O 62: Metal Substrates: Adsorption of Inorganic Molecules

Time: Thursday 9:30–12:30 Location: MA 042

O 62.1 Thu 9:30 MA 042

Tuning Surface Energy Landscapes in Metallic Quantum Films using Alkali Adsorbates — •Alexander Khajetoorians[1], Shengyong Qin[1], Wenguang Zhu[2], Holger Eisele[1], Zhenyu Zhang[2], and Chih-Kang Shih[1] — [1]Department of Physics, University of Texas at Austin, Austin, Texas, USA — [2]Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

Quantum confinement shows a strong interplay with growth and kinetics in thin metal systems where the Fermi wavelength has a special relationship to the surface normal lattice constant. In the case of Pb/Si(111) systems, this relationship reveals an interesting thickness-dependent bilayer oscillation in the density of states up to a phase. In the limit where surface energy oscillations are strong, this interplay can result in the formation of magic quantum stable islands and film thicknesses. In this paper, we report on a novel effect: tuning of the energy landscape of a flat-top quantum Pb mesa using Cs adsorbates. Using STM/STS, we show that depositing Cs adsorbates on a thin Pb mesa promotes quantum stable Pb nanoislands on preferentially unstable thicknesses. Thickness-dependent nanoisland densities show a strong bilayer oscillation correlating with quantum stability. By modifying the Cs coverage on the mesa surface, we can tune the lateral size distribution of the nanoislands and the overall amplitude of the island density oscillation. Nanoisland formation seems intricately linked to a step decoration of Cs adatoms along the step edge of the nanoisland. The role of surface reactivity on these properties will also be discussed. Support: NSF-IGERT DGE-0549417; NSF-FRG 26-1126-8750

O 62.2 Thu 9:45 MA 042

Quantum size effects on the adsorption of rare gases on Ag monolayer covered noble metal surfaces — •Frank Forster, Andreas Nuber, Hendrik Bentmann, Johannes Ziroff, and Friedrich Reinert — Universtät Würzburg, Experimentelle Physik II, 97074 Würzburg, Germany

In the recent past it has been demonstrated that Shockley states on (111) surfaces of Cu, Ag, and Au are a sensitive probe for interactions between surfaces and adsorbates. Their significant change in binding energy, band mass and spin-orbit coupling allows an access to the comprehension of adsorption mechanisms like physisorption. On the example of Xe monolayers on noble metal surfaces we show vice versa that the Shockley states influence the adsorption dynamics of rare gas atoms. For that purpose we present real-time and high resolution ARPES investigations on Xe adsorption on Cu(111) and Au(111) substrates with Shockley states modified by a pre-adsorption of layer-by-layer grown Ag-films of various thickness. In the case of Xe on Ag/Cu(111) we found that the rare gas prefers the adsorption on the thickest Ag film to the disadvantage of thinner layers or the clean substrate. A similar behaviour could be observed for Ag/Au(111) with the exception of a single Ag layer, which is always unfavoured for Xe coverage. Within a simplified model, the local DOS of the Shockley state at the modified surfaces are compared to the obtained ARPES results.

O 62.3 Thu 10:00 MA 042

Insight into water molecules bonding on 4*d* metal surfaces — •Javier Carrasco[1], Angelos Michaelides[1,2], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — [2]London Centre for Nanotechnology and Department of Chemistry, University College London, London WC1E 6BT, United Kingdom

H_2O-metal interactions are of capital importance to a wide variety of phenomena in materials science, catalysis, corrosion, electrochemistry, etc. Here we address the nature of the bond between water molecules and metal surfaces through a careful systematic study. Specifically, the bonding of isolated H_2O molecules to a series of close-packed transition metal surfaces—Ru(0001), Rh(111), Pd(111) and Ag(111)—has been examined in detail with density functional theory (DFT). Aiming to understand the origin behind energetic and structural trends along the 4*d* series we employ a range of analysis tools, such as decomposition of the density of states, electron density differences, and inspection of individual Kohn-Sham orbitals. The results obtained allow us to rationalize the bonding between water and transition metal surfaces as a balance of covalent and electrostatic interactions. A frontier orbital scheme based on so-called two-center four-electron interactions between molecular orbitals of H_2O— mainly $3a_1$ and $1b_1$—and d band states of the surface proves incisive in understanding these systems.

