

O 12: Metal substrates: Adsorption of O / H and inorganic molecules I

Time: Monday 15:00–17:00

Location: WIL A317

O 12.1 Mon 15:00 WIL A317

Adsorption of atomic oxygen on PdAg/Pd(111) surface alloys and coadsorption of CO — ●ARNOLD P. FARKAS^{1,2}, JOACHIM BANSMANN¹, THOMAS DIEMANT¹, and R. JÜRGEN BEHM¹ — ¹Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany — ²Reaction Kinetics Research Group at the University of Szeged, Chemical Research Center of the Hungarian Academy of Sciences, H-6720 Szeged, Hungary

The interaction of dissociated oxygen with structurally well-defined PdAg/Pd(111) surface alloys and the coadsorption of CO was studied by high resolution electron energy loss spectroscopy (HREELS) and temperature-programmed desorption (TPD). After oxygen saturation of the non-modified Pd(111) surface at RT, we observed the formation of a prominent peak in the HREEL spectra at 60 meV corresponding to the perpendicular vibration of oxygen atoms adsorbed in threefold hollow sites. Deposition of small Ag amounts does not change the signal intensity of this peak; it decreases only above 20% Ag. Beyond this Ag content, the peak intensity steeply declines and disappears at around 55-60% Ag. CO coadsorption on the oxygen pre-covered surfaces at 120 K leads to the formation of additional features in HREELS. For a surface alloy with 29% Ag, three loss features due to CO adsorption in on-top, bridge, and threefold-hollow sites can be discriminated already after the lowest CO exposure. Annealing of the co-adsorbed layer to 200 K triggers a decrease of the oxygen concentration due to CO₂ formation. These findings are corroborated by TPD spectra of the CO desorption and CO₂ production.

O 12.2 Mon 15:15 WIL A317

Adsorption and reaction of sulfur dioxide on clean and oxygen precovered Pd(100) — ●KARIN GOTTERBARM, REGINE STREBER, CHRISTIAN PAPP, OLIVER HÖFERT, MICHAEL PETER ANDREAS LORENZ, and HANS-PETER STEINRÜCK — Lehrstuhl für physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91052 Erlangen

Sulfur and its oxides are well-known poisons in large scale applications of heterogeneously catalyzed reactions. We studied the adsorption and thermal evolution of SO₂ on a clean and oxygen precovered Pd(100) surface by in-situ high-resolution XPS applying synchrotron radiation at BESSY II, Berlin. Adsorption of SO₂ on the clean Pd(100) surface at 130 K leads to formation of two different SO₂ species: a highly populated upright standing SO₂ species and a small amount of flat lying SO₂. Upon annealing the sample standing SO₂ is transformed into lying SO₂, which is ultimately reduced to atomic sulfur. On the oxygen precovered surface a fraction of SO₂ reacts to SO₃ immediately upon adsorption, even at temperatures as low as 130 K. Heating of the resulting mixed adsorbate layers first results in the conversion of all remaining SO₂ species to SO₃ followed by subsequent oxidation to SO₄ above 300 K.

This work was supported by the BMBF under grant 05 ES3XBA/5 and by the Cluster of Excellence 'Engineering of Advanced Materials'.

O 12.3 Mon 15:30 WIL A317

Coadsorption of CO and hydrogen on submonolayer Pt/Ru(0001) films — ●HEINRICH HARTMANN, THOMAS DIEMANT, JOACHIM BANSMANN, and R. JUERGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

Due to their high CO tolerance, bimetallic Pt-Ru catalysts are an attractive electrode material for the oxidation of H₂-rich fuel gases prepared by reforming of fossil fuels in low-temperature polymer electrolyte fuel cells. This makes the adsorption properties of PtRu systems an interesting topic for fundamental studies on model systems.

