

O 46 Adsorption VI

Time: Friday 11:15–13:00

Room: TRE Phys

O 46.1 Fri 11:15 TRE Phys

The Structure of O-p(4x4)/Ag(111): results from surface sensitive x-ray techniques — ●A. STIERLE¹, A. REICHO¹, I. COSTINA¹, S. THIESS², J. ZEGENHAGEN², and H. DOSCH¹ — ¹MPI für Metallforschung, Heisenbergstraße 3, D-70569 Stuttgart — ²ESRF, B.P. 220, F-38043 Grenoble

Silver plays an important role as an oxidation catalyst and therefore many fundamental studies have been devoted to Ag surfaces. One important finding is that after oxidation of Ag(111) at 500 K either at O₂ pressures in the mbar regime, or using NO₂ at lower pressures a p(4x4) superstructure is formed, which was believed to be a prototype for a surface oxide O-Ag-O trilayer. The proposed models for this structure [1] are incompatible with the surface x-ray diffraction data obtained at the MPI-MF beamline at ANKA and the normal incidence x-ray standing wave results from ID32, ESRF. Instead, a model is favoured, that includes Ag adatoms on hcp and fcc sites and oxygen atoms filling the rows in between, which is also supported by recent scanning tunneling microscopy and core level spectroscopy results, combined with density functional theory calculations*.

*M. Schmid, et al., contribution at this conference

[1] A. Michaelides, K. Reuter, and M. Scheffler. *J. Vac. Sci. Technol. A* 23, 1487-1497 (2005).

O 46.2 Fri 11:30 TRE Phys

The p(4x4) structure of Ag(111): A soft O-induced reconstruction — ●MICHAEL SCHMID¹, GEORG KRESSE², JAN KLIKOVITS¹, OR-EST DUBAY², and PETER VARGA¹ — ¹Inst. f. Allgemeine Physik, TU Wien — ²Inst. f. Materialphysik and CMS, Universität Wien

Silver is a well-known catalyst for selective oxidation reactions, e.g., of ethylene (epoxidation). The phase on the (111) surface usually associated with this reaction is a p(4x4) superstructure, which has been studied since 1972 [1] and considered a surface oxide similar to a layer of the Ag₂O bulk structure since 1974. An X-ray diffraction study by A. Stierle et al. [2] has disproved essentially all Ag₂O-based models [3] so far. We have studied the mass transport during reduction of the p(4x4) structure by scanning tunneling microscopy (STM) to determine the number of Ag atoms per cell. Based on this input and the STM images, a structural model very different from Ag₂O emerges. The model is compatible with high-resolution core level spectroscopy data and was confirmed by surface x-ray diffraction [4]. The structure does not have the lowest energy of all possible models in density functional theory (DFT) calculations, a fact attributed an inherent problem of today's DFT calculations. Nevertheless, DFT is valuable for a detailed study of this structure and shows that it is very soft, exhibiting extremely high vibration amplitudes.

[1] G. Rovida et al., *J. Vac. Sci. Technol.* 9, 796 (1972).

[2] A. Stierle et al., contribution at DPG Frühjahrstagung 2004.

[3] A. Michaelides et al., *J. Vac. Sci. Technol. A* 23, 1487 (2005).

[4] A. Stierle et al., contribution at this conference.

O 46.3 Fri 11:45 TRE Phys

H-Induced Symmetry Break of the Hexagonal Surface Reconstruction of Ir(100) — ●D. LERCH¹, A. SCHMIDT¹, A. KLEIN¹, L. HAMMER¹, S. MÜLLER¹, K. HEINZ¹, H.-C. POON², and D. SALDIN² — ¹Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7, D-91058 Erlangen — ²Univ. Wisconsin-Milwaukee

Upon H adsorption the (quasi-)hexagonal 5x1-reconstruction of clean Ir(100) is lifted. Yet, as this process is thermally activated the hexagonally close-packed surface Ir-layer persists as a metastable phase for sample temperatures below 200 K. We have investigated this 5x1-hex-H phase by the combined application of quantitative LEED and DFT. Using LEED spectra as a structural fingerprint we find that hydrogen considerably modifies the complex reconstruction pattern of the surface. Yet, though the clean surface structure could be reliably solved by quantitative LEED, the method fails to produce a satisfactory theory-experiment fit as long as all symmetry elements of the clean surface are enforced. Only by breaking the mirror symmetry of the 5x1 unit cell the reproduction of measured intensity data is possible. DFT calculations corroborate this symmetry break as well as the experimentally estimated H coverage of 0.6 ML. The calculations show that the symmetry break is due to only one of the three hydrogen atoms per unit cell which assumes an asymmetric hollow site near the centre of the troughs of the surface reconstruction. The

resulting 33 (!) geometrical parameters describing the surface and sub-surface Ir structure are in quantitative agreement with those determined by the LEED analysis. The H-induced structure can be interpreted as a precursor phase for the reconstruction lifting transition.

