



## Chemical properties of structurally well-defined PdRu/Ru(0001) surface alloys – Interaction with CO

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### ABSTRACT

The chemical properties of structurally well-defined PdRu/Ru(0001) monolayer surface alloys [H. Hartmann, T. Diemant, A. Bergbeiter, J. Bansmann, H.E. Hoster, R.J. Behm, *Surf. Sci.* in press, doi:10.1016/j.susc.2008.10.055.] and a Pd monolayer on Ru(0001) were studied by temperature programmed desorption and infrared reflection absorption spectroscopy using CO as probe molecule. IR experiments on the PdRu/Ru(0001) surface alloys demonstrate that CO adsorption on Ru sites resembles that on pure Ru(0001) (on-top adsorption), while adsorption on the Pd sites occurs on both multifold coordinated and on-top sites, similar to CO on Pd(111). A significant destabilization of CO adsorption on Pd sites for both, surface alloys and the Pd monolayer film, compared to pure Pd(111) surfaces is attributed to a combination of geometric strain and vertical electronic ligand effects; an additional variation in the CO adsorption bond strength in the surface alloys is attributed to changes in the neighboring surface atom shell (lateral ligand effects). The chemical modifications introduced by PdRu surface alloy formation are compared with findings for deuterium adsorption on the same surface alloys; effects of the two-dimensional (2D) distribution of surface atoms are illustrated by comparison with CO adsorption on PtRu/Ru(0001) surface alloys, where in contrast to the pronounced 2D phase segregation in PdRu/Ru(0001) the surface atoms are essentially randomly distributed.

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### 1. Introduction

The systematic modification of the physical and chemical properties of metals upon alloy formation is of considerable interest both from a fundamental point of view as well as for various applications. One of the earliest and still dominant applications is the use of bimetallic catalysts in heterogeneous catalysis, whose catalytic performance was found to be distinctly different from that of the individual components and often superior to that of monometallic supported catalysts [1–3]. The modified chemical and catalytic properties were explained by various structural and electronic effects such as electronic ligand effects, geometric ensemble effects and, more recently, electronic strain effects [4–6]. A more detailed introduction to these effects is given in a preceding paper [7]. Main problem in the unambiguous experimental identification and quantification of the different effects for supported bimetallic catalysts is the lack of structural information, in particular the missing knowledge of the exact concentration and even more of the two-dimensional (2D) distribution of the respective atomic species in the surface of the bimetallic nanopar-

ticles. A basic understanding of the effects modifying the chemical/catalytic properties of bimetallic nanoparticle surfaces can be obtained, however, from model studies on bimetallic planar surfaces of massive solids with well-defined surface structure. Recently, we performed a number of studies on the chemical and electrochemical properties of PdAu/Au(111) [8], PdAu/Pd(111) [9], PdCu/Ru(0001) [10–12] and PtRu/Ru(0001) [13–19] monolayer surface alloys, where the surface composition and the 2D distribution of surface atoms was quantitatively determined by atomic resolution scanning tunneling microscopy (STM). In combination with theoretical studies (density functional theory (DFT) calculations) [9,20–27], these studies allowed to clearly identify and distinguish between geometric ensemble effects, electronic ligand effects, and electronic strain effects, and even quantify the order of magnitude of the different contributions.

In the present paper, we report results of a similar type study on the correlation between surface structure and chemical properties on structurally well-defined PdRu/Ru(0001) monolayer surface alloys. Here, we focus on the interaction of CO with these surfaces, which was studied by temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS). This publication follows a preceding paper where we prepared a series of monolayer surface alloys with varying Pd content and character-

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ized the atom distribution by STM and the deuterium adsorption behavior by TPD [7]. This system turned out to be particularly interesting, since despite the rather similar chemical properties of the platinum group metals Pt and Pd the distribution of surface atoms is distinctly different for PtRu/Ru(0001) and PdRu/Ru(0001) monolayer surface alloys. While for PtRu/Ru(0001) the surface atoms are essentially randomly distributed [18], PdRu/Ru(0001) surface alloys tend to phase segregation and formation of 2D domains [7]. CO and deuterium adsorption complement each other in so far as CO is largely adsorbed in on-top sites, and hence is expected to be more sensitive to ligand effects, while deuterium, which is adsorbed in threefold hollow sites, is more sensitive to the elemental composition of the adsorption ensemble, i.e., to ensemble effects.

Previous studies of bimetallic PdRu surfaces were carried out on Ru(0001) substrates covered by Pd overlayers. Based on TPD, Auger electron spectroscopy (AES), and low energy electron diffraction (LEED) experiments, Park concluded that the growth of the first few monolayers proceeds via a layer-by-layer growth process with the first layer being pseudomorphic with respect to the Ru(0001) surface [28]. Furthermore, the  $\text{CO}_{\text{ad}}$  saturation coverage for adsorption at room temperature was found to be significantly reduced compared to adsorption on the unmodified substrate. Campbell et al. came to similar results, and concluded that the change in adsorption properties of a Pd monolayer on Ru(0001) compared to pure Pd(111) is caused by transfer of electron density from Pd to Ru, leading to a greater fraction of empty states in the valence band of the Pd layer [29].

DFT calculations of CO adsorption on Ru(0001), Pd(111), and a Pd monolayer on Ru(0001) ( $\text{Pd}_{\text{ML}}/\text{Ru}(0001)$ ) yielded identical CO adsorption geometries on Pd(111) and  $\text{Pd}_{\text{ML}}/\text{Ru}(0001)$  [24]. The adsorption energy, however, is significantly lower on the Pd monolayer compared to Pd(111), which was attributed to a shift of the d-band center to lower energies. This conclusion is corroborated by DFT calculations on the interaction between a Pd monolayer and the Ru(0001) substrate, which indicate a depopulation of the d-states of Pd atoms and a charge transfer to the substrate [30,31].