We have investigated the coadsorption of CO and hydrogen on submonolayer Pt films deposited on the Ru(0001) surface with TPD and IRAS under UHV conditions. Adsorption of either of the two molecules on the Pt covered parts of the bimetallic surface is weaker compared to adsorption on the remaining uncovered Ru parts. Coadsorption of hydrogen and CO leads to a displacement of hydrogen from the Ru areas to the energetically less favourable Pt islands. At the same time a further weakening of the hydrogen-Pt bond is observed, which is attributed to repulsive interactions between adsorbed hydrogen and CO molecules.

O 12.4 Mon 15:45 WIL A317

Non-adiabatic Effects during the Dissociative Adsorption of O₂ at Ag(111)? A first-principles Divide & Conquer Study — ●ITZIAR GOIKOETXEA^{1,2}, JUAN BELTRÁN¹, JÖRG MEYER^{1,3}, MAITE ALDUCIN², IÑAKI JUARISTI², and KARSTEN REUTER^{1,3} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Centro de Física de Materiales, San Sebastian, Spain — ³Technische Universität München, Germany

A predictive materials science modeling based on microscopic understanding requires a thorough knowledge of all underlying elementary processes at the atomic scale. The adsorption of individual oxygen molecules at metal surfaces is one example -crucially relevant not only but in particular in heterogeneous catalysis. Recent work on the dissociative adsorption of O₂ at Al(111) has severely challenged its prevalent understanding: A non-adiabatic transition of the molecular spin state favored by low density of states at the Fermi-level has been proposed to reconcile experimental observations with ab-initio theory [1]. Consequently, coinage metal surfaces might be further good candidates for such effects. With this motivation, we have used a first-principles based divide and conquer approach to study O₂ on Ag(111). Experimental observables like e.g. (initial) sticking and scattering turn out to be semi-quantitatively reproduced with adiabatic dynamics already. Finally, the emerging picture for the interaction of oxygen molecules with this surface is compared to the low-dimensional model originally proposed by Kleyn et al. [2]. [1] J. Behler et al., Phys. Rev. Lett. 94, 036104 (2005). [2] A. W. Kleyn et al., Surf. Sci. 363, 29 (1996).

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In-situ oxidation study of Pd(100) by surface x-ray diffraction — ●VOLKAN KILIC¹, NATALIA MARTIN², MIGUEL MANTILLA³, DIRK FRANZ¹, EDVIN LUNDGREN² und ANDREAS STIERLE¹ — ¹AG Grenzflächen, Universität Siegen, Germany — ²Department of Synchrotron Radiation Research, Lund University, Sweden — ³MPI für Metallforschung, Stuttgart, Germany

The oxidation of the Pd(100) surface at oxygen pressures in the 10⁻⁶ mbar to 10³ mbar range and temperatures up to 1000 K has been studied in-situ by surface x-ray diffraction (SXRD). The SXRD experiments were performed at the MPI beamline at the Angstrom Quelle Karlsruhe (ANKA). We present the surface and crystal truncation rod (CTR) data from the ($\sqrt{5} \times \sqrt{5}$) surface layer. We show that the transformation from the surface oxide to PdO bulk oxide can be observed in-situ under specific pressure and temperature conditions. We will compare our results with previously proposed structure models based on low energy electron diffraction (LEED) I(V) curves and density function theory calculations [1,2]. Finally, we will elucidate the question of commensurability of the surface oxide layer with respect to the Pd(100) substrate.

[1]P. Kostelnik, N. Seriani, G. Kresse, A. Mikkelsen, E. Lundgren, V. Blum, T. Sikola, P. Varga, M. Schmid, Surf. Sci. 601 (2007) 1574-1581

[2]M.Todorova, E. Lundgren, V. Blum, A. Mikkelsen, S. Gray, J. Gustafson, M. Borg, J. Rogal, K. Reuter, J. N. Andersen, M. Scheffler, Surf. Sci. 541 (2003) 101-112

O 12.6 Mon 16:15 WIL A317

Electron-Hole Pairs during Adsorption Dynamics of O₂ on Pd(100) – Exciting or not? — ●JÖRG MEYER^{1,2} and KARSTEN REUTER^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Technische Universität München, Germany