O 62.4 Thu 10:15 MA 042

Adsorption and thermal decomposition of NO_2 on two stepped platinum surfaces — •Michael Peter Andreas Lorenz[1], Regine Streber[1], Christian Papp[1], Andreas Bayer[1], Reinhard Denecke[2], and Hans-Peter Steinrück[1] — [1]Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen — [2]Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstr. 2, 04103 Leipzig

The adsorption of NO_2 on stepped Pt surfaces, namely Pt(322) and Pt(355), and its behaviour during heating to elevated temperatures was studied by in-situ high resolution XPS using synchrotron radiation at BESSY II. The motivation for our study was to obtain high oxygen precoverages, in order to study CO oxidation on stepped surfaces in this coverage regime. For the flat Pt(111) surface, Dahlberg et al. [1] showed that by dosing NO_2 oxygen coverages can be obtained, which are three times higher than those obtained by conventional exposure to O_2; for the more reactive stepped surfaces one could expect even higher coverages. Our study shows that at low temperatures, up to 250 K, NO_2 molecularly adsorbs on both surfaces as could be observed in the O 1s and N 1s regions. During heating, NO_2 starts to decompose to NO and O above 270 K. Thereby, NO desorbs completely up to 400 K. Significantly higher oxygen coverages than those formed by dissociation of O_2 can only be reached by adsorption of NO_2 at 400 K, resulting in the formation of clean oxygen layers without any nitrogen impurities. Supported by BMBF (05 ES3XBAI5).

[1] D. Dahlgren, J. C. Hemminger, Surf. Sci. 123 (1982) L739

O 62.5 Thu 10:30 MA 042

Kinetic passivation of steps with sulfur and CO/S site exchange processes on stepped Pt surfaces — •Regine Streber[1], Christian Papp[1], Michael Peter Alexander Lorenz[1], Andreas Bayer[1], Reinhard Denecke[2], and Hans-Peter Steinrück[1] — [1]Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen — [2]Willhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstrasse 2, 04103 Leipzig

We studied the influence of sulfur on the adsorption and thermal evolution of CO on the stepped Pt(355) and Pt(322) surfaces by in-situ XPS. At low temperatures, we observe a passivation of the step sites for both surfaces, along with a decrease of the total CO coverage. Upon heating the CO covered surfaces a repopulation of the step sites with CO occurs at 185 K for Pt(355) and 240 K for Pt(322). For Pt(355), finally the same step coverage as for the clean surface is obtained, whereas for Pt(322) only half the value of the clean surface is found. This behavior is attributed to the S induced formation of double steps on Pt(322), which are stable in the investigated temperature range. From the lifting of the step passivation by sulfur upon heating for both surfaces we conclude that, under the experimental conditions applied, an occupation of steps sites by CO is energetically favored over occupation with S, with the CO-S site exchange process being kinetically hindered at low temperatures. The differences found for the two different step orientations are attributed to differences in the electronic structure and local adsorption sites. Supported by BMBF (05 ES3XBA/5).

O 62.6 Thu 10:45 MA 042

Adsorption of CO on Ni decorated Rh(553) — Priyanka Singnurkar, Hans Peter Koch, and •Robert Schennach — Instiute of Solid State Physics, Graz University of Technology, Austria

Carbon monoxide is a widely used probe molecule in surface science. In addition, it is an important reactant and intermediate in several catalytic reactions (e.g. oxidation of carbon monoxide to carbon dioxide in automotive catalysts), making the adsorption and reaction of carbon monoxide a thoroughly investigated system on many different metal surfaces. In the work presented here, the adsorption and desorption of carbon monoxide on Ni decorated steps on Rh(553) has been studied using reflection absorption infra red spectroscopy (RAIRS) and thermal desorption spectrometry (TDS). Previous scanning tunneling microscopy (STM) experiments have shown, that the Rh(553) surface has rather stable mono atomic steps. The steps are (111) oriented and the (111) terraces are 4 atomic rows wide, as can be predicted from the crystal structure. The steps of the Rh(553) surface can be decorated by evaporating about 0.2 mono layer Ni under ultra high vacuum conditions and at a substrate temperature of 150°C, leading to one to two atoms wide Ni wires running along the steps of the Rh(553) substrate, according to STM data. No carbon monoxide dissociation is found when the steps are decorated with Ni. TDS results and RAIRS results on the Ni decorated surface are discussed with respect to the results obtained with the clean Rh(553) surface.

