

## O 64: Metal substrates: Adsorption of inorganic molecules

Time: Friday 11:15–12:45

Location: SCH A215

O 64.1 Fri 11:15 SCH A215

**Angle Resolved Photoelectron Distribution of the  $1\pi$  Resonance of CO/Pt(111)** — ●THORBEN HAARLAMMERT<sup>1</sup>, SEBASTIAN WEGNER<sup>1</sup>, GRIGORIUS TSILIMIS<sup>1</sup>, HELMUT ZACHARIAS<sup>1</sup> und ALEXANDER GOLOVIN<sup>2</sup> — <sup>1</sup>Physikalisches Institut, Westfälische Wilhelms Universität, Münster — <sup>2</sup>Institute of Physics, St. Petersburg State University

The CO  $1\pi$  level of a  $c(4\times 2)$ -2CO / Pt(111) reconstruction shows a significant resonance when varying the photon energy between  $h\nu=23$  eV and  $h\nu=48$  eV. This resonance has not been observed in gas phase measurements or on the Pt(110) surface. To investigate the photoelectron distribution of the  $1\pi$  level High Harmonic Radiation has been used. By conversion in rare gases like Argon, Neon, or Helium photon energies of up to 100 eV have been generated at repetition rates of up to 10 kHz. The single Harmonics have been separated and focused by a toroidal grating and directed to the sample surface. A time-of-flight detector with multiple anodes registers the kinetic energies of the emitted photoelectrons and enables the simultaneous detection of multiple emission angles.

The angular distributions of photoelectrons emitted from the CO  $1\pi$  level have been measured for a variety of initial photon energies. Further the angular distributions of the CO  $1\pi$  level photoelectrons emitted from a CO-Pt<sub>7</sub> cluster have been calculated using the MSX $\alpha$ -Method which shows good agreement with the experimental data.

O 64.2 Fri 11:30 SCH A215

**Coadsorption of CO and hydrogen on PtRu/Ru(0001) surface alloys** — ●THOMAS DIEMANT<sup>1</sup>, JOACHIM BANSMANN<sup>1</sup>, HUBERT RAUSCHER<sup>1,2</sup>, and R. JUERGEN BEHM<sup>1</sup> — <sup>1</sup>Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany — <sup>2</sup>Institute for Health and Consumer Protection, Joint Research Centre, European Commission, I-21020 Ispra (VA), Italy

Due to their superior CO tolerance, bimetallic platinum-ruthenium catalysts are one of the most promising materials for the anodic hydrogen oxidation reaction in low-temperature polymer electrolyte fuel cells in the presence of small CO amounts. Therefore, the study of the adsorption properties of PtRu systems is of high interest. We have investigated the coadsorption of CO and hydrogen on PtRu/Ru(0001) surface alloy model systems by TPD and IR spectroscopy under UHV conditions. While hydrogen adsorption on the bimetallic surface alloys is already weakened in the absence of CO compared to the case of unmodified Ru(0001) [1], the addition of CO to the surface leads to a further significant weakening of hydrogen adsorption, caused by the repulsive interaction between the adsorbed species. Furthermore, post-adsorbed CO displaces hydrogen to energetically less favourable Pt-rich adsorption sites. The implications of our results for fuel cell applications will be discussed.

[1] T. Diemant et al., J. Phys. Chem. C 112 (2008) 8381.

O 64.3 Fri 11:45 SCH A215

**Interaction of CO with PdAg/Pd(111) surface alloys** — YUNSHENG MA, ●JOACHIM BANSMANN, THOMAS DIEMANT, ALBERT ENGSTFELD, HARRY HOSTER, and BEHM BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

The surface composition, distribution of different Pd ensembles and adsorption properties of PdAg/Pd(111) surface alloys have been investigated by Scanning Tunneling Microscopy (STM), Temperature Programmed Desorption (TPD) and High Resolution Electron Energy Loss Spectroscopy (HREELS) using CO as a probe molecule. The statistical analysis of atomic resolution STM images with chemical contrast reveals a nearly random distribution of the surface atoms on PdAg/Pd(111) surface alloys. The presence of Ag on the surface first suppresses the adsorption of CO on the preferred Pd threefold-hollow sites. For these sites, the adsorption energy does not change for small Ag coverages, indicative for a geometric (ensemble) effect. With increasing Ag surface concentration, CO mostly adsorbs on bridge sites of Pd dimers and top sites of Pd monomers surrounded by Ag atoms. At higher CO coverage, a transition of CO adsorption from bridge to top sites occurs on Pd dimers to accommodate more CO molecules, similar to the case on PdAu/Pd(111) surface alloys [1].

