XPS INVESTIGATIONS OF Pt AND Rh SUPPORTED ON $\gamma$-$\text{Al}_2\text{O}_3$ AND TiO$_2$

Eindhoven University of Technology, Laboratory of Inorganic Chemistry, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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An XPS investigation of Pt and Rh supported on $\gamma$-$\text{Al}_2\text{O}_3$ and TiO$_2$ was performed in order to establish the differences in metal-support interactions. The binding energies of the core levels of the supported metal particles were found to vary as a function of the dispersion of the supported metal, with the highest binding energy for the highest dispersion. This binding energy variation is caused by differences in the extra-atomic relaxation of metal particles of different sizes. In small particles there is a less effective screening of the core holes created during photoemission. For Pt/TiO$_2$ catalysts pretreated below 1015 K, slightly higher binding energies were found than for Pt/Al$_2$O$_3$ catalysts after comparable pretreatments. No differences in binding energies could be observed between Rh/TiO$_2$ and Rh/Al$_2$O$_3$ over a wide range of dispersions. In situ reduction of M/TiO$_2$ at 523 or 823 K led to essentially the same binding energy. These results show that there is no significant electron transfer from Ti$^{3+}$ to metallic platinum or rhodium. Consequently the strongly reduced chemisorption properties of metals on TiO$_2$, observed after high temperature reduction (SMSI), cannot be due to negatively charged metal atoms. For M/TiO$_2$ samples pretreated above 1015 K, an increase in binding energy of the metal core levels is found in combination with a decrease in dispersion of the metal. This behaviour is explained by encapsulation and spalling of the metal particles during an observed anatase-to-rutile phase transformation.

1. Introduction

The importance of X-ray Photoelectron Spectroscopy in the characterization of supported catalysts has been demonstrated by several authors. For instance Shpiro et al. used XPS to determine differences in the reduction behaviour of Re/SiO$_2$ and Re/Al$_2$O$_3$ catalysts [1]. Chin and Hercules [2] used XPS to follow the extent of diffusion of Co ions into the $\gamma$-$\text{Al}_2\text{O}_3$ matrix as a function of calcination temperature and metal loading. Recently Carvalho et al. [3] presented XPS evidence for the existence of two different rhodium species in

* Present address: Koninklijke/Shell-Laboratorium, Badhuisweg 3, 1031 CM Amsterdam, The Netherlands.
** To whom correspondence should be sent.
Wilkinson's catalyst. The authors concluded that apart from RhCl(PPh₃)₃ also a Rh(III)-oxygen complex is present, which is relatively inactive as a hydrogenation catalyst. Apart from monometallic also bimetallic catalysts have been investigated with XPS. Especially surface enrichment phenomena have been studied extensively [4–6].

XPS can also be used in the study of the electronic structure of monometallic catalysts. Such a study is hampered, however, by the difficulty of separating the influences of metal particle size and of metal–support interactions on the observed binding energy [7]. In 1973 Ross et al. [8] presented XPS data for reduced Pt/SiO₂ samples. The Pt 4f electron binding energy in Pt/SiO₂ indicated an apparent chemical shift of +1.5 eV (to higher binding energy) as compared with platinum foil. On a conductive carbon support this shift was only 0.4 eV. The shift in Pt/C might indicate a net electron transfer from platinum to the support, whereas most of the shift in Pt/SiO₂ was, according to Ross et al., produced by partially uncompensated charging. Also in other papers, higher core level binding energies than that of the bulk metal have been presented for supported metal catalysts. Thus Vedrine et al. [9] reported for atomically dispersed Pt⁰ and Pd⁰ in Y zeolites a shift of +1.3 eV for the Pt 4f and of +1.4 eV for Pd 3d levels and ascribed them to relaxation effects. Aggregates of platinum in the zeolite were found to have a shift of 0.7 eV, but in this case charge transfer from the aggregates to the Lewis acid sites of the zeolite framework was claimed to be important as well. Pederson and Lunsford [10] observed for ruthenium systems in Y zeolites, in analogy with Vedrine et al., a shift of +0.9 eV. Biloen et al. [11] observed shifts of +0.6 eV in binding energies for Pt 4f electrons in reduced Pt/SiO₂ systems. Addition of rhenium to this catalyst further increased the shift to 1.0 eV. In all these studies the influences of metal–support interaction and of metal particle size on the binding energy could not be separated.

