Axel Gross — Institut für Theoretische Chemie, Universität Ulm, Germany

Strain effects in the adsorption on transition metal surfaces have recently attracted a lot of attention. Strain can significantly change the electronic structure and thus the reactivity and catalytic properties of these metals. These effects occur, e.g., if a metal grows pseudomorphically on another metals. In this context, only late transition metals have been investigated so far [1] because they are the common catalytically active metals. However, early transition metals such as titanium or manganese represent promissing candidate materials in light intermetallic compounds for hydrogen storage.

Compressive strain leads to a reduced overlap of the wave functions and thus to a narrowing of the d-band. Charge conservation leads either to a downshift of the d-band in early transition metals or to an upshift in late transition metals because of the different degree of filling. According to the d-band model, a downshift of the d-band should cause weaker interactions with adsorbates [1]. We performed density functional theory calculations to study for the first time strain effects in several early transition metals using hydrogen and CO adsorption energies as a probe for their reactivity. The DFT results confirmed the predictions of the d-band model, thus providing guidance for a rational modification of the chemical properties of early transition metals. [1] M. Mavrikakis, B. Hammer, and J.K. Nørskov, Phys. Rev. Lett. **81**, 2819 (1998).

O 74.9 Thu 17:00 MA 141

Femtosecond laser desorption of atomic hydrogen from graphite in the visible and in the XUV using FLASH

— •Robert Frigge[1], Tim Hoger[1], Björn Siemer[1], Carsten Thewes[1], Marcus Rutkowski[1], Helmut Zacharias[1], Stefan Düsterer[2], and Rolf Treusch[2] — [1]Physikalisches Institut, Münster, Germany — [2]Hasylab, Hamburg, Germany

The desoption of hydrogen from HOPG is of great interest in astrophysics. In so called H-I-clouds particles form areas of higher density in which protostars develop. The rise of protostars out of H clouds is not yet fully understood. This talk presents the laser desorption of hydrogen from HOPG. The velocity distribution of atomic hydrogen from HOPG is examined after surface excitation with fs pulses of 800 nm and 400 nm from a Ti:Sa laser system and 32 nm from a free electron laser(FLASH).

The atomic hydrogen is ionised via the 1s → 2s transition using a 2+1 REMPI detection scheme. Ionised H atoms are detected by a time-of-flight mass spectrometer. The arrival time distribution of H atoms at the ionised volume is measured by varying the delay between the pump and the probe laser. The transformation into a velocity distribution yields extremely slow velocities. The results are discussed more generally with the two temperature model and also in light of a recent DFT calculation. [Hornekaer et al., Phys. Rew. Lett.**97**, 186102 (2006)]