



Formation, stability and CO adsorption properties of PdAg/Pd(1 1 1) surface alloys

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ABSTRACT

The formation, stability and CO adsorption properties of PdAg/Pd(1 1 1) surface alloys were investigated by X-ray photoelectron spectroscopy (XPS) and by adsorption of CO probe molecules, which was characterized by temperature-programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS). The PdAg/Pd(1 1 1) surface alloys were prepared by annealing (partly) Ag film covered Pd(1 1 1) surfaces, where the Ag films were deposited at room temperature. Surface alloy formation leads to a modification of the electronic properties, evidenced by core-level shifts (CLSs) of both the Pd(3d) and Ag(3d) signal, with the extent of the CLSs depending on both initial Ag coverage and annealing temperature. The role of Ag pre-coverage and annealing temperature on surface alloy formation is elucidated. For a monolayer Ag covered Pd(1 1 1) surface, surface alloy formation starts at ~450 K, and the resulting surface alloy is stable upon annealing at temperatures between 600 and 800 K. CO TPD and HREELS measurements demonstrate that at 120 K CO is exclusively adsorbed on Pd surface atoms/Pd sites of the bimetallic surfaces, and that the CO adsorption behavior is dominated by geometric ensemble effects, with adsorption on threefold hollow Pd₃ sites being more stable than on Pd₂ bridge sites and finally Pd₁ a-top sites.

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1. Introduction

In the past decades, bimetallic surfaces have attracted considerable attention since they often exhibit distinctly different chemical and physical properties compared to those of the respective pure components. Single-crystalline bimetallic bulk alloy surfaces and/or surface alloys can be used as model systems for a detailed understanding of the surface properties of these bimetallic systems [1–3]. In the present contribution, we report first results of an ongoing study on the correlation between surface structure and adsorption properties/reactivity of bimetallic PdAg surfaces. Scanning tunneling microscopy (STM) measurements on the distribution of the Pd and Ag atoms in the surface layer after different treatments are currently underway and will be published later [4]. This is part of a comprehensive study on the chemical properties of structurally well-defined bimetallic surfaces, in particular surface alloys, in our laboratory, which aims at elucidating the structure–reactivity correlation on the respective surfaces on a quantitative scale [5–9]. PdAg alloys have been used as hydrogen separator and catalytic membrane reactor, due to their superior hydrogen permeability and stability [10], and also as selective hydrogenation catalysts owing to their enhanced selectivity and stability [11–13].

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PdAg surface alloys can be prepared by deposition of Ag on Pd(1 1 1) and subsequent controlled annealing. Ag growth on Pd(1 1 1), surface segregation of Ag in PdAg alloys and the electronic structure of PdAg alloys have been studied both experimentally and theoretically [14–32]. Ag growth on Pd(1 1 1), by physical deposition of Ag at room temperature, was reported to proceed via layer-by-layer growth and without any interdiffusion [19–21,33]. Annealing the Ag covered Pd(1 1 1) surfaces at above 500 K results in a narrowing of the Pd(4d) band due to Ag–Pd interdiffusion and surface alloy formation, i.e., intermixing of Ag and Pd only in the topmost layer(s) [20,22,30]. Ag and Pd, which are both 4d transition metals with fcc structure, are completely miscible. Segregation studies on bulk PdAg alloys revealed a significant Ag enrichment on the surface [29,31], reflecting the significantly lower surface energy of Ag compared to Pd (1.3 J m⁻² vs. 2.0 J m⁻²) [34]. Both experimental and theoretical data showed a negative shift of the Ag(3d_{5/2}) peaks in PdAg alloys compared to the pure components. In contrast, differing results were reported for the binding energy (BE) shift of the Pd(3d_{5/2}) peaks [15,28,30,32,35,36]. Steiner et al. reported an almost linear decrease of the Ag(3d_{5/2}) BE by ~0.95 eV with increasing Pd concentration in PdAg alloys, while the Pd(3d_{5/2}) BE showed a positive and non-linear shift by ~0.5 eV compared to pure Pd [32]. On the other hand, Pervan et al. measured negative BE shifts for both the Ag(3d) and Pd(3d) signals upon PdAg/Pd(1 1 0) surface alloy formation [30], which is consistent with the results on PdAg bulk alloys reported by Slusser and Winograd who observed lower BEs for the Pd(3d) and Ag(3d)

