XPS and TDS study of CO interaction with Pd–AlOₓ systems

V. Matolín *, I. Stará, N. Tsud, V. Johánek

Department of Electronics and Vacuum Physics, Charles University, V Holešovičkách 2, 18000 Prague 8, Czech Republic

Abstract

The metal–substrate and metal–metal interactions (MSI, MMI) represent important effects determining the properties of supported catalysts, gas sensors and gettering alloys. We investigated the MSI and MMI effects by the X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) in the case of Pd films deposited on Al₂O₃ and Al substrates. The study shows that the particle-size dependent metal–substrate interaction plays an important role in CO–Pd chemisorption, namely, in the case of “aluminium rich” Pd–aluminium oxide interface. CO chemisorption exhibits a low-temperature desorption feature at 360 K characteristic for Pd–Al and very small Pd particles. The MSI is explained by the formation of a Pd–Al intermetallic interface exhibiting a strong bimetallic Pd–Al interaction. © 2001 Elsevier Science Ltd. All rights reserved.

PACS: 86.65.Jv; 86.65.My; 82.80.Pv; 61.46.+w

Keywords: Pd; Al; Al₂O₃; XPS; TPD; Metal–substrate interaction; CO adsorption; Bimetallic interaction; Model catalysts; Heterogeneous catalysis

1. Introduction

Modern catalysts are generally composed of several elements in precise proportions. They are optimised in order to give the highest reaction rate and to have the best selectivity. The optimisation is mainly based on empirical approaches and often it is not possible to describe the details of the reaction mechanisms taking place during catalytic reaction. This is partially due to the complexity of the catalysts,

*Corresponding author. Tel.: +420-2-2191-2323; fax: +420-2-688-5095.
E-mail address: matolin@mbbox.troja.mff.cuni.cz (V. Matolín).

0079-6816/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PH: S 0 0 7 9 · 6 8 1 6 ( 0 1 ) 0 0 0 2 2 - 3
small particles supported by more or less inert porous oxide substrates, and also to the lack of their characterisation.

For this reason, the adsorption and reaction studies are often performed on well-defined model systems, i.e., on single-crystals and supported ultra-thin metallic layers, often epitaxial, under in situ low-pressure reaction conditions. Model catalysts can be fully characterised by the numerous surface-science techniques available.

The most important metals for catalysis are those of groups VIII to IB of the periodic table, the most important crystal structure being face-centred cubic (Ni, Cu, Rh, Pd, Pt, Ag, Ir, Au). Each atom in the interior of fcc crystal has 12 nearest neighbours. By cutting a crystal along different planes we can create surfaces of different atomic arrangements, as can be seen in Fig. 1(a). The difference between the bulk (12) and surface atom co-ordination number gives us the number of missing neighbours \(Z_m\) of an atom in each surface plane. An atom in fcc \((1\ 1\ 1)\) has \(Z_m = 3\), in \((1\ 0\ 0)\) \(Z_m = 4\), while fcc \((1\ 1\ 0)\) is a corrugated surface and contains two types of atoms with \(Z_m = 6\) and 2, respectively. The number of missing neighbours corresponds to the number of broken (unsaturated) bonds that can determine the reactivity of surfaces. For this reason, the surface morphology, namely, the existence of surface irregularities, such as step sites with low co-ordination number, can influence the mechanism of chemisorption and catalytic processes [1–6].

Adsorption and reaction on small supported particles often differ strongly from the behaviour of macroscopic metal surfaces. The recent review of Henry [7] shows

![Diagram](image)

Fig. 1. Schematic view of main surface plans of fcc (a) and corundum \(\alpha-\text{Al}_2\text{O}_3\) (b) crystals.
how extensively is the field of model supported catalysts studied by surface scientists. The interaction of CO with highly dispersed platinum metals on non-metallic supports is of special interest, because CO is involved in many practical reactions and its relatively simple and well-known molecular structure enables it to be used as a probe for adsorption mechanism studies. Many studies have been performed on Pd model catalysts, supported by $\text{Al}_2\text{O}_3$ and MgO, due to the great importance of Pd in heterogeneous catalysis [7–21]. While the adsorption behaviour of large crystals is usually well understood from numerous studies on single-crystals, very little is known about supported metals, investigations have been devoted namely, to the investigation of the so-called size effect – size and morphology dependent properties. The results have often been rather contradictory, showing the complexity of the problem.