Diminishing resources have made energy research become more and more prominent over the recent years. Energy conversion and dissipation at interfaces are two examples about which microscopic knowledge is limited at best – despite their fundamental importance e.g. during catalytic reactions at surfaces. Theoretical first-principles based modeling can provide important insights on corresponding underlying elementary processes. Non-adiabatic excitations of electron-hole pairs during adsorption of molecules on metal surfaces fall into this category and have been controversially discussed only recently [1]. Therefore, we have investigated their importance for O₂-adsorption on Pd(100), a representative showcase for heterogeneous catalysis. Using our efficient implementation of a computationally appealing perturbative approach [2], we have obtained electron-hole pair spectra for several trajectories

of different statistical relevance. Concomitant non-adiabatic energy losses do not exceed 4% of the available chemisorption energy, pointing towards other more dominant energy dissipation channels for this system. The role of the spin transition will be critically discussed.

[1] J. I. Juaristi et al., Phys. Rev. Lett. **100**, 116102 (2008); A. C. Luntz et al., *ibid.* **102**, 109601 (2009); J. I. Juaristi et al., *ibid.* **102**, 109602 (2009).

[2] M. Timmer and P. Kratzer, Phys. Rev. B **79**, 165407 (2009).

O 12.7 Mon 16:30 WIL A317

Surface oxidation of planar and stepped Pt(111) surfaces studied by DFT — •JOCHEN BANDLOW, PAYAM KAGHAZCHI, and TIMO JACOB — Abteilung Elektrochemie, Universität Ulm, Germany

The surface oxidation of Pt(111) plays an important role for a wide range of catalytic reactions in gas-phase surface science and electrochemistry. Despite the fact that many experimental studies are focused on single crystal systems with almost perfect surfaces, realistic catalysts always contain step edges, kinks, vacancies and other imperfections on the surface. Especially these lower-coordinated sites are believed to play a decisive role for surface reactions and the catalytic performance.

In the present work we investigated the adsorption of oxygen on perfect and stepped Pt(111) using density functional theory and the extended *ab initio* thermodynamics approach. [1] By comparing the (p, T) phase diagram for the system in contact with a gaseous O₂ atmosphere with the corresponding electrochemical (a, T, φ) phase diagram, characteristics of the surface morphology under specific conditions were evaluated. It turned out that the model of a pure and perfect Pt(111)

surface, which is often used to study this reaction, is clearly incomplete.

[1] T. Jacob, *J. Electroanal. Chem.*, **607**, 158 (2007).

O 12.8 Mon 16:45 WIL A317

First-Principles Diffusion Barrier of O at Pd (100): A Benchmark beyond LDA/GGA — •WEI-BING ZHANG^{1,2}, YONGSHENG ZHANG¹, JÖRG MEYER^{1,2}, and KARSTEN REUTER^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — ²Technische Universität München

The diffusion of adsorbates at a solid surface is a core elementary process of critical relevance for many functionalities. The accurate determination of diffusion barriers is correspondingly an important aspect in first-principles kinetic modeling. At extended metal surfaces the state-of-the-art for this is still local (LDA) and semi-local (GGA) density-functional theory. Critically scrutinizing the reliability of such description for the diffusion of O atoms at Pd(100) we first use a cluster expansion approach to separate the overall diffusion barrier into the isolated-adatom limit and contributions arising from lateral interactions with other O adsorbates. Comparing LDA and GGA data suggests that the latter component is surprisingly well described already at this level of theory. However, comparison against experiment reveals a significant error for the barrier in the isolated O adatom limit. We therefore use an exchange-correlation correction approach based on finite cluster calculations [1] to assess the performance of higher level theory, including hybrid and RPA functionals. [1] Q.M. Hu, K. Reuter, and M. Scheffler, Phys. Rev. Lett. **98**, 176103 (2007).