After a brief description of the experimental procedures and set-up, we will first report results of CO TPD measurements on PdRu/Ru(0001) surface alloys of different composition, complemented by similar measurements on bare Ru(0001) and on  $\text{Pd}_{\text{ML}}/\text{Ru}(0001)$ . In Section 3.2, we present results of IRAS measurements, performed after increasing adsorption of CO at 100 K. In the last section (discussion), we compare the present results with those obtained for deuterium adsorption on similar surfaces [7] and with those of previous studies on deuterium and CO adsorption on PtRu/Ru(0001) [13–19], and PdCu/Ru(0001) [10] surface alloys, and finally summarize the complementary results of these studies on the correlation between structural, electronic and chemical properties.

## 2. Experimental

The experimental set-up and the procedures for sample cleaning/sample preparation were described in a preceding paper [7]. PdRu surface alloys were prepared by evaporation of sub-monolayer amounts of Pd from an electron beam evaporator (Omicron, EFM 3) at a substrate temperature of 300 K and subsequent flash annealing of the sample to 1150 K for 10 s. The Pd monolayer film was prepared by annealing to 800 K for 30 s after evaporating a corresponding Pd amount. The Pd surface concentration was determined by calibrated X-ray photoelectron spectroscopy (XPS) measurements, using the intensity ratio of the 3d-states of Pd and Ru. The Pd amount in the alloy surface is linearly related to the ratio of the two peaks. The calibration was done using the Pd/Ru ratio of a

closed Pd monolayer (ML) on Ru(0001) as upper reference point [28].

Gas exposures were performed by backfilling of the chamber via a glass tube (inner diameter 8 mm), whose open end was positioned about 30 mm in front of the sample. Therefore, the actual CO pressure at the sample position was about five times higher than that measured at the ion gauge. This factor was determined using the well-known adsorption kinetics on Ru as a reference [32]. All pressure and exposure values in the paper were corrected for this effect. TPD spectra were recorded with a heating rate of  $5 \text{ K s}^{-1}$  using a quadrupole mass spectrometer (Pfeiffer Vacuum, QMS 200), after adsorbing CO at a sample temperature of 100 K. To reduce undesired contributions to the signal (from the sample holder, etc.), the QMS was shielded by a cap with an aperture of 4 mm. The distance between cap and sample could be adjusted reproducibly via an electrical contact [33]. For the XPS measurements, we used non-monochromatic Al  $K_{\alpha}$  radiation and a hemispherical sector analyzer (CLAM 2, VG Scientific) operated in the fixed transmission mode at pass energy of 20 eV. The IRAS measurements were carried out with a Bruker Tensor 27 spectrometer at incidence and detection angles of  $7^{\circ}$  with respect to the surface plane, the resolution was set to  $4 \text{ cm}^{-1}$ . Two-thousand scans (14 min) were collected for an IR spectrum. Reference spectra of CO-free surfaces were recorded at temperatures sufficient to remove all CO from the surface.

## 3. Results

### 3.1. Interaction of CO with PdRu/Ru(0001) surface alloys – TPD results

For comparison, we start with CO TPD spectra of the unmodified Ru(0001) surface, which are displayed in Fig. 1a. For small CO exposures, only a single peak ( $\alpha_1$  peak) at 487 K is observed. With increasing coverage it shifts to lower temperatures and is centered at 460 K for 0.33 ML CO. At CO coverages above 0.33 ML, a second peak develops with the maximum at 402 K ( $\alpha_2$  peak). The spectra are identical to those reported previously [13,16,34,35]. The  $\alpha_1$  state is associated with the formation of a  $(\sqrt{3} \times \sqrt{3})\text{-R}30^{\circ}$  structure, with CO molecules linearly adsorbed in an on-top configuration on Ru atoms, while the  $\alpha_2$  peak is formed at higher coverage [35]. Using the value for the preexponential factor for desorption of  $10^{16} \text{ s}^{-1}$ , which was reported previously by Pfnür et al. [34,35] for small  $\text{CO}_{\text{ad}}$  coverages on Ru(0001), a Redhead analysis yields an activation energy for desorption of  $155 \text{ kJ mol}^{-1}$  for the  $\alpha_1$  peak.

Sets of desorption spectra from PdRu/Ru(0001) surface alloys with varying Pd concentrations and from a closed Pd monolayer on the Ru(0001) substrate ( $\text{Pd}_{\text{ML}}/\text{Ru}(0001)$ ) are collected in Fig. 1b–h. The respective CO TPD spectra at saturation coverage are additionally compiled in Fig. 2 to illustrate the changes of the CO adsorption behavior more clearly. The TPD sets of PdRu/Ru(0001) surface alloys with Pd contents below 64% (Fig. 1b–f) show for small CO exposures a single desorption peak  $\beta_1$ , which shifts from 491 K at 9% Pd to 459 K at 64% Pd. Since its position is almost identical to that of the  $\alpha_1$  peak on Ru(0001), it is assigned to desorption from Ru sites of the surface alloy. For CO saturation, the desorption maximum of the  $\beta_1$  peak shifts only little with increasing Pd content to low temperatures, from 460 K at 9% Pd to 454 K at 64% Pd (Fig. 2). At the same time, also the trailing edge of this peak shifts to lower temperatures with increasing Pd content, and this shift is more pronounced than that of the peak maximum. As one would expect from the diminishing Ru fraction in the topmost layer, the  $\beta_1$  peak decreases in intensity with increasing Pd concentration, and is finally (for a surface alloy with 87% Pd) only visible as a small high temperature shoulder to the desorption states related to Pd. In the TPD spectra of surface alloys

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