peaks than in the respective pure components [36]. Based on STM and TPD measurements, it was determined that for a $\text{Ag}_{33}\text{Pd}_{67}(111)$ bulk alloy the Pd surface concentration is only $\sim 5\%$ after equilibration at 820 K and that, because of the very low concentration of larger Pd ensembles on these surfaces, CO desorption mostly arises from isolated Pd atoms [37,38]. In an earlier study, Soma-Noto et al. investigated CO adsorption on supported PdAg/SiO₂ catalysts as model system for ensemble effects in bimetallic systems [39]. While the IR band frequencies of linear and bridge-bonded CO_{ad} molecules remained, independent of the Ag content, almost constant for Pd/SiO₂ and PdAg/SiO₂ catalysts, the relative intensity of linear to bridge-bonded CO_{ad} increased with increasing Ag concentration [39]. Recently, Khan et al. studied CO adsorption on PdAg nanoparticles of different bulk composition supported on an Al₂O₃ film by STM, TPD, XPS and IR spectroscopy [40]. They could demonstrate that the addition of Ag to the Pd particles first suppresses CO adsorption on threefold hollow sites of the Pd surface and that a-top CO adsorption on isolated Pd surface atoms becomes dominant with increasing Ag coverage.

PdAg surface alloys with a well-defined composition of the underlying substrate, where the interpretation of the chemical surface properties is much simpler than for bulk alloys with unknown neighborhoods of the respective surface atoms in the subsurface layer(s), have not found much interest so far. Most studies available on PdAg surface alloys focused on their electronic structure and the surface segregation behavior [16,27,30,41]. Data on the chemical properties and on the structure–reactivity correlation of these surfaces are completely missing.

In the present paper, we report on the formation, stability and CO adsorption properties of PdAg/Pd(111) surface alloys, which were prepared by Ag deposition on Pd(111) at room temperature and subsequent annealing at higher temperatures. After a brief description of the experimental facilities and procedures (Section 2), we will first discuss briefly XPS and CO TPD results on the room temperature growth of Ag films on the Pd(111) substrate (Section 3.1). In the next section, XPS data on the formation of PdAg/Pd(111) surface alloys upon annealing are presented (Section 3.2). Third, using CO as probe molecule, the Pd surface concentration and the adsorption strength of different Pd ensembles were investigated after different annealing steps by TPD and HREELS (Section 3.3). The data are discussed in comparison with previous results on PdAu surface alloys [6,42–48].

2. Experimental

The experiments were carried out in an ultrahigh vacuum (UHV) system consisting of two connected chambers [42]. One chamber is equipped with facilities for XPS, low energy electron diffraction (LEED) and TPD measurements with a base pressure of 2×10^{-10} mbar. The second chamber contains a HREELS spectrometer (Delta 0.5 spectrometer, VSI), its base pressure is about 1×10^{-10} mbar. The (111) oriented Pd single crystal has a hat shape, with a smaller diameter (5 mm) in the upper part. It is mounted at the end of a long-travel manipulator (Omniac, VG Scientific) which allows facile transport of the sample between both chambers, and can be cooled down to 90 K by liquid N₂ or heated up to 1200 K by electron bombardment. The sample temperature was monitored by a K-type thermocouple spot-welded to the crystal edge. The surface was cleaned by cycles of Ar⁺ sputtering (1 kV, room temperature), oxygen treatment ($p_{\text{O}_2} = 5 \times 10^{-8}$ mbar, 900 K), and annealing to 1100 K. Surface order and cleanliness were checked by XPS and LEED. The clean surfaces were characterized by a sharp (1 × 1) LEED pattern and the absence of any features other than Pd related signals in the XP spectra. STM measurements on similarly prepared surfaces showed atomically smooth terraces

(terrace width between 50 and 100 nm) separated by monoatomic steps [4].

