CO adsorption on Al₂O₃-supported Pd clusters: XPS study

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Abstract

The adsorption of carbon monoxide on small alumina-supported Pd particles have been studied by X-ray photoelectron spectroscopy (XPS). The results showed clearly different surface properties of bulk metal and supported clusters. The effect of partial CO dissociation was observed on Pd deposited on γ-alumina and on clean aluminium, but not on small Pd particles prepared on thin amorphous oxide film on Al substrate. CO–Pd interaction was determined from C 1s photoelectron spectra that exhibited two CO-related components. The dissociation activity was monitored as a rise of C 1s signal at 285 eV, while the molecularly adsorbed CO exhibited the intensity at 287 eV. The study showed that beside the particle size, the metal–substrate interaction (MSI) plays an important role in CO–Pd adsorption process. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Oxide-supported small metal particles are systems that have attracted a lot of attention because of their catalytic activity. However, studies of the industrially manufactured catalysts are not easy to perform due to their amorphous structure and great complexity. The need to understand the fundamental phenomena of catalytic behaviour of supported catalysts leads to using more simple and well-defined, so-called model catalysts.

The adsorption of CO on transition metals is the important process connected with many practical applications. Especially, the oxidation reaction:

\[ 2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2, \]

is of the particular importance in many practical applications. However, CO molecule may also dissociate partially on the surface of the catalyst, following the reaction:

\[ 2\text{CO} \rightarrow \text{CO}_2 + \text{C}. \]

Since one of the products of this reaction is carbon that remains on the surface and, consequently, occupies the chemically active surface positions, this process leads to the decay of catalytic properties. Therefore, also the investigation of eventual CO dissociation is essential in the study of a particular model catalyst.
The electronic and geometrical structure of thin metal overlayers grown on chemically dissimilar substrates which is mainly determined by the interaction with the substrate may strongly influence the mechanisms of adsorption of gases and surface catalytic processes. In recent studies, Staša et al. [1–3] reported the influence of deposit particle size and surface structure and/or stoichiometry of the substrate [4] on the mechanism of CO adsorption and catalytic oxidation on small alumina-supported Pd particles. Surprising effect of partial CO dissociation was observed on small (2.5 nm) Pd particles deposited on γ-alumina, prepared by thermal oxidation of aluminium, but not on large (27 nm) Pd particles, Pd/α-alumina model catalysts, and continuous Pd surfaces [1,2,5].

However, the question of the mechanism of dissociation process enhanced by this unexpected behaviour has not been explained yet. The possible origin of this phenomenon could be linked to the metal–substrate interaction (MSI), which may be influenced by the thickness, surface structure, and/or stoichiometry of the alumina support.

Therefore, the purpose of this work is to outline the influence of MSI on adsorption and dissociative activity of CO in the case of Pd/Al₂O₃ model catalysts. To study CO interaction with small Pd particles deposited on Al, α-Al₂O₃/Al (amorphous), and γ-Al₂O₃ substrates we have used X-ray photoelectron spectroscopy (XPS) as a powerful tool of a surface chemistry study. XPS is particularly important in this work because it probes only a few top layers of the surface and besides it gives the image of the electronic structure of the sample it is highly sensitive to the processes at gas–solid phase interface. Analysing the XP spectra detailed information regarding the chemical state, adsorption geometries, interaction strengths, etc., may be obtained.

2. Experimental

XPS spectra were collected on a vacuum system equipped with the Omicron spectrometer using dual (Al/Mg) anode X-ray monochromatized excitation source. In this work the Mg Kα line (1253.6 eV) was used for all measurements. The sample position provided 90° take-off angle between direction of analysed photoelectrons and substrate surface, whereas the incidence angle of X-ray contained 15° to the surface plane. Typical background pressures in the system during the measurements were in the range of 1–3 × 10⁻⁷ Pa.

The electron spectra were accumulated by means of a multichannel hemispherical electrostatic analyser Omicron EA 125. The analyser was operated in the retarding-field mode applying the pass energy of 20 eV. Since alumina was an insulator it induced different surface charging which led to shifts in the energy scale of the XP spectra. Therefore, the shifted spectra were referenced to the 1s line of the oxygen, which was assigned a value of 531 eV (with respect to the Fermi level).

Besides the overall wide spectrum (0 to 1000 eV BE), the valence band (VB) spectrum, photoelectron peaks of Al 2p₁/₂, O 1s, Pd 3d₅/₂, C 1s, and Auger peaks of Al (KLL) and Pd (MNN) were recorded in detail. The probable electron energy uncertainty of the spectrometer amounted to about 0.1 eV.