[1] M. Ruff et al., ChemPhysChem 8 (2007) 2068.

O 64.4 Fri 12:00 SCH A215

**CO adsorption on bimetallic PtRu/Ru(0001) surfaces - the influence of surface structure** — ●HEINRICH HARTMANN, THOMAS DIEMANT, JOACHIM BANSMANN, and R. JUERGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

To study the influence of the surface structure on the adsorption properties of PtRu/Ru(0001) surfaces, two types of bimetallic model systems with significantly different surface structure were prepared and studied by a combination of TPD and IR spectroscopy using CO and deuterium as probe molecules. While the first type of surface, a sub-monolayer Pt film on Ru(0001), shows Pt islands on the Ru substrate, the second type is a PtRu surface alloy with an almost random distribution of the components in the surface layer. For both surface types, a marked weakening of the adsorption strength of both CO and deuterium is evidenced by TPD experiments. While the CO TPD measurements show only minor differences for the two surface types, the surface structure has a clear influence on the D<sub>2</sub> TPD spectra, which is most pronounced for intermediate Pt concentrations. These results demonstrate the special importance of ensemble effects for deuterium adsorption, where mixed threefold adsorption ensembles are occupied, while such effects are absent for CO with exclusive adsorption in on-top sites. For CO, the influence of ligand and strain effects for the CO adsorption on the bimetallic surfaces will be discussed.

O 64.5 Fri 12:15 SCH A215

**Ordered Iodine Adsorption as Fingerprint of (111) Orientation of Pt Thin Films** — ●BJÖRN BRAUNSCHWEIG, ALEXEJ MITIN, and WINFRIED DAUM — Institut für Physik und Physikalische Technologien, TU Clausthal, Leibnizstrasse 4, D-38678 Clausthal-Zellerfeld

Well-ordered Pt films deposited on re-usable substrates find applications such as inexpensive replacements for bulk single crystals or ultrathin transparent electrodes for spectro-electrochemical applications. While morphological properties of such films - roughness, atomic steps and spatial extent of atomically flat terraces - are easily imaged with the STM, atomic resolution of the Pt surface is often not attainable under environmental conditions. We demonstrate that the atomic surface structure of (111)-oriented Pt thin films deposited on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) substrates is clearly revealed after adsorption of ordered iodine adlayers. In comparative STM studies with Pt thin films and with (111)-oriented bulk single crystals we observed the same coexisting ( $4 \times 3\sqrt{3}$ ) and ( $\sqrt{43} \times \sqrt{43}$ ) iodine superstructures which indicates that our Pt films are highly ordered and (111)-oriented.

O 64.6 Fri 12:30 SCH A215

**Monte-Carlo lattice gas simulation of adsorption and desorption at disordered surface alloys** — ●MARKUS MAUKSCH<sup>1</sup>, ANDREAS BERGBREITER<sup>1</sup>, HARRY E. HOSTER<sup>1</sup>, YOSHIHIRO GOHDA<sup>2</sup>, AXEL GROSS<sup>2</sup>, and R. JÜRGEN BEHM<sup>1</sup> — <sup>1</sup>Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm — <sup>2</sup>Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm

The atom distribution in disordered surface alloys like PtRu/Ru(0001) or PdAg/Pd(111) is known from STM imaging with chemical contrast. The interaction of model adsorbates like H<sub>ad</sub> or CO with many of these surfaces were probed by thermal desorption and infrared spectroscopy [1]. Based on experimentally determined atom distributions in the surface alloys, we will model the adsorption properties of selected systems by lattice gas Monte-Carlo simulations including (i) site-specific molecule-substrate, (ii) molecule-molecule interaction energies and (iii) site-specific vibrational entropy [2]. Where available, molecule-substrate interactions are derived from DFT results, in other cases they are fitted to experimental data. The molecule-molecule interactions and site specific entropies are assumed to be close to those for Pt(111) [2] and Ru(0001) [3].

[1] H. Rauscher et al., Surf.Sci. 601 (2007) 4608.

[2] J.-S. McEwen et al., Surf.Sci. 545 (2003) 47.

[3] J.-S. McEwen et al., J.Chem.Phys. 126 (2007) 094701.