O 62.7 Thu 11:00 MA 042

Towards a full undertanding of the "CO Adsorption"puzzle: advanced many-body electronic structure calculations of CO-adsorbed Cu custers — •Xinguo Ren[1], Patrick Rinke[2], and Matthias Scheffler[1,2] — [1]Fritz-Haber-Institut der MPG, 14195 Berlin, Germany — [2]Materials Reserach Lab, University of California at Santa Babara, CA 93106

Density functional theory, within its present-day local/semi-local approximations (LDA/GGA), has known difficulties for describing certain surface chemical processes. For instance, for a CO molecule adsorbed at the Cu(111) surface, both LDA and GGA predict the wrong adsorption site, favoring the threefold-coordinated hollow site rather than the onefold-coordinated top one [1]. The energetic order of these two adsorption sites can be correctly reversed by applying a "local XC correction"scheme [2], in which an exchange-correlation (XC) energy correction can be obtained by using an improved XC treatment for relatively small clusters. However, such single-point total energy calculations do not reveal the underlying mechanism behind the improved description. To shed new light on the "CO adsorption puzzle"we have performed quasiparticle energy calculations for CO adsorbed on selected Cu clusters in second-order Møller-Plesset perturbation theory and the *GW* approach. The resultant energy spectra are analyzed in terms of charge transfer and energy level shifts with respect to LDA/GGA. [1] Feibelman *et al.*, J. Phys. Chem **105**, 4018 (2001). [2] Q.-M. Hu, K. Reuter, and M. Scheffler, Phys. Rev. Lett **98**, 176103 (2007); **99**, 169903(E) (2007).

O 62.8 Thu 11:15 MA 042

New adsorption states of carbon monoxide on Cu(110) — •Erkan Demirci and Adolf Winkler — Graz University of Technology, Institute of Solid State Physics, Graz, Austria

The adsorption of carbon monoxide on a Cu(110) surface has been investigated by Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS) and low energy electron diffraction (LEED). The carbon monoxide desorption spectra as known from literature exhibit only a peak at 210K (α state) when adsorption takes place at T = 100 K -150 K, correlated with a (2x1) superstructure [1,2]. When CO is adsorbed at 180 K and using high enough exposure the TDS clearly shows additional peaks at 245 K, 290 K and 355 K (β_1, β_2, β_3 states). The population of these peaks is adsorption temperature dependent. The peak maxima of β_1 and β_2 shift to higher temperature with increasing coverage, in contrast to the α and β_3 peaks, which show coverage independent peak maxima. LEED shows a (1x2) superstructure when CO is adsorbed at 300 K. From these results we conclude that a missing row reconstruction is induced by CO, which leads to the new adsorption states. Additional quantitative TDS and angle resolved TDS measurements were performed to support this idea. *Financial support by the Austrian Science fund (FWF), Proj. No. P 20026 is gladly acknowledged.*

[1] C. Harendt, J. Goschnick and W. Hirschwald, Surf. Sci. 152/153 (1985) 453

[2] K. Horn, M. Hussain and J. Pritchard, Surf. Sci. 63 (1977) 244

O 62.9 Thu 11:30 MA 042

Monte-Carlo lattice gas simulation of the thermal desorption behavior of CO from Pt_xAu_{1-x}/Pt(111) surface alloys — •Harry E. Hoster[1], Yoshihiro Gohda[2], Andreas Bergbreiter[1], Menhild Eyrich[1], Joachim Bansmann[1], Axel Gross[2], and R. Jürgen Behm[1] — [1]Institute of Surface Chemistry and Catalysis, Ulm University, 89069 Ulm, Germany — [2]Institute of Theoretical Chemistry, Ulm University, 89069 Ulm, Germany

The thermal desorption behavior of CO adsorbed on Pt_xAu_{1-x}/Pt(111) surface alloys was studied by Monte Carlo simulations in a lattice gas approximation [1,2], comparing different Pt:Au ratios and initial CO_{ad} coverages. Based on thermal desorption data and DFT calculations, the CO molecules preferentially occupy Pt on-top sites of Pt_xAu_{1-x}/Pt(111) surface alloys, and the adsorption energies are approximately constant for different numbers of neighboring Au atoms (ligands). Au sites are not occupied at room temperature. The atomic distribution in the surface layer used in the simulations was derived from STM data with chemical contrast, and the adsorption energies stem from DFT calculations. At higher CO_{ad}-coverages, the CO-CO repulsions are considered via a pair interaction parameter determined by fitting to the experimental data. The accuracy of the lattice gas approach for inhomogeneous surfaces is discussed by comparing with the experimental thermal desorption data.

