

O 3 Adsorption I

Time: Monday 11:15–12:45

Room: TRE Phys

O 3.1 Mon 11:15 TRE Phys

Ligand Effects Observed For The CO Adsorption At CoPt-Alloys — •DANIELA FENSKE, DIRK HOOGESTRAAT, DENIS GRESHNYK, STEFANIE NEUENDORF, HOLGER BORCHERT, WAI-LEUNG YIM, THORSTEN KLÜNER, and KATHARINA AL-SHAMERY — Carl v.Ossietzky University Oldenburg, Faculty V, Institute of Pure and Applied Chemistry, Germany

The use of bimetallic compounds instead of monometallic catalysts can strongly enhance the efficiency of heterogeneous catalysts which may be attributed either to structural and/or to ligand effects. Results on the influence of the adsorption of CO at CoPt-alloys will be reported as a function of surface composition. The alloys were obtained by evaporating a thin film of Co-atoms onto a Pt(111) crystal under UHV-conditions and subsequent annealing to various temperatures. The final composition of the surface itself could be tuned because Pt tends to segregate at the surface as a function of temperature. The exact surface composition of the different alloys was investigated by XPS. FT-IRAS as well as TPD measurements exhibited that CO-adsorption strongly depends on the actual surface composition which is mainly attributed to strong ligand effects (either preferential adsorption at Pt- (Pt rich surfaces) or Co-sites (Co rich surfaces)). Within TPD desorption peaks are lower than for pure platinum but larger than for pure cobalt sites. Supplementary data on a Co₃Pt(111) single crystal will be presented. Theoretical calculations (DFT) reveal the dependence between surface composition, the composition of the second and third layer and changing IR-frequencies and desorption temperatures.

O 3.2 Mon 11:30 TRE Phys

Changes in CO adsorption behavior on stepped platinum surfaces induced by preadsorbed silver — •BARBARA TRÄNKENSCHUH, REGINE STREBER, JOHANNES SCHÖCK, CHRISTIAN PAPP, REINHARD DENECKE, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

The influence of preadsorbed silver on the adsorption of CO on stepped platinum surfaces was studied using a combination of high-resolution X-ray photoelectron spectroscopy (XPS) and a supersonic molecular beam set-up. Gambardella et al. [1] have shown that on stepped Pt surfaces silver grows via an 1D row-by-row growth mode for small coverages (< 0.5 ML), starting at the step edges. In our study we deposited different amounts of silver onto Pt(355)=[5(111)x(111)] and Pt(644)=[5(111)x(100)] at 300 K and monitored the growth behavior by XPS in the Ag 3d and Pt 4f binding energy region. Thereafter, CO was dosed at low temperatures and simultaneously C 1s spectra were measured to determine the time-dependent occupation of the different adsorption sites, which can be distinguished by high-resolution XPS. For Ag coverages up to one monatomic row at the step edges, mainly the occupation of the CO step adsorption sites is changed. For higher Ag coverages, also changes in the CO adsorption behavior on the terraces were observed, due to the decreasing free Pt terrace width. Supported by the DFG (STE 620/4-3).

[1] P. Gambardella et al., Physical Review B 61 (2000) 2254.

O 3.3 Mon 11:45 TRE Phys

The influence of steps on the activated adsorption of methane on platinum: a molecular beam / high-resolution XPS study. — •CHRISTIAN PAPP, BARBARA TRÄNKENSCHUH, REGINE STREBER, THOMAS FUHRMANN, REINHARD DENECKE, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen.

We investigated the activated adsorption of methane on Pt(644) and Pt(355) to examine the influence of steps on the sticking coefficient and, thus, on the reactivity of these surfaces. Both samples have (111) terraces and differ only in the step orientation: Pt(644) has (100) steps and Pt(355) has (111) steps. To overcome the barrier for methane dissociation at UHV conditions, we used a supersonic molecular beam set-up. From measurements on Pt(111)[1], methyl (CH₃) has been identified as the product of the dissociative adsorption. By using high resolution in-situ XP spectroscopy we are able to distinguish between methyl adsorbed at step and terrace sites. The adsorption processes were analysed separately, leading to relative sticking coefficients for step and terrace

adsorbed molecules, with a different kinetic energy dependence. Additionally, we investigated the thermal evolution of the adsorbed species to study the influence of the steps on the dehydrogenation process. A comparison to corresponding results for flat Pt(111)[2] will be presented. Supported by the DFG (STE 620/4-3).

[1] Fuhrmann et al., Chem. Phys. Lett. 390 (2004) 208.

[2] Fuhrmann et al., New J. Phys. 7 (2005) 107.

