Role of Pd–Al bimetallic interaction in CO adsorption and catalytic properties of bulk PdAl alloy: XPS, ISS, TDS, and SIMS study

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Abstract

CO adsorption on the bulk PdAl bimetallic systems has been studied using XPS, ISS, TDS, and SIMS under UHV conditions.

Pd exhibits strong interaction with Al atoms resulting in the formation of noble metal-like electronic structure of PdAl alloy. The shifts of both Pd core levels and of Pd valence d-band centroid towards higher binding energies compared to bulk Pd were observed. The surface structure of the alloy changes with temperature (Al surface segregation), ion bombardment (preferential Al sputtering), and is also strongly affected by the presence of ambient CO. The Pd–Al bond is weakened upon the interaction with CO, which tends to dissociate on the surface even at room temperature, with carbon fraction bonding to Pd atoms and oxygen to Al.

The TDS of CO spectra consisted of one to three desorption peaks, all lying lower than those from Pd foil, indicating a distinct weakening of the Pd–CO chemisorption bond. Moreover, the partial CO dissociation on PdAl was indicated both as adsorption capacity decay and CO₂ and H₂O production.

Keywords: Ion scattering spectroscopy; X-ray photoelectron spectroscopy; Secondary ion mass spectroscopy; Thermal desorption spectroscopy; Carbon monoxide; Alloys; Aluminum; Palladium

1. Introduction

During the last years much effort has been devoted to the study of the electronic structure of transition metals and their alloys, especially in connection with the modification of chemical bonding due to the presence of different atomic species. It has been shown that the structure of deposited thin layers differs considerably from the bulk overlayer material due to the interaction with the substrate [1–3]. Likewise, the gas interaction with transition metal alloys shows a strong dependence on surface composition when compared to the pure component [4,5]. Bimetallic Pd–Al systems pertain to the above-mentioned group.

Results for Pd–Al systems [2,3] showed Pd (3d) core levels and Pd (4d) valence bands (VBs) at higher binding energies (BE) than those corresponding to bulk Pd. The shift of the Pd core levels
and of the VB centroid to higher BE and their narrowing with increasing Al content, due to the formation of bimetallic bond, were also observed in [6–8].

Carbon monoxide interaction with single- and polycrystalline Pd has already been studied in detail [9–18]. On pure Pd surfaces CO adsorbs molecularly at room temperature (RT) with desorption occurring around 480 K. It is generally accepted that the CO molecule is chemisorbed through the carbon atom with the molecular axis perpendicular to the surface plane [11]. Another binding state around 385 K on polycrystalline Pd at higher CO exposures was assigned to bridge (two-fold) bonded CO [13]. In general, CO adsorption on Pd is strongly dependent on surface plane orientation [9,14], sample preparation conditions [15,16], and adsorption temperature [17].

Much less work has been performed on the interaction of gases with simple (s,p-) metals. Paul and Hoffmann [19] have shown that CO chemisorption on clean Al(110) was characterised by desorption at 125 K, and no TDS peak was observed above RT. Studies of CO interaction with Al substrates [20,21] reported CO dissociation at RT accompanied by a progressive incorporation of oxygen and carbon with aluminum oxide and carbide formation. The kinetics of the formation was strongly influenced by the initial state of the Al(1 0 0) surface, when CO was reduced to carbon atom by the surface reactions 2 CO $\rightarrow$ CO$_2$ + C, CO + H$_2$ $\rightarrow$ H$_2$O + C. The remaining carbon poisoned the reaction sites, resulting in the reduction of CO chemisorption probability during the next stage [22].

Even though the electronic structure of Pd–Al bimetallic systems was investigated [2,3,6–8], the CO adsorption properties of such systems remained unexplored. The aim of this work is to contribute to the elucidation of the mechanism of CO interaction with PdAl alloys which can be used as novel bimetallic catalysts and/or can appear as interfacial compounds in the case of supported Pd/alumina catalysts [23].

In this paper, the results of the study of CO adsorption properties of PdAl system during heating procedures and adsorption/desorption cycles are reported. The main experimental techniques used were ion scattering spectroscopy (ISS), X-ray photoelectron spectroscopy (XPS), thermal desorption spectroscopy (TDS) and static secondary ion mass spectroscopy (SSIMS).