Determination of core-level peak positions and spectral intensities (peak areas) was accomplished after subtracting a smooth background. Peaks in a spectrum were fitted by a combination of Gauss and Lorentz curves, which also allowed one to separate overlapping peaks.

There were three different substrates [12 × 12 mm in size] studied: the pure aluminium foil (99.999%), polycrystalline Al₂O₃ (γ-Al₂O₃), and the thin amorphous Al₂O₃ (α-Al₂O₃) on Al. This oxide layer was prepared by the oxidation of a clean Al foil (natural oxide overlayer was removed by the Ar⁺ sputtering) in the pure oxygen atmosphere (5 × 10⁴ Pa) at room temperature (RT) for 10 min. The γ-Al₂O₃ substrate was prepared by heating of chemically polished Al foil in air at 900 K for 24 h before inserting into vacuum.

In order to remove surface impurities (consisting mainly of carbon), all the samples were treated by sequential annealing cycles (T = 700 K, 20–30 min, eventually in oxygen at P₀₂ = 1 × 10⁻³ Pa) and argon sputtering (P Ar⁺ = 2.5 × 10⁻³ Pa, 500 eV, 1.5 μA cm⁻², 20–30 min). Higher sputtering energies (1000–1500 eV) were applied to obtain bare aluminium surface without oxide layer. The cleanliness of the surface as well as the eventual effect of preferential sputtering of surface components, which
may cause the changes in surface stoichiometry, was monitored within the cleaning cycles by means of XPS.

Small Pd clusters were deposited on the samples in situ at RT using the micro electron beam evaporation source (MEBES) [6]. During the deposition the background pressure in the vacuum chamber was lower than $1 \times 10^{-6}$ Pa. Although this procedure caused a partial contamination of the sample with carbon, no other cleaning procedure could be applied henceforward because it could induce the modifications in the structure and/or morphology of the sample surface. The evaporation parameters (i.e., emission current and time of deposition) were kept identical for all Pd depositions although the real structure of the deposit may vary in fact, depending on the actual growth mode and the sticking probability of Pd atoms on a specific substrate. After the whole experiment the particle size was controlled by means of the Transmission Electron Microscopy using the method of the transfer carbon replica. Firstly, the XP spectra of the bare clean substrates were taken, both before and after CO exposition at partial pressure of $10^{-5}$ Pa for 100 s, corresponding to 10 L (langmuir) [1 L = $10^{-6}$ Torr s], in order to obtain the information about the interaction of the bare substrate alone with CO. After Pd deposition, the samples were exposed to 10 L of CO at RT and the XP spectra were measured. Then thermal CO exposures (i.e., continuous heating of the sample up to 600 K in the CO atmosphere, $P_{CO} = 10^{-5}$ Pa, for about 3 min) were performed.

3. Results and discussion

The XP spectra of three different samples Pd/(Al$_2$O$_3$) as well as of the reference bulk polycrystalline Pd were measured. The interaction of CO with Pd was determined from 1s line of carbon in photoelectron spectra that exhibited two CO-related components. Since the production of carbon was directly consequent to CO dissociation, the dissociation activity was monitored as a rise of C 1s signal (with peak at about 285 eV BE), while the molecularly adsorbed CO exhibited the intensity at BE of 287 eV. In some cases also metal-carbide peak appeared towards lower energies from C peak (at position of about 282 eV) but we did not use it neither for qualitative nor for quantitative analysis.

Fig. 1a and b illustrates the result of decomposition and fitting of the overlapping C-related peaks in XP spectra. The first one is the example of the sample with capability to CO molecular adsorption, therefore a distinct CO peak shifted from C 1s peak towards higher binding energies can be seen. On the contrary, the second example describes the situation when no CO adsorption at RT is observed.

From the point of view of MSI, the samples studied in this work represent three basic model situations. In the case of Pd/Al sample Pd atoms are in direct contact with Al metal support, whereas on
Pd/a-Al₂O₃/Al the Pd clusters are separated from the metal by a very thin oxide layer (1.5 nm). Finally, zero interaction with Al is provided by thick γ-Al₂O₃ substrate (approximately 10 nm). Apart from this, the latter two samples also differ from each other in their surface structure. While low temperature prepared oxide layer on Al is amorphous, γ-alumina is a polycrystalline compound with cubic structure [7].

Because in our previous TPD study the partial CO dissociation and the consequent carbon contamination have been found by cyclic CO adsorption and desorption [1], we repeated the same treatment in this work.