O 3.4 Mon 12:00 TRE Phys

Buckled iodine layers on Pt(100): evidence of a charge density wave? — •BJÖRN BRAUNSCHWEIG and WINFRIED DAUM — Institut für Physik und Physikalische Technologien, TU Clausthal, Leibnizstrasse 4, D-38678 Clausthal-Zellerfeld

The atomic structure of well-defined iodine-covered Pt(100) surfaces was examined by scanning tunnelling microscopy (STM) in air and electrolyte. At high iodine coverage the well-known ($\sqrt{2} \times 5\sqrt{2}$)R45°-I adlattice on an unreconstructed Pt(100) substrate is observed. The adlayer consists of iodine rows which predominantly run along the [010] direction and form a characteristic double-row structure. Our STM images of the I-Pt(100) surface obtained in air show that the surface is covered with two distinctly different ($\sqrt{2} \times 5\sqrt{2}$)R45°-I phases: one phase with weak buckling of the double-rows parallel to the steps along the [010] direction, and a second phase of strongly buckled iodine double-rows perpendicular to the steps. The buckling of both domains strongly depends on the tunneling resistance and is reversible. No buckling is observed in a 0.1M HClO₄ electrolyte for a wide range of tunneling conditions, in accordance with previous work. We suggest that the iodine adsorbate induces a periodic lattice distortion (Peierls distortion) of the substrate yielding a charge density wave. The distortion of the charge density may be lifted or enhanced by the strong electric field of the electric double layer of the Pt/electrolyte interface and by the tip-induced field at the Pt/air interface, respectively.

O 3.5 Mon 12:15 TRE Phys

Adsorption modes of ethene on Pt(111) and Cu₃Pt(111) from vibrational spectroscopy and DFT calculations — •CONRAD BECKER, JAN HAUBRICH, THOMAS PELSTER, and KLAUS WANDEL — Institut für Physikalische und Theoretische Chemie der Universität Bonn, Wegelestr. 12, 53115 Bonn

The adsorption of ethene on Pt(111) and Cu₃Pt(111) at 100K has been investigated experimentally using high resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD). The spectra suggest two significantly different adsorption modes, which can be characterized as a bridged di-σ-mode on Pt(111) and a more weakly bound atop mode on Cu₃Pt(111). Using the Vienna ab initio simulation package (VASP) we have computed the bonding geometries and energies as well as the vibrational spectra of the di-σ-mode and the atop mode. As expected the di-σ-mode is the strongest bonding mode on Pt(111). When the molecule is, however, forced to an atop position - a situation that corresponds to the bonding on the Cu₃Pt(111) surface - the most favourable configuration is a metalla cycle, which is characterized by two σ-bonds on a single Pt atom. Furthermore, the adsorption energy of the metalla cycle is significantly smaller than that of the di-σ-mode, which reflects the findings of the TPD experiments. Based on DFT calculations a complete assignment of the modes in the HREELS spectra is performed.

O 3.6 Mon 12:30 TRE Phys

Investigations on segregation in modern hydrogen storage alloys — •MARK SCHÜLKE¹, JANOS GIBER², GABOR KISS², MARTIN LAMMERS³, KARL-HEINZ MÜLLER^{1,3}, and HUBERT PAULUS³ — ¹University of Applied Sciences of South Westphalia, Luebecker Ring 2, 59494 Soest, Germany — ²Technical University of Budapest, Institute of physics, Chair of atom physics, H-1111 Budapest, Budafoki ut 8, Hungary — ³Institute for Technology and Knowledge Transfer (TWS), Luebecker Ring 2, 59494 Soest, Germany

Before the first use hydrogen storage alloys have to be activated by means of several heating cycles combined with hydrogen flushing. According to former publications, the key mechanism to the understanding of the activation process is surface segregation induced by selective oxidation. [1] But it is also known from previous experiments with model

systems that the thermodynamic segregation of alloy components and of oxygen solved in the bulk influences the hydrogen absorption as well.

Samples of the AB₂ Laves phase alloy Ti_{0.95}Zr_{0.05}Mn_{1.53}V_{0.47}Fe_{0.08}Al_{0.02} with an oxygen content of ca. 0.9 at% (from manufacturing) were tempered for different periods of time (30 s, 1 min, 1 h, 5 h) at 100 °C and 200 °C and analyzed by means of different surface analysis methods (SNMS, XPS, AES, depth profiles) afterwards. In addition to oxygen, Mn and Fe are enriched in a surface layer with a thickness of about 20 nm.

In future investigations the influence of defined surface conditions on the hydrogen absorption shall be examined.

[1] L. Schlapbach in: Hydrogen in Intermetallic Compounds II, Topics in Applied Physics, vol. 67, ed. L. Schlapbach, Springer, 1992.