O 46.4 Fri 12:00 TRE Phys

CO adsorption and CO and O coadsorption on Rh(111) — ●ROBERT SCHENNACH¹ and IMRE BAKO² — ¹Institute of Solid State Physics, Graz University of Technology, Graz, Austria — ²Chemical Research Institute of the Hungarian Academy of Sciences, Budapest, Hungary

The adsorption of CO and the coadsorption of CO and O on Rh(111) at 123 K was studied using reflection absorption infra red spectroscopy (RAIRS) and density functional theory (DFT). CO adsorption on Rh(111) proceeds via adsorption at on top sites at low coverages (less than 0,33 monolayer (ML)) and by on top and hollow site occupation at higher coverages (more than 0,33 ML). Evidence from the RAIRS measurements shows that also some bridge sites are occupied from intermediate coverages up to a full monolayer. A new vibration in the on top region around 2085 cm⁻¹ is found in the IR spectra at higher coverages, which has not been detected in high resolution electron energy loss spectroscopy (HREELS) studies. The origin of this new vibrational feature is discussed in detail using the results from DFT calculations. Experiments show that this new vibration vanishes during CO adsorption at elevated temperatures. Coadsorption of oxygen generally leads to a shift to higher wavenumbers of the CO vibrations. This is explained in terms of increased repulsive interactions between the adsorbed species. The adsorption sequence does not influence the vibrational spectra, however, the CO to O ratio and the surface temperature during adsorption show an influence. Thermal desorption from the coadsorbed layers shows some reaction between CO and O to form CO₂.

O 46.5 Fri 12:15 TRE Phys

STRUCTURE AND PROPERTIES OF K-O COADSORBATE PHASES ON RH(110): CHEMICAL PATTERNS AND LOW PRESSURE PATHWAY TO SURFACE OXIDE FORMATION

— ●SEBASTIAN GÜNTHER¹, FRIEDRICH ESCH², GIOVANNI COMELLI², and MAYA KISKINOVA³ — ¹Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstr. 11 E, 81377 München, Germany — ²Laboratorio TASC-INFN, Area Science Park, 34012 Trieste, Italy — ³Sincrotrone Trieste, Area Science Park, 34012 Trieste, Italy

The present study of K-O coadsorbate system on Rh(110) has been inspired by the peculiar chemical wave patterns observed during the H₂ + O₂ reaction on the K-covered Rh(110) surface. Using Low energy electron diffraction (LEED), Scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) we found that coadsorption of O and K at T > 450 K leads to a variety of ordered phases, all of them involving missing-row reconstructions of the substrate. The building blocks of these surface structures were determined. The massive restructuring of the surface at high K coverage is followed by growth of a surface oxide phase, which cannot be formed on a K-free surface under UHV conditions. The surface composition and activity of the coadsorbed phases were characterized by XPS, which revealed that although K adatoms promote the O₂ adsorption and oxidation of the substrate, they act as deactivators for the H₂ + O₂ reaction.

O 46.6 Fri 12:30 TRE Phys

An *ab initio* Study of Topographical Defects on NaCl(100) — ●BO LI, ANGELOS MICHAELIDES, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft Faradayweg 4-6, D-14195 Berlin, Germany

Ab initio calculations based on density-functional theory (DFT) within the plane-wave pseudopotential formalism have been performed for a wide variety of defects on NaCl surfaces. Specifically, Na and Cl vacancies and adatoms as well as neutral and polar steps have been examined.

These DFT calculations have yielded several interesting results, such as the first *ab initio* determinations of the surface energy of NaCl(100) and monatomic step formation energies. In addition, it is found that Cl adatoms exhibit a preference for adsorption on top of Cl substrate sites, rather than above Na substrate sites as might be anticipated. A series of second order Møller-Plesset perturbation theory (MP2) calculations for Cl adatoms on small NaCl clusters show the same binding site preference,

thus lending support to this “non-textbook” result. The explanation for this unusual result is, however, perfectly textbook: a weak covalent bond that forms only when Cl adatoms reside above Cl substrate atoms.

O 46.7 Fri 12:45 TRE Phys

Tensor LEED and PIRS study of the monolayer C_2D_2 adsorbed on KCl(100) — •JOCHEN VOGT and HELMUT WEISS — Chemisches Institut der Universität Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany

Growth and structure of the monolayer C_2D_2 adsorbed on KCl(100) single crystal surfaces were investigated by means of polarization infrared spectroscopy (PIRS) and low-energy electron diffraction (LEED). PIRS spectra in the region of the ν_3 fundamental mode show a sharp singlet absorption near 2396 cm^{-1} at 75 K. The ratio of the integrated intensities in s- and in p-polarization is consistent with a parallel orientation of the molecules with respect to the surface plane. LEED experiments indicate a $(\sqrt{2} \times \sqrt{2})R45^\circ$ lattice with two glide-planes under the same conditions. Integrated intensities of 5 beam orders were recorded as a function of electron energy and analyzed using the tensor LEED approach. Based on a structure model with two molecules in the surface unit cell the I(E) analysis supports an adsorption site 3.15 \AA above the K^+ cations. In the best-fit geometry the molecular axes of the two molecules enclose an angle near 60° . In contrast the appearance of the singlet absorption in the infrared spectra strongly support this angle to be 90° . These deviating results are discussed by taking into account the influence of frustrated rotations of the molecules on the LEED intensities within the model of ‘split positions’ [1].

[1] H. Over, M. Gierer, H. Bludau, G. Ertl, Phys. Rev. B 52, 16812 (1995)