In this investigation we will present data for series of platinum and rhodium catalysts supported on γ-Al₂O₃ and TiO₂. By varying systematically the dispersion of the metals on the supports we have tried to separate the effects of metal particle size and of metal–support interaction. Differences, if found, between the binding energies of metal particles of the same size but on different supports can be indicative for metal–support interactions. A special reason for choosing TiO₂ as a support is the fact that the so-called strong metal-support interaction (SMSI) [12], which is very pronounced with this support, is not well understood yet.

2. Experimental

The aluminum oxide used was γ-Al₂O₃ (Akzo 000-1.5 E) with a surface area of 195 m² g⁻¹ and a pore volume of 0.6 cm³ g⁻¹. The titanium dioxide used
was anatase (Tioxide Ltd. CLDD 1367) with a surface area of 50 m² g⁻¹ and a pore volume of 0.9 cm³ g⁻¹. Platinum was deposited on the supports by means of a combined ion exchange and wet impregnation method: known amounts of Pt(NH₃)₄(OH)₂ solutions were added to well-stirred aqueous slurries of supports and stirring was continued for 6 h. Subsequently the water was evaporated by slowly heating to 363 K at reduced pressure. Rhodium samples were prepared by the standard pore volume impregnation method. The samples were dried at 393 K after impregnation.

To obtain a variety of dispersions, two methods were used. The γ-Al₂O₃ supported samples were sintered in a flow of hydrogen at different temperatures, always for 1 h. After sintering the samples were cooled in hydrogen and then passivated at room temperature in nitrogen by slowly admitting small amounts of oxygen. In another method, a dispersion variation was obtained by changing the metal content in Rh/TiO₂ samples. These samples were reduced at 773 K and passivated as described above. Metal contents for all the samples were determined spectrophotometrically [13]. Following on the reduction and passivation, the dispersion (total amount of chemisorbed hydrogen atoms per metal atom (H/M)ₜ) was determined with hydrogen chemisorption in a conventional volumetric system, after rereduction in situ at 473 K. According to our TPR studies of passivated catalysts this temperature is sufficient to attain a complete reduction of the Pt as well as the Rh particles.

XPS measurements were carried out on a Physical Electronics 550 XPS/AES spectrometer equipped with a magnesium anode (hv = 1253.6 eV) and a double pass cylindrical mirror analyzer. A PDP 11-04 computer interfaced with the XPS apparatus enabled signal averaging to be carried out. Prior to the measurements, the passivated powdered samples were pressed on a stainless steel grid, which was mounted onto a heatable transfer rod (fig. 1). The samples were rereduced in flowing hydrogen at various temperatures on the transfer rod in a preparation chamber attached to the UHV work chamber.

![Fig. 1. Heatable sample holder in its experimental set-up during XPS measurements.](image)
After reduction the samples were cooled under hydrogen to 293 K and evacuated in the preparation chamber to 66 mPa (0.5 m Torr). Then the transfer rod was transported via a gate valve to the work chamber and positioned in front of the analyzer and X-ray source with the aid of a 2000 eV electron beam. The pressure during the measurements did not exceed $6.6 \times 10^{-6}$ Pa and the temperature was approximately 313 K. The analyzer was frequently and carefully calibrated with a gold sample (Au 4f$_{7/2}$ at 83.8 eV) and with a copper sample (Cu 2p$_{3/2}$ at 932.4 eV and Cu 3p$_{3/2}$ at 74.9 eV). During the measurements a flood gun was used to avoid charging. The binding energies referenced to the Fermi level were calibrated by putting the C 1s energy at 284.6 eV. The Al 2p (74.40 eV) and the Ti 2p$_{3/2}$ (458.70 eV) levels were used as an additional check on the carbon reference level. Binding energies for these levels were found to be constant within 0.1 eV. For instance for six samples of the same TiO$_2$ catalyst the Ti 2p$_{3/2}$ level was found at 458.70 ± 0.04 eV.