The CO adsorption on Pd, investigated via temperature programmed desorption (TPD), showed similar trends in CO desorption spectra – apart from a peak at 470 K, governing the spectrum for crystals and large particles, features at 350–380 K [5,13,14,19], (or below room temperature for experiments with cooled samples [15]) gained intensity with decreasing particle size.

In order to explain this size dependence, it is useful to remember the interaction mechanism between CO and metal as first described by Blyholder [22] in the molecular-orbital model, involving a $5\sigma$ CO donation to the metal associate with a back-donation to the empty $2\pi^*$ CO orbital. When an atom (or molecule) is adsorbed onto a simple metal surface such as Al, without d states, the adsorbate electronic states are broadened and shifted down in energy by the interaction with the broad continuum of metal sp states [23]. Hybridisation of adsorbate and metal states build up bonds to many adsorbates, including CO [24,25]. The surfaces of transition metals possess between 6 and 10 d-electrons, which are much more localised on the atoms than the s-electrons are, and spread over the crystal in well-defined bands which retain the characteristics of the atomic d-orbitals. However, the presence of the d-states enables a further bonding interaction between metal and adsorbate via the formation of new molecular orbitals. The subtle balance between the filling of these orbitals, as well as the population of $2\pi^*$ CO antibonding level (that weaken, i.e., activate, C–O bond), influence the strength of the metal–CO bond and determines whether the adsorption is molecular or dissociative. Pd has the electronic configuration $4d^{9.5}5s^{0.5}$ in the bulk that is characterised by a narrow high-lying d-band that allows important back-donation to $2\pi^*$ CO orbital, which favours adsorption in the highly co-ordinate sites with high-binding energy.

Another important behaviour of CO adsorption on Pd is the strong repulsive CO–CO interaction at high CO coverage that is responsible for the weakness of the Pd–CO bond. On Pd(1 1 1), CO–CO repulsion leads to the occupation of new adsorption sites – identified as on-top sites – that can be seen as a formation of a shoulder below the main desorption peak [1]. The similar, but more pronounced, peak-like shoulders can be seen on open Pd(1 1 2) surfaces [5], which clearly indicate the morphological dependence of this effect. Thus CO chemisorption reflects a complicated balance of different factors, such as the metal–CO bonding character of the orbitals and also the CO–CO intermolecular interactions.
In the case of supported catalysts, another effect, the metal–substrate–interaction (MSI), can influence the adsorption and morphological size dependent properties of particles. The smaller the particles are, the more important the MSI should be. While alumina is considered by some authors as an inert, non-reactive substrate, others classify it as more or less reactive. The thin film of Al$_2$O$_3$(1 1 1) on NiAl(1 1 0) has been found to be non-reactive [26] and low-temperature CO desorption features, from very small Pd particles, were explained by CO adsorption on low co-ordination adsorption sites influenced by a strong repulsive CO–CO interaction [15]. In contrast, the Pd–Al$_2$O$_3$ interaction, resulting from charge transfer between Al cations to deposited Pd atoms, was found [27,28].

Investigation of size effect upon CO adsorption on alumina supported particles showed a surprising effect – CO partially dissociated on small Pd clusters deposited on mica [29], γ-alumina [13] and thin aluminium-oxide film [30]. It was found that smaller particles exhibited higher dissociative activity. On the other hand, CO adsorption was molecular on Pd clusters deposited on sapphire [19,31] and Al$_2$O$_3$(1 1 1)/NiAl(1 1 0) [15]. However, the question of the mechanism of dissociation process, enhanced by this unexpected behaviour, has not been answered yet. The possible origin of this phenomenon could be linked to the MSI, which may be influenced by the thickness, surface structure, and/or stoichiometry of the alumina support, which could be related to the MS charge transfer. This assumption is supported by the recent observation of Pd 3d$_{5/2}$ initial state shift for Pd on γ-alumina, prepared by thermal oxidation, which was associated to electron transfer in the direction of the substrate-deposit [32]. Beside the above-mentioned observations of CO dissociation on Pd model catalysts, a similar effect has been observed on real Pd/SiO$_2$ [33] and Pd/Al$_2$O$_3$ and Pd/TiO$_2$ [34] catalysts, where this behaviour was attributed to the MSI effect.