[1] J.L.Sales, G.Zgrablich, V.P.Zhdanov, Surf.Sci 209(1989)208

[2] V.P.Zhdanov, J.L.Sales, R.O.Unac, Surf.Sci.Lett.381(1997)L599

O 62.10 Thu 11:45 MA 042

CO adsorption on bimetallic Au_xPt_{1-x} surface alloys studied by TPD and IRAS — •Menhild Eyrich, Heinrich Hartmann, Thomas Diemant, Andreas Bergbreiter, Harry Hoster, Joachim Bansmann, and Rolf Juergen Behm — Institute of Surface Chemisty and Catalysis, Ulm University, D-89069 Ulm, Germany

The interaction of CO with bimetallic Au_xPt_{1-x} surface alloys supported on Pt(111) is investigated by temperature programmed desorption and infrared reflection absorption spectroscopy to study the influence of the Au content on the chemical properties of the surface alloys. The surface composition and the distribution of surface atoms were determined by scanning tunnelling microscopy, showing a tendency for the segregation of both metals on the surface. Due to the preference for the formation of homo-atomic domains, the adsorption of CO on the Pt part of the surface alloys is only weakly affected up to very high Au concentrations and very similar to the pristine Pt(111). This behaviour is manifested in an almost constant initial CO desorption energy and the successive occupation of on-top and bridged adsorption sites with increasing CO coverage. Since the adsorption of CO is not possible on the Au part of the surface alloys under the conditions of this study, a decrease of the CO saturation coverage and of the initial sticking coefficient are observed with increasing Au content.

O 62.11 Thu 12:00 MA 042

CO adsorption on Ag/Pd(111) surface alloy — •Yunsheng Ma, Joachim Bansmann, and Rolf Jürgen Behm — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

The growth of Ag on Pd(111), Ag/Pd surface alloy formation and the chemical properties of these surfaces using CO probe molecules were studied by X-ray Photoemission Spectroscopy (XPS), CO Temperature Programmed Desorption (TPD) and High Resolution Electron Energy Loss Spectroscopy (HREELS). At room temperature, thermal evaporation of Ag leads to a layer-by-layer growth mode on Pd(111) [1]. Annealing the Ag film induces a down-shift of the binding energy of the Ag 3d peak by 0.6 eV, indicating surface alloy formation. CO desorption peaks in the temperature range between 350 K and 500 K are observed upon varying the Ag/Pd ratio of the surface alloy. The different CO TPD peaks obtained on Ag/Pd surface alloys can be attributed to CO desorption from different Pd/Ag or Pd ensemble. The results are discussed in comparison with previous experimental and theoretical results on Au/Pd(111) [2].

[1] B. Eisenhut, J. Stober, G. Rangelov, Th. Fauster, Phys. Rev. B 47 (1993) 12980

[2] M. Ruff, N. Tahehiro, P. Liu, J.K. Norskov, R.J. Behm, Chem. Phys. Chem. 8 (2207) 2068

O 62.12 Thu 12:15 MA 042

Interaction of CO and H_2 with Zn/ZnO modified Pd(111) surfaces — •Markus Kratzer[1], Anton Tamtögl[1], Jörg Killmann[1], Robert Schennach[1], Adolf Winkler[1], Gunter Weirum[1], and Svetlozar Surnev[2] — [1]Institute of Solid State Physics, Graz University of Technology — [2]Department of Physics, Karl-Franzens University Graz

Due to its increased use in methanol reforming the Zn/Pd and ZnO/Pd system came to the fore of surface science. Especially, the interaction with CO and hydrogen with these surfaces is of specific importance. In this work the adsorption/desorption kinetics of CO and H_2 on Zn and ZnO thin film covered Pd(111) was studied using TPD, LEED, AES and STM. TPD, LEED and AES results show that the ZnO modified palladium surfaces undergo a change in the surface configuration during CO and H_2 desorption due to reduction of the ZnO layer. In case of CO-TPD temperatures up to 650 K are required, which additionally lead to the formation of a ZnPd alloy. In the literature one can find UPS measurements as well as DFT based calculations that point out that ZnPd alloys should have similar electronic properties as the Cu(111) surface [1]. Indeed, CO desorption on Zn covered Pd(111) shows a similar low temperature desorption peak at 220 K as measured on Cu-surfaces [2].

This work was supported by the Austrian Science Fund: Project Nr. P20016 and P19198.

[1] A. Bayer et.al. Surface Science, 600 (2006) 78

[2] S. Vollmer et.al. Catalysis Letters 77 (2001) 97