3. Results and discussion

3.1. Pt/Al$_2$O$_3$

The impregnated and dried Pt/Al$_2$O$_3$ sample gave an XPS spectrum with clearly resolved O 1s, 2s and KLL peaks, Al 2s and 2p peaks, N 1s and C 1s peaks, and Pt 4d peaks. The Pt 4f doublet in Pt/Al$_2$O$_3$ could not be observed because it was completely masked by the Al 2p line. Therefore for quantitative measurements of Pt on Al$_2$O$_3$ the Pt 4d doublet had to be used. From the intensities of the various lines and using Scofield’s cross sections [14] we calculated an atomic N/Pt ratio of 1.4. This is in agreement with our expectation for adsorption of the Pt(NH$_3$)$_2^{2+}$ complex in aqueous solutions onto the Al$_2$O$_3$ support. For it is likely that an acidic hydroxyl group of the γ-Al$_2$O$_3$ surface protonates a NH$_3$ ligand, while the complex is anchored to the surface [15]:

$$x [O_s]H + Pt(NH_3)_2^{2+} \rightarrow [O_s]_xPt(NH_3)_{(2-x)}^{(2-x)+} + x NH_4^+,$$

where $[O_s]$ stands for a surface anion. The low N/Pt ratio indicates that already two to three NH$_3$ ligands have been removed from the original complex. For the untreated Pt/TiO$_2$ we find a N/Pt ratio of 3.3, which means that in this case on the average only about one NH$_3$ ligand has left the complex. This difference in N/Pt ratio can be understood when taking into account the difference in surface areas and in acidity of the OH groups of both supports.

In table 1 the XPS results are presented for the Pt/Al$_2$O$_3$ samples which had been prereduced, passivated and rereduced in situ in the XPS apparatus.
Table 1
Hydrogen chemisorption data and binding energies of 5.2 wt% Pt/Al₂O₃ catalysts with different dispersions obtained by sintering at varying temperature

<table>
<thead>
<tr>
<th>Prereduction temperature (K)</th>
<th>Dispersion (H/M)</th>
<th>$E_b$ (eV) Pt 4d$_{5/2}$ reduced in situ at 583 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>588</td>
<td>0.99</td>
<td>314.45</td>
</tr>
<tr>
<td>908</td>
<td>0.87</td>
<td>314.35</td>
</tr>
<tr>
<td>1003</td>
<td>0.79</td>
<td>314.30</td>
</tr>
<tr>
<td>1058</td>
<td>0.55</td>
<td>314.15</td>
</tr>
<tr>
<td>1100</td>
<td>0.45</td>
<td>314.10</td>
</tr>
</tbody>
</table>

a) Untreated sample.
b) Pt foil.

In all samples the 4d$_{5/2}$–4d$_{3/2}$ doublet separation is the same (17.1 eV). After the primary reduction no nitrogen is found anymore in the XPS spectrum. After reduction at 588 K the position of the Pt 4d$_{5/2}$ level shifted from 315.50 eV for the unreduced sample to 314.45 eV, which means that the electronic configuration had changed. From temperature programmed reduction studies we know that at this temperature the complex is completely reduced to metallic platinum.

When plotting the 4d$_{5/2}$ binding energy as a function of dispersion a continuous decrease in 4d binding energy with decreasing dispersion for the

![Graph](image-url)  

Fig. 2. Pt 4d$_{5/2}$ binding energy of Pt/Al₂O₃ catalysts as a function of dispersion. Spectra have been taken after in situ rereduction at 583 K.
Pt/Al₂O₃ samples is observed (fig. 2). Note that the more severely sintered platinum particles had the lower binding energy. The Pt 4d₅/₂ value of the sputter cleaned foil (314.00 eV) measured with the same experimental set up was not reached with this series. This observation can be explained in four different ways, of which the first three are based on initial-state effects.

At the metal-support interface, charged platinum species are present as has previously been demonstrated by ESR [16]. Assuming that the metal-support interface determines the number of Pt ions, this means that the electrostatic potential of the metal particles (and consequently the binding energy) is a function of the metal crystallite size. However, the total number of platinum ions is limited. From ESR measurements it has been concluded that 0.4% of the platinum atoms were in the +1 oxidation state while Pt²⁺ ions (diamagnetic) cannot be detected with ESR. Therefore the resulting shift in binding energy cannot be as large as 0.5 eV because as a rule of thumb in XPS, core-levels shift 1 eV per oxidation step. This is particularly true for platinum [17].