MSI-induced changes in the Pd–CO interaction are much more important in the case of Pd films deposited on metallic supports. The combined X-ray photoelectron (XPS), ultra-violet photoelectron spectroscopy (UPS) and CO–TPD studies have been performed on Pd overlayers on transition metals Ta [35], Mo [36] or W, Re and Ru [37], as well as on Rh, Pt [37,38], and noble metals, such as Au [39]. The common feature of Pd deposited on transition metals was the shift of Pd core levels and the centre of Pd d-band toward higher binding energies, due to the formation of a bimetallic bond. Pd 4d orbitals were pushed away from the 2π* CO orbitals which led to a weakening of the Pd 4d–CO 2π* bonding interactions. It was shown that the d-band centroid shift was in direct correlation to the decrease of CO desorption temperature [23]. Hence, beside the CO–CO repulsion and low co-ordination site effect, the bimetallic interaction represents a further effect responsible for the weakening of the Pd–CO chemisorption bond.

In order to explain a possible bimetallic MSI effect, in the case of Pd deposited on “aluminium-rich” substrates, the Pd–Al interaction was considered. Even though the electronic structure of Al–Pd bimetallic systems has been investigated [40–42], the CO adsorption properties of such systems remained unexplored. Pd–Al studies showed that the evolution of the Pd d-band was very similar as to that of Pd–transition metals interactions. At room temperature, Pd intermixed with the Al
polycrystalline substrate forming a thin surface alloy up to 5 ML thick [41] and 8 ML thick [42] for the Al(0 0 1) single-crystal, respectively. Photoemission results showed a strong interaction between Pd and Al, through the hybridisation of the Pd d and Al s states, leading to the formation of PdAl alloy of noble metal-like electronic structure with the d-band centred at 4 eV below the Fermi level.

The CO adsorption–desorption studies on Pd/Al systems [43] showed an important decrease in the CO desorption temperature accompanied by partial CO dissociation and formation of Al-related oxidic and carbidic species.

In this paper, the different CO desorption features, obtained for small Pd particles deposited on different aluminium oxide supports, are compared and discussed in relation to possible MSI and particle-form effects.

2. Experimental

Experiments have been carried out in ultra-high vacuum (UHV) chambers. For TPD studies, the UHV system was equipped with a specially designed desorption spectrometer, described elsewhere [13]. Pd–Al desorption studies were performed using the spectrometer described in [43]. CO exposure was provided by a molecular beam doser direct to the surface, so that relatively high exposures of the sample were possible, while a low pressure in the chamber was maintained. The intensity of the molecular beam was about 5 × 10^{12} molecules cm^{-2} s^{-1} at the sample surface. The desorbed molecules were monitored with a differentially pumped quadrupole mass spectrometer. A linear heating rate was achieved with a thermoelectric programmer.

XPS experiments were performed using the OMICRON EA 125 multichannel hemispherical analyzer and a dual Al/Mg X-ray source. The substrates were cleaned by Ar^+ ion bombardment using a differentially pumped ion gun. The substrate cleanliness, stoichiometry and amount of deposited Pd were checked by XPS. The deposited layer morphology was investigated using QUASES™ software (the software package for quantitative XPS of surface nanostructures by analysis of the peak shape and background) made by Quases Tougaard ApS. The principles of the method were explained in [44,45].

Before the experiments, the reference Pd(1 1 1) single-crystal surface was cleaned by cycles of argon ion bombardment (900 eV, 2 μA cm^{-2}) and heating in oxygen (3 × 10^{-6} Pa) at 900 K during 1 h.