2. Experimental

Experiments were carried out in two ultra-high vacuum (UHV) systems. For XPS and ISS studies, the UHV system (background pressure 1–3 $\times$ 10$^{-7}$ Pa) was equipped with the multichannel hemispherical electrostatic analyser Omicron EA 125, a dual (Al/Mg) anode X-ray source and a differentially pumped sputter ion source Omicron ISE 10. In this work the MgK$\alpha$ line (1253.6 eV) was used for XPS measurements, with the incidence angle of X-ray 15° to the surface plane. The analyser was operated in the retardation-field mode, applying a pass energy of 20 eV. For ISS measurements a He$^+$ ion beam with a primary energy of 2 keV was used at the incidence angle of 130°.

Another UHV system used for TDS and SIMS measurements (with background pressure 2 $\times$ 10$^{-8}$ Pa) consisted of quadrupole mass spectrometer Balzers QMS 200 Prisma (for collecting TDS spectra) and SIMS analyser Perkin-Elmer 06-600 with mass range of 0–250 amu. All TDS spectra presented here were collected in the temperature range from 293 to 600 K with heating rate of 2 K/s. For SIMS measurements, the unfocused primary ion beam with energy of 1000 eV was applied at the incidence angle of the ion beam to the analysed surface of 20°.

Bulk PdAl sample was alloyed by melting the proper weights of high-purity Pd (99.99 +%, Goodfellow) and Al (99.999%, Goodfellow) in clean argon discharge. However, bulk homogeneity of the alloy was not controlled by any independent analytical technique.

In order to remove surface impurities (mainly oxygen and carbon), the sample was treated by sequential cycles of argon sputtering ($P_{Ar} = 2–3 \times 10^{-3}$ Pa, 1000 eV, 1–2 μA/cm$^2$, 20–30 min) and heating to 600 K. Cleanliness and actual composition of sample surface were monitored during the cleaning cycles by means of XPS or SIMS, respectively.
3. Results and discussion

3.1. X-ray photoelectron spectroscopy and ion scattering spectroscopy characterisation of PdAl alloy

In comparison to bulk palladium, XPS results from PdAl alloy (Fig. 1) showed that the Pd 3d peaks were shifted by 0.8 eV towards higher BE as a result of Pd–Al chemical bonding, which was formerly reported before in [7]. No splitting of Pd 3d doublet due to the possible simultaneous presence of both Pd and Pd–Al states was observed. The VB centroid shift of 1.8 eV towards higher energies reflected the reduction of electron density near the Fermi level due to the hybridisation having an origin in highly localised 4d electrons of Pd and widely spread sp states of Al.

The measured VB of PdAl (Fig. 1b) disclosed a slight shape difference in comparison to the one presented in [6]. The VB edge near Fermi level was more precipitated in our case, i.e., closer to Pd than it was expected. Similarly, the BE of Pd 3d core levels were lower than published data [7]. Thus, the prepared PdAl alloy seems to be enriched with Pd with the (at least surface) stoichiometry different from the reported one.

PdAl alloy surface stability was controlled by means of ISS and XPS techniques during several different treatments. The increase of surface concentration of Al atoms and the decrease of Pd signal during heating procedure up to 600 and 670 K were observed in ISS spectra. It may be assigned to the process of Al segregation and/or interchange of Al sub-surface and Pd surface atoms. Considering the lower free surface energy of Al compared to Pd [24], that result is in the agreement with thermodynamics. The relative surface concentration of Al measured with ISS increased by 41% while Pd concentration dropped about 36%.

The same behaviour was found in XPS spectra where the relative intensity of Pd to Al dropped after heating the sample. The interchange effect was more pronounced in ISS, which is the consequence of higher surface sensitivity of ISS compared to XPS.