After exposing the pure reference Pd bulk sample by 10 L of CO, it gave a significant C CO 1s signal (relative to the CO carbon) while the atomic carbon signal was negligible. The relative “CO” intensity was constant during four adsorption/desorption cycles and kept the value \( \frac{I_C}{I_{Pd}} = 0.005 \pm 0.0002 \). It should be noted that the relative values of \( \frac{I_C}{I_{Pd}} \) better expresses the surface composition than the absolute adsorbate signal because there is not influence of possible fluctuation of the primary X-ray source intensity. We can see that this “reference” experiment confirmed well-known fact that CO adsorption on bulk Pd is molecular. At the same time it proved a good stability of our experiment and no contamination given by the vacuum system hydrocarbons, etc.

The plot in Fig. 2 presents the relative quantity of atomic carbon relative C 1s intensity on the surface for all studied samples. The starting points \( (n = 0) \) of each curve correspond to the initial situation, i.e., immediately after the Pd deposition and consequent adsorption of 10 L of CO \( (P_{CO} = 10^{-5} \text{ Pa}) \) for 100 s. The next points were obtained after the cycles of CO desorption (heating up to 600 K) followed by the simple CO exposition of 10 L after cooling down the sample to ambient temperature. The quantities are calculated as the C peak area related to the peak area of the palladium, in order to make them mutually comparable in the meaning of relative surface concentration of carbon. The direct comparability of the results for different samples is not possible due to the different structure of Pd deposits for different samples. Pd formed an alloy with the Al substrate, the average particle size for γ-alumina and a-alumina substrate was 2.5 and 6 nm, respectively. All the substrates exhibited a specific initial contamination with carbon (given by the cleanliness of substrates, methods of sample preparation) which contribution was not separated from the measured values.

There are several eventual contributions to changes of C 1s photoelectron signal. Firstly, the change of C 1s peak intensity can be partially caused by the effect, which is linked to the thermally and adsorption induced changes in palladium deposit population. The freshly deposited Pd particles are not stable and therefore the thermal and/or adsorption treatments may lead to the particle coalescence and structure rebuilding (i.e., atomic reordering, changes in the Pd island shape, etc.) [7,8]. This effect corresponds to the changes of photoelectron signal from Pd relative to the Al signal, \( \frac{I_{Pd}}{I_{Al}} \), which were observed for all investigated samples, as can be seen in Table 1. Because these changes were not important we can suppose that the \( \frac{I_C}{I_{Pd}} \) ratios were not affected by the Pd surface structure changes.

Secondly, the possibility of the eventual contribution of Pd-uncovered substrate surface to the photoelectron signals of C and CO evocated the need for some few assumptions in order to allow clear interpretation and quantification of the results. It was presumed that the only localities for eventual CO adsorption and dissociation are the “active” sites,
Table 1
The changes in relative Pd signal after several treatments

<table>
<thead>
<tr>
<th>Treatment procedure</th>
<th>(R_{\text{Pd}}/R_{\text{Al}})</th>
<th>(\text{Pd/Al})</th>
<th>(\text{Pd/}\alpha\text{-Al}_2\text{O}_3/\text{Al})</th>
<th>(\text{Pd/}\gamma\text{-Al}_2\text{O}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd deposition</td>
<td>0.216</td>
<td>0.631</td>
<td>0.258</td>
<td></td>
</tr>
<tr>
<td>CO exposition</td>
<td>0.215</td>
<td>0.617</td>
<td>0.252</td>
<td></td>
</tr>
<tr>
<td>10 L at RT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heating to 600 K</td>
<td>0.207</td>
<td>0.546</td>
<td>0.233</td>
<td></td>
</tr>
<tr>
<td>+ CO exposition</td>
<td></td>
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</tr>
</tbody>
</table>

i.e., these on the surface of Pd islands and/or at the Pd–Al atomic interface. This assumption was easy to verify performing the CO exposition to the bare substrate under the same conditions as described for a regular experiment. None of the three samples exhibited CO adsorption or CO dissociation.

The other contribution could be the contamination with carbon due to the thermal diffusion from bulk to the surface. This was checked by making the same heating procedure as described above, only without CO exposition, with a clean substrate (without deposited Pd). The increase of C signal (relative to Al signal) was, if any, so small that any eventual bulk diffusion of carbon may be omitted. Furthermore, it was assumed that carbon atoms do not diffuse along the surface in so far as they would move away from the positions of their origin.

3.1. Pd/Al

At RT, the deposited Pd intermixes with the Al substrate and forms a thin surface alloy which consists of PdAl\(_x\) and PdAl intermetallic compounds [9] having “noble metal” properties. This phenomenon was indicated in XP spectra by the large positive shifts of core and valence levels of Pd adatoms with respect to those of pure bulk Pd [10]. For deposited Pd, a correlation has been found between the electronic perturbations in the Pd 3d\(_{1/2}\) core level and the strength of the bimetallic bond. The charge redistribution from Pd toward the Al substrate weakens the strength of CO–Pd bonding and, consequently, decreases the adsorption energy [10]. For this reason, the CO adsorption may appear below RT. It corresponds to our results showing no evidence for molecular CO adsorption at RT after the dosing of 10 L of CO, whereas CO adsorbs on bulk Pd at RT.