The aluminium oxide substrates, with various surface structure and/or stoichiometry, were used as a model support. The (0 0 0 1) and (1 − 1 0 2) α-alumina substrates with more or less stoichiometric surfaces were prepared by heating in the air (at 1620 K during 2 h), in vacuum (10^{-6} Pa, 1970 K, 30 min) and by argon ion bombardment (1 keV, 1 μA cm^{-2}, 15 min). Polycrystalline γ-alumina supports, composed of grains of cubic structure [8], were obtained by thermal oxidation in the air at 900 K during 24 h.

Small Pd clusters were deposited on the samples in situ at room temperature using the micro electron beam evaporation source (MEBES) [46] which enable the evaporation rate to be controlled by monitoring the Pd^+ ion current.
3. Results

3.1. Pd particles deposited on aluminium oxide substrates

3.1.1. CO adsorption study – TPD

In Fig. 2(1–6), we compare the CO desorption spectra from Pd(1 1 1) single-crystal and small particles deposited on aluminium oxide surfaces prepared in different ways. Beside the polycrystalline, several tens nm thick \( \gamma \)-Al\(_2\)O\(_3\) sample (sample 2), we used two orientations of \( \alpha \)-alumina surfaces, (0 0 0 1) – samples 3,4 and (1 1 0 2) – samples 5,6. Samples 3 and 5 (4 and 6) were prepared by heating in air (vacuum). The heating was performed in a special vacuum chamber, and the samples were then transferred into the analysis chamber. During the transport the samples were exposed to the atmosphere. The crystallographic structure of these surfaces can shown in Fig. 1(b). Before Pd deposition, the surfaces were cleaned by a small dose of argon ion bombardment (500 eV, 2 \( \mu \)A cm\(^{-2}\) during 5 min) in order to remove surface impurities. After the experiments, the average particle size was determined by transmission electron spectroscopy, using the method of transport carbon replica. Auger electron spectroscopy (AES) and Electron Energy Loss Spectroscopy (EELS) investigations [47] showed that the samples heated in vacuum exhibited “aluminium-rich” surfaces due to partial thermal reduction. Similarly, the \( \gamma \)-alumina sample prepared by thermal oxidation of aluminium revealed a nonstoichiometric alumina with a lack of oxygen or excess of aluminium in the layer.

All TPD spectra (Fig. 2) possesses the “low-temperature” desorption feature discussed in the introduction. While Pd(1 1 1) desorption spectra exhibited a typical CO–CO repulsion shape, small particles had a more developed desorption peak between 330 and 400 K. These peaks were pushed to lower temperatures in the case of particles deposited on vacuum annealed supports, see samples (4) and (6), in spite of their relatively larger size. The filling of lower-lying peaks started at lower CO coverages than in the case of Pd(1 1 1), which made the simple CO–CO repulsion less likely.

The CO desorption from \( \gamma \)-Al\(_2\)O\(_3\) supported particles, presented in Fig. 2(2), was accompanied by CO\(_2\) production via the CO disproportionation reaction that involved the CO dissociation step [13]. On the other hand, CO dissociation was not observed on \( \alpha \)-Al\(_2\)O\(_3\) supported particles.

3.1.2. Pd growth and CO adsorption study – XPS

In order to elucidate the difference between the most distinct cases of CO chemisorption, we investigated Pd particle growth and CO adsorption by XPS for Pd/air annealed (0 0 0 1) \( \alpha \)-Al\(_2\)O\(_3\) and Pd/\( \gamma \)-Al\(_2\)O\(_3\) systems. The Pd 3d\(_{5/2}\) peak intensity variations as a function of the deposition time, obtained at the same evaporation rates, had nearly identical shape for both investigated substrates [32], showing the identical growth mode. More detailed information about the layer parameters was obtained using the Pd peak background analysis. It was found that Pd formed small three-dimensional islands during the early stages of growth up to particle height \( h \) of 1.1 nm. Thereafter, particles formed flat islands by lateral growth
Fig. 2. CO–TPD spectra for CO saturation coverage on Pd(111) single-crystal (1), and supported Pd particles on different aluminium oxides (2)–(6).
at constant $h$ (stage II), which was characterised by a linear coverage increase. These results were supported by the dependence of Pd 3d$_{5/2}$ peak FWHM on coverage. FWHM, which generally depends on the average co-ordination number of cluster atoms, decreased rapidly in stage I, whereas it remained constant in stage II.