Ag was evaporated at room temperature from a resistively heated Knudsen cell (WA Technology), the deposition rate was 0.1–0.15 monolayers (ML) min⁻¹. During Ag deposition, the background pressure remained in the 10⁻¹⁰ mbar range. XP spectra (using Al K_α radiation for excitation) were recorded with a hemispherical analyzer (CLAM2, VG Scientific) at a pass energy of 25 eV. All binding energies (BEs) were calibrated with respect to the Pd(3d_{5/2}) BE of the clean surface of 334.9 eV [49]. For TPD measurements, CO adsorption started at ~ 120 K during cool down of the sample, the heating rate was 4 K s⁻¹. Desorption signals were monitored by a differentially pumped quadrupole mass spectrometer (QMS) (Balzers QMA 125), which is shielded against background desorption by a closed cover with an aperture of 2 mm in diameter pointing towards the sample. The HREELS measurements were performed using a primary energy of 4 eV. The spectra were collected in a specular reflection geometry, with an angle of about 60° between analyzer and surface normal; the typical resolution of the elastic peak (full width at half-maximum, FWHM) was about 5–7 meV.

3. Results and discussion

3.1. Growth of Ag on Pd(111)

To calibrate the Ag coverage, we first monitored the growth of Ag on Pd(111) at room temperature by XPS. The XPS intensities of the Ag(3d) and Pd(3d) peaks are shown in Fig. 1 as a function of Ag deposition time. These intensities were determined from the respective peak areas after a Shirley background subtraction [50]. The Ag(3d) signal intensity initially increased linearly with Ag deposition time. Breaks in the approximately linear increase were observed at deposition times of about 7 (±1) min and 15 (±1) min, corresponding to completion of the first and second monolayer, respectively. This behavior is characteristic for an initial layer-by-layer growth and agrees well with results of previous investigations on the growth of Ag on Pd(111) at room temperature [19–21,33]. Based on photoelectron forward scattering and LEED measurements, Eisenhut et al. concluded that the first Ag layer is pseudomorphic with respect to the Pd(111) surface, while the bilayer film adopts a lattice constant close to that of bulk Ag. They suggested that the lattice mismatch between Ag and Pd is accommodated by a stacking fault between the first and the second

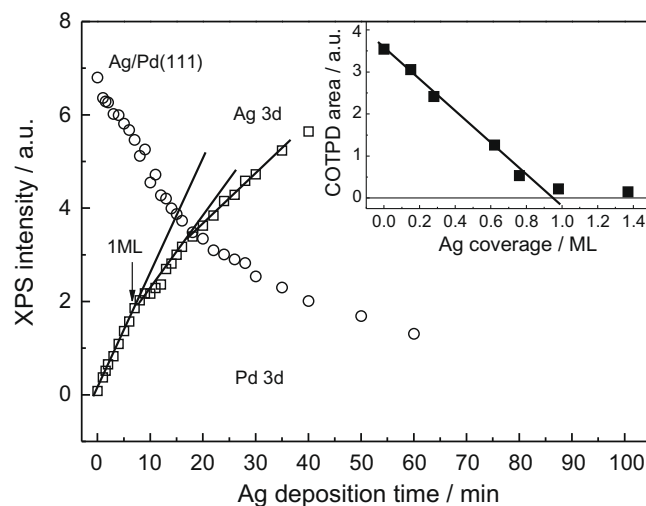


Fig. 1. XPS intensities of the Ag(3d) and Pd(3d) peaks as a function of Ag deposition time on Pd(111) at room temperature. The inset shows the CO TPD peak area vs. the Ag coverage.

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