As can be seen in Fig. 2, the relative changes in \(I_{\text{C}}(\text{CO})/I_{\text{Pd}}\) intensity indicated that the catalytic activity of the Pd–Al bimetallic surface for the CO dissociation was relatively large even though CO did not adsorb at RT. It can be explained by the fact that the decrease of the activation energy of CO desorption is accompanied by a simultaneous decrease of the activation energy of dissociation on the bimetallic Pd/Al system.

3.2. Pd/\(\gamma\text{-Al}_2\text{O}_3\)

The only molecular CO adsorption was observed on \(\gamma\)-alumina-supported Pd clusters reaching the value \(I_{\text{C}}(\text{CO})/I_{\text{Pd}} = 0.03\). During the adsorption/desorption cycles the carbon relative ratio \(I_{\text{c}}(\text{CO})/I_{\text{Pd}}\) increased from the initial value of 0.047 to the final value of 0.077 (see Fig. 2), which was in agreement with previous studies [1,3] giving a clear evidence for CO dissociation. Considering the initial value given by the residual carbon remaining on the alumina substrate only, the \(I_{\text{c}}(\text{CO})/I_{\text{Pd}}\) variations corresponded to the increase of carbon concentration on the Pd particle surface. Because of known CO adsorption stoichiometry on 2.5 nm particles supported on \(\gamma\text{-Al}_2\text{O}_3\) [1] giving the relative CO coverage \(\theta_{\text{CO}} = 0.5\) at the CO saturation, we were able to use the \(I_{\text{c}}(\text{CO})/I_{\text{Pd}}\) value for the carbon concentration calibration (0.03 corresponded to \(\theta_{\text{CO}} = 0.5\)). In Fig. 3, we plotted the relative atomic carbon coverage.

![Fig. 3. Relative carbon surface coverage after cycles of CO adsorption on Pd/\(\gamma\text{-Al}_2\text{O}_3\) sample.](image-url)
(with respect to the Pd surface atoms) vs. number on cycles $n$. It can be seen that after five cycles, the carbon $\theta_C$ reached the value of 0.5 indicating relatively high dissociation activity of Pd clusters. It should be noted that the particle structure and size stability was the necessary condition permitting this quantification of the XP signal ratios.

3.3. Pd/$a$-Al$_2$O$_3$/Al

The Pd/$a$-Al$_2$O$_3$/Al model system can be considered as a bimetallic system where the two metals are separated by a thin oxide. Applying the quantitative analysis [11] of both Al metallic and oxide peaks in XP spectra, the thickness of the alumina layer was estimated at 16 Å. Therefore, an indirect interaction of Pd clusters with Al underlying substrate may be expected, apart from the influence of the oxide structure alone.

The $I_C$ (CO)/$I_{Pd}$ ratio exhibited the value of 0.035 indicating the ability of the Pd/$a$-Al$_2$O$_3$/Al sample toward CO adsorption. On the other hand, the appropriate curve in Fig. 2 shows no variation of surface atomic carbon concentration — the intensity of C peak remained constant after both CO expositions at room and elevated 600 K temperatures. It indicated the lack of CO dissociative process on the surface of Pd/$a$-Al$_2$O$_3$/Al, which was probably the result of Pd–Al electronic interaction mentioned above, only in some way modified by the presence of separating thin oxide film. This hypothesis was supported by the considerable differences in the valence band structure of the three samples (not presented in this paper).

4. Summary

There were three model catalysts, based on Pd-supported particles, studied by means of photoelectron spectroscopy. The capability for molecular adsorption of CO at RT was observed on both Pd/$a$-Al$_2$O$_3$/Al and Pd/$\gamma$-Al$_2$O$_3$ samples, but not on Pd/Al because of the strong electronic interaction of deposited Pd with Al that weakened the strength of CO–Pd bonding.

There is an evidence for partial CO dissociation on Pd/$\gamma$-Al$_2$O$_3$ and Pd/Al, while no dissociative activity was observed on Pd/$a$-Al$_2$O$_3$/Al sample.

One can conclude that Al–Pd bimetallic interaction affects considerably the CO adsorption and dissociation properties of catalysts. The different behavior of the “thin” and “thick” alumina film substrates could be explained by both bimetallic interaction and/or substrate structural effect. However, an extended experimental study is needed to distinguish and better understand these effects.

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References