The metal–substrate interaction for small Pd particles deposited on both alumina substrates was investigated in terms of initial state effect, which is sensitive to MSI-induced cluster-substrate charge transfer [32]. $\Delta \varepsilon$ was found to be shifted to higher positive values for more strongly interacting substrate ($\gamma$-Al$_2$O$_3$) whilst, for the inert-like sapphire substrate, the MSI was less important. The initial state shift value was associated with the electron transfer in the substrate-clusters direction. We advanced the hypothesis of the link between charge transfer and CO dissociation.

![Graph](image-url)

Fig. 3. Evolution of valence band measured by XPS excited with Mg K$\alpha$ source for Pd clusters supported on $\alpha$-Al$_2$O$_3$(0001) surface during Pd deposition. Final spectra correspond to the deposition of 3 ML of Pd.
Evolution of XPS valence band spectra are presented in Fig. 3. Fig. 3(a) shows formation of the Pd d-band (close to the zero binding energy (BE) corresponding to the Fermi level) that overlaps the alumina valence band. The difference spectra obtained by subtracting the aluminium oxide background spectrum showed that, for very low deposits, the d-levels are centred at the BE of 3 eV and move to 2 eV for large Pd islands. By comparing the valence band spectra of other alumina substrates discussed here, we find identical shape evolution.

3.2. Pd/Al bimetallic systems

3.2.1. CO adsorption study – TPD

The polycrystalline aluminium substrate was cleaned by Ar ion bombardment until natural oxide layer was completely removed. Pd was deposited as in the case of the aluminium oxide samples, in order to compare the adsorption properties of both systems. Fig. 4 shows a typical set of CO desorption curves obtained for the sample prepared by depositing approximately 0.7 ML of Pd. After the Pd deposition, several cycles of adsorption–desorption was performed at the CO exposures of 10 Langmuirs (10 \times 10^{-6} \text{ Torr s}), corresponding to a saturation CO coverage. The first curve differs from others by the dominant maximum at 420 K. The following curves exhibited a temperature stable maximum at 360–370 K, while the higher peak decreased rapidly in intensity and moved down to 400 K. All curves exhibited the common trend of decreasing of desorption peak area, i.e., of the total CO uptake. An increase of the desorption peak area was obtained by adding Pd by new evaporation and the CO desorption features followed the same evolution trend as before [43].

![Fig. 4 Set of CO–TPD spectra obtained during adsorption–desorption cycles for CO saturation exposure on Pd–Al bimetallic surface prepared by deposition of 0.7 ML of Pd. Amount of desorbed CO decreases with increasing number of cycles.](image-url)
3.2.2. Pd growth and CO adsorption study – XPS

In order to explain the above mentioned results of CO adsorption, we investigated Pd growth and CO adsorption–desorption on Pd/Al by XPS. For comparison, we also performed CO desorption studies, for the same exposures, on a bare Al substrate. In agreement with previous AES investigations [26], we found the CO dissociation was followed by an increase of carbon and Al oxide (at 75 eV) intensities [48].

The two most spectacular effects of Pd/Al growth were the 2.5 eV shift of the Pd 4d-centroid and the 2 eV shift of Pd 3d$_{5/2}$ core level to higher BE. The growth of the 4d-band is shown in Fig. 5. In Fig. 6 we compared the core level XPS of Pd/Al and bulk Pd samples. Fig. 5 shows that the 4d-band kept a constant shifted value during whole growth process. Similarly, the BE of the core level Pd 3d$_{5/2}$ peak was constant, contrary to the typical variations of the Pd 3d$_{5/2}$ peak BE, obtained for Pd/alumina system [32]. Energy and FWHM variations of the Pd 3d$_{5/2}$ peak on alumina supported particles were given mainly by final state variations, which corresponded to the evolution to bulk metal properties [32,49–51] and by increase of average coordination number of the particle atoms during the growth. For the Al substrate, the situation was different. The constant BE showed the intermixing of Pd and Al atoms, where the BE value was determined by the ultimate contact of both species and by the formation of bimetallic bonds. Heating of the samples, during TPD experiments, led to the diffusion of a Pd atom in the subsurface region, which was accompanied by a decrease in the Pd 3d$_{5/2}$/Al 2p intensity ratio [43], which fitted well with the observed variation of the CO Pd/Al TPD spectra in Fig. 4. After Pd deposition at room temperature, a surface overlayer of Pd was formed, the adsorption properties of which were determined, more or less, by the strong bimetallic interaction. Heating