The adsorption/desorption procedure was applied to examine the PdAl alloy in order to study the substrate interaction with CO, from which XPS and ISS results can be seen in Fig. 2a and b. The clean sample, exposed to 10 L of CO at partial pressure of $10^{-5}$ Pa (1 L (langmuir) = $10^{-6}$ Torr s) at the RT, was heated up to 600 K. The composition and the surface cleanliness of the alloy was finally restored by means of short 10 min Ar$^+$ bombardment.
The similar behaviour of Al and Pd signals during the heating procedure as well as during the CO adsorption/desorption cycle was observed. However, the CO-induced relative changes of ISS and XPS intensities of Pd and Al were more pronounced compared to the effect of heating. The relative surface concentration of Al measured with ISS increased by 51\% while Pd concentration decreased by 81\%. Simultaneous slight rise of oxygen signal was also observed in the ISS spectra as a result of CO interaction with PdAl sample surface. XPS analysis showed the presence of Al–O bond (leading to the appearance of Al 2p (73 eV) peak satellite at about 75 eV, labelled herein Al\textsuperscript{ox}) while no Pd 3d peak splitting related to the possible oxidation was observed. Furthermore, both CO adsorption and consequent desorption led to the increase of C XPS signal. The carbon presence could not be determined from ISS spectrum due to the very low intensity.

CO adsorption/desorption cycle results in the interchange of Pd and Al atoms as well as the increase of surface oxygen amount and the carbon contamination, which gives the evidence for—at least partial—CO dissociation. These observations suggest that the part of CO molecules dissociates on the surface and the dissociatively adsorbed O atoms can form Al–O bonds even at RT, lifting the Al atoms from underlayer onto the surface. The both phenomena of CO adsorption induced Al segregation and partial CO dissociation at RT were also described in [25] for interfacial Al-alloyed Pd(001) surface.

The last points in Fig. 2a and b were measured after Ar\textsuperscript{+} cleaning bombardment. The original values of the surface concentrations of all the atomic compounds were restored, which was not exactly the case Al\textsuperscript{ox} of XPS data where relative intensity of Al\textsuperscript{ox}/Al decreased less than expected. Considering the different surface sensitivity of both XPS and ISS methods it could be explained by the partial diffusion of oxygen atom to the sub-surface region. It was already reported in the case of Ni{001}/(2\times2)–Al [26], the system similar to Pd–Al.

### 3.2. Secondary ion mass spectroscopy

The temperature influence on surface structural changes of PdAl alloy was also studied by means of SIMS during sample heating sequentially from RT up to 600 and 670 K. The drop in the relative Pd\textsuperscript{+}/Al\textsuperscript{+} signal intensity was observed. However, the signal of PdAl\textsuperscript{+}/Al\textsuperscript{+} did not change and remained constant indicating enhancement of surface concentration of Pd–Al bimetallic species. Both these results cohered well with ISS and XPS measurements supporting the idea of temperature induced Al surface segregation and/or Al and Pd atomary interchange. The interesting fact was that the changes did not come during but immediately after the heating, when the sample started to cool down.
In Fig. 3 the relative ratios of ion signals of AlO\(^+\), AlOH\(^+\), PdAl\(^+\), Pd\(^+\), and PdC\(^+\) during adsorption/desorption cycles are plotted. Note that absolute intensity of SIMS peak is not directly proportional to the actual surface concentrations of particular elements and compounds because of the different sputtering yields and ionisation probability for every single ionic species released from the surface. For example, the CO bonding on Pd atoms could increase the local work function and, consequently, the Pd\(^+\) yield.

When performing the TDS experiments, distinct drop of PdAl\(^+\)/Al\(^+\) and PdAl\(^+\)/Pd\(^+\) relative signals was observed. The accrual of atomic species in the spectra to the detriment of PdAl\(^+\) clusters suggests the formation of “single” Al and Pd atoms being the pathway for disappearance of Pd–Al bonds on the surface. The quantities of AlO\(^+\) and AlOH\(^+\) related to Al\(^+\) increased with the number of adsorption/desorption cycles, corresponding with the similar results obtained by means of XPS and ISS, mentioned above.