![Figure 5](image_url)

**Fig. 5.** Evolution of valence band measured by XPS excited with Mg Kα source for Pd overlayer on polycrystalline Al surface as function of amount of deposited Pd. First (lowest) spectra corresponds to bare Al surface, final spectra corresponds to deposition of 3 ML of Pd.
induced alloying, which led to the disappearance of the higher-lying Pd metal-like desorption feature. The decrease of the total CO uptake corresponded to the decrease of the Pd atom concentration on the surface, which is schematised in Fig. 7. This hypothesis is in agreement with LEIS study of Pd overlayer growth on Al [42] and with the results of RHEED observations of the formation of Pd/Al (001) clusters on KCl (001) substrate [52]. Beside the diffusion of Pd atoms into the subsurface, CO dissociation and subsequent Pd surface contamination by diffusing carbon is probably an additional effect responsible for the decrease of CO adsorbed molecules. Since the alloying process is more important, during only two firsts desorption heatings, the contamination could be the most important effect responsible for decrease of the CO adsorption capacity during the further heating cycles.

Variation of CO adsorption properties can be explained by the formation of a noble metal-like alloy characterised by a lower-lying d-band and a low density of states at the Fermi level, which weakens the Pd 4d–CO 2π* bonding interactions. The higher desorption temperature for deposited Pd should correspond to a more

---

**Fig. 6.** Comparison of Pd 3d₅/₂ peaks for Pd overlayer on Al (a) and bulk Pd crystal (b).

---

**Fig. 7.** Schema of formation of surface Pd–Al alloy.
metallic than bimetallic electronic character of the upper Pd overlayer. This behaviour was not seen for the valence band spectra, due to the low “surface sensitivity” of the valence band XPS.

4. Discussion

The use of supported model catalysts, elaborated and characterised in UHV, is a necessary step towards the understanding of heterogeneous catalysis. Their role is essential in the elucidation of size effects in the activity and selectivity of catalytic reactions and in the investigation of the metal–support interaction. As shown in numerous studies [12], small particles grown at low temperature (RT or below) do not have well-defined shapes and are metastable. Upon heating, for example during a TPD or catalytic reaction, their shape evolves and tends more or less rapidly towards the equilibrium shape. By changing the crystallographic orientation, and/or the nature of the substrate, it is possible to alter the ratio of the different exposed planes. The model studies of CO chemisorption on single-crystals of different orientation confirm the general trend of increase of CO metal bond strength on more opened surfaces [53]. It also explains that, for clusters having the same morphology, the average desorption energy generally increases with decreasing size, due to the increase of the proportion of low co-ordinated edge and corner sites, as can be seen, for example, for CO on Pt/Al₂O₃ [54] and/or on Pd/MgO [12]. The CO adsorption energy \( E_a \) for MgO(100) supported Pd particles, measured by a molecular beam method [12], showed an increase from 30 to 40 Kcal/mol with decreasing particle size from 5 to 2 nm. The answer to the question why should CO be more strongly bonded on low co-ordinated Pd atoms is given in [55], where the shift of the d-band center towards the Fermi level, calculated for edge and corner Pd adsorption sites, is linked to the increase of CO–Pd bond strength.

However, Pd/alumina particles do not follow the above mentioned rule. The evolution of low-temperature lying CO desorption features with decreasing particle size, which dominates in certain cases, shows it very clearly. Assuming that the calculated tendency is correct (even though some small divergences from the theory are possible, due to the neglect of some properties of real systems, such as relaxation during adsorption), another factor explaining the above mentioned discrepancy should be proposed. It could be the interaction between the metal cluster and the substrate that is only important for very small clusters. The MSI could influence the electronic structure of supported catalyst, what in turn, influences its reactivity. The importance of MSI effects depends, not only on chemical composition of interface, but also on its crystallographic structure. The influence of \( \alpha \)-Al₂O₃ surface structure on the Pd/alumina interface structure can be seen in [56,57], where the models of interface formation determined by RHEED are presented. The growth on \( \alpha \)-Al₂O₃ (0001) is characterised by the formation of a commensurate Pd overlayer, with respect to the oxygen closed packed surface lattice, while Pd forms on the more opened (1−100) and (11−20) surfaces incommensurate deposits. The theoretical predictions [58] of a (0001) surface structure show that an \( \alpha \)-Al₂O₃ bulk crystal is
formed by Al-terminated stacking sequences Al–O–Al in [0 0 0 1] direction. The Al-terminated surface is expected to be more stable, because of its non-polar character. The Al–O inter-layer spacing is reduced from the bulk value of 0.08 nm to 0.03 nm. This large relaxation of the first–second layer spacing results in the formation of nearly coplanar Al–O charge neutral structure. Although the unit cell should contain one Al and three O atoms, experimental studies show that the Al–O surface stoichiometry, as well as the surface roughness, depend considerably on the surface treatment – heating under air or vacuum gives different surface stoichiometry [47,58] and morphology [59]. Concerning the more opened $\alpha$-Al$_2$O$_3$ (1 1 0) and (1 1 –20) surfaces, reliable experimental data are limited but we can expect the same (or probably more pronounced) dependence of the surface structure on different surface treatments.

Comparison of $\gamma$-alumina with $\alpha$-alumina shows a decrease of the ionicity through the series $\alpha$-alumina, reduced $\alpha$-alumina, $\gamma$-alumina surfaces [60], i.e., an increase in electronic exchanges with other species present on the surface.

Electronics structure calculations of transition metal–alumina interfaces [61] show that, for early transition metals, there is strong metal–surface oxygen interaction. On the other hand, in the case of late transition metals, such as Ni or Pd, the metal–O interaction is relatively weak, while the metal–Al interaction starts to play a more important role in metal–aluminium oxide bonding. Calculations [61] show that, in this case, the surface bands consist mainly of surface Al orbitals that are slightly hybridised with the deposited metal d-bonding, and that covalent or metallic interactions, similar to the bond in intermetallic compounds or alloys, might be possible. The results of these calculations are supported by study [62], where the Ni–Al intermetallic formation, via deposition of Ni onto an alumina substrate in the absence of oxygen, has been found. Summarising, we conclude that Pd–alumina MSI depends strongly on the type of alumina and on its surface structure, given by its annealing, through the formation of different Pd–AlO$_x$ interfaces that are more or less aluminium rich. The notable similarity between CO–TPD spectra, obtained for Pd deposited on alumina and aluminium substrate, can be explained by the formation of Pd–Al intermetallic interface, in the case of Pd/Al$_2$O$_3$ model catalysts.

5. Conclusion

The TPD results of CO adsorption on Pd particles, supported on different AlO$_x$ ($x$ between 0 and 1.5) surfaces, are compared. We see that there is notable similarity – a more or less pronounced desorption feature, around 350 K. The XPS study shows that, in the case of Pd–Al, an alloy with a strong bimetallic interaction is formed, having a noble metal-like electronic structure characteristic of a deeper-lying d-band. CO chemisorption on these alloy exhibits a weaker CO bond, due to the d-band shift to a higher BE.

Lowering of CO desorption temperature with decreasing size of Pd–alumina supported particles, which is inconsistent with the general prediction, is explained by
a possible formation of a Pd–Al intermetallic interface and formation of bimetallic like adsorption sites.

These results should be taken into account in explaining not only the different CO bonding on Pd model catalysts, but also in explaining the different “reactive properties” of technological alumina powders used as supports in heterogeneous catalysis.

Acknowledgements

This work was supported by the Czech Grant Agency under the Grants No. 202/99/1714, and by the Czech Ministry of Education, Youth and Sports under the Project No. VS97116.

References