On the base of these results, we can pronounce the hypothesis that in the presence of CO the individual Pd and Al atoms tend to create chemical bonds to carbon and oxygen species, respectively, which causes the weakening in Pd–Al bonding, probably leading to the breaking of the bimetallic bond finally. CO molecule dissociates on the surface, which gives the reason for AlO\(^+\)/Al\(^+\) and AlOH\(^+\)/Al\(^+\) ratios growth during TDS treatments. Without the presence of CO on the surface, the only temperature-induced change of AlO\(^+\)/Al\(^+\) is negligible. On the other hand, the steady decrease of PdC\(^+\)/Pd\(^+\) with the number of TDS cycles was observed (Fig. 3) which did not agree with XPS results presented in Fig. 2b. That effect will be discussed later.

The inset of Fig. 3 illustrates the behaviour of PdAl within a single adsorption/desorption experiment, demonstrating the partial development of the mentioned effects even upon CO adsorption at RT, not only during the following desorption.

### 3.3. TDS results

The TDS spectra of CO from PdAl bulk alloy for several adsorption/desorption cycles are presented in Fig. 4. The PdAl alloy exhibited low temperature CO desorption peaks in comparison to bulk Pd [9–18]. This is in agreement with generally proposed correlation of weakening of CO bond with shifts in electronic structure of Pd upon alloying with Al [5,27].

![Fig. 4. The evolution of CO TDS spectra from bulk PdAl alloy after its exposition of about 10 L CO at RT during three adsorption/desorption cycles. The inset presents CO\(_2\) and H\(_2\)O production during and after a single CO TDS cycle.](image)
We performed more TDS cycles in order to explore CO dissociation. The shape and the total area of desorption spectra remarkably changed with the number of cycles. Low-temperature peak at 325 K dropped in its intensity and simultaneous development of two peaks located at higher temperatures (375 and 410 K) was found. The total adsorption capacity progressively vanished with additional TDS cycles which was accompanied by gradually increasing production of CO$_2$ and H$_2$O as results of surface reactions: $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$, $\text{CO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{C}$. The remaining carbon poisoning the surface was partially reacted off in the form of CH$_4$ molecules, as indicated by TDS. The dissolution of hydrogen into PdAl bulk and/or adsorption of H$_2$ from residual atmosphere could be the probable origin of hydrogen atoms. Note that CO$_2$, H$_2$O and CH$_4$ production was observed not only during desorption but also after heating off, when the sample was cooled down, as well as during the CO exposition. An example of CO$_2$ and H$_2$O production as an evidence for CO dissociation on PdAl surface during and after TDS cycle is presented in the inset of Fig. 4.

From a balance of PdAl surface reactions it was found that the amount of molecules containing oxygen atoms desorbing from the surface was lower than the amount of incoming oxygen in the form of CO. Thus, this observation elucidates the reason for oxygen accumulation observed as the increase of AlO$^+$/Al$^+$ and AlOH$^+$/Al$^+$ in Fig. 3.

Similarly, the balance of incoming and outgoing carbon showed an accumulation of surface carbon which explained the enhancement of XPS carbon signal during the first TDS cycle. The SIMS PdC$^+$/Pd$^+$ intensity ratio decrease during the following TDS cycles showed that the accumulated carbon was partially removed from the surface. Apart from the species that were reacted off in the form of CH$_4$, another pathway of carbon sub-surface diffusion could be considered.

4. Summary

The CO interaction with PdAl alloy was investigated by means of XPS, ISS, SIMS and TDS.

- The electronic structure of the alloy was affected by the strong bimetallic bonding between Pd and Al. The sample was probably surface-enriched with Pd in respect to the intended stoichiometry.
- PdAl alloy surface exhibited stoichiometry changes induced by heating. Al sub-surface atoms tend to interchange with Pd surface atoms.
- The weakening of CO bond to PdAl alloy compared to pure Pd was observed.
- CO dissociation on PdAl sample during adsorption/desorption cycles, causing the CO$_2$ and H$_2$O production, was observed. CO partially dissociated even at RT.
- The presence of oxygen atoms on PdAl surface caused the lifting of Al atoms from underlayer towards surface in order to create Al–O chemical bond and weakening of Pd–Al bond.

Acknowledgements

This work was supported by the Czech Grant Agency under the Grants nos. 202/01/P091 and 202/99/1714.

References