A second initial state explanation might be found in the chemisorption of hydrogen. Since hydrogen is thought to be slightly electronegative [18] it might draw electronic charge from the surface metal atom to which it is bound, thereby inducing a shift towards higher binding energy. Note that this shift will follow the observed trend of increasing magnitude with increasing dispersion. For single crystals of W and Ir the negative surface core-level shift is indeed diminished by hydrogen chemisorption [19]. We do not favour this explanation because the hydrogen coverage is not enough to account for the observed shifts. Although we did not intend to desorb hydrogen from the surface of the noble metal particles in the catalyst samples, the low pressure during the XPS measurements (p < 6.6 × 10⁻⁶ Pa) took care of substantial desorption. From results published by Crucq et al. on Pt/Al₂O₃ over a large pressure range [20], we infer that in our samples the metal surface coverage by hydrogen was smaller than 30%. Since full coverage is expected to lead to shifts of a few tenths of an eV [19], the low hydrogen coverages present during our experiments will at maximum only have contributed 0.1 eV to the shift of the catalysts with the highest dispersion. The observed shifts being much larger, we reject the residual chemisorbed hydrogen as the cause of the core-level shifts.

A third initial state effect that might play a role in determining the binding energy of small metal particles is the phenomenon of surface core-level shifts [18,19,21–23]. We may speculate whether or not surface core-level shifts play a role in our systems. To be able to observe surface core-level shifts a surface sensitive mode of measurement is of primary importance. Thus mean free paths for inelastic scattering of the ejected photoelectrons of 3 Å are required. This certainly cannot be attained with the Mg Kα XPS measurements of Pt 4d core-levels. Electrons from this level have a kinetic energy of 940 eV and hence their mean free path will be much too large to allow surface sensitive
measurements. On the other hand, our systems are in some cases highly dispersed, so that a substantial fraction of the Pt 4d electrons comes from surface atoms. However, the shifts measured in Pt/Al₂O₃ samples as well as in Pt/TiO₂ are “positive” (towards higher binding energies), while the core-level shifts observed for the surface atoms in single crystals were negative (towards lower binding energy). We therefore conclude that the observed shifts in binding energy of our samples are not due to initial state effects caused by surface band narrowing.

This leaves the fourth explanation, a final state effect, as the most probable and main origin of the observed core-level shifts. Because of screening of the core-hole by the electrons of neighbouring atoms the apparent binding energy is lowered. This lowering is maximum for bulk metal atoms, because there are more neighbouring atoms and thus more electrons to screen. In smaller particles this core-hole screening will be less effective than in larger particles [24,25]. Consequently the apparent binding energies of core-levels in small particles will be higher than those in large particles. This interpretation is consistent with those of Oberli et al. [7] for Au/C and of Mason et al. [26] for Ag/C. Recently Baetzold measured the 5d band of platinum as a function of particle size [27]. Again, as in our case, the d-band shifted towards lower binding energy with increasing size of the metal particles, independent of the type of carrier, initial state, etc., as one would expect for a final state effect.

3.2. Pt/TiO₂

The results for the TiO₂-supported platinum samples are presented in table 2. For Pt/TiO₂ samples there is no overlap between Pt 4f and substrate lines so

<table>
<thead>
<tr>
<th>Prereduction temperature (K)</th>
<th>Dispersion (H/M)₁</th>
<th>$E_b$ Pt 4d$_{5/2}$ (eV)</th>
<th>$E_b$ Pt 4f$_{7/2}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>RIS $^a$ RIS</td>
<td>523 K 823 K</td>
</tr>
<tr>
<td>818</td>
<td>0.65</td>
<td>315.60 $^b$</td>
<td>314.60</td>
</tr>
<tr>
<td>945</td>
<td>0.27</td>
<td>314.35 314.30</td>
<td>314.30</td>
</tr>
<tr>
<td>1015</td>
<td>0.27</td>
<td>314.25 314.20</td>
<td>71.10 71.00</td>
</tr>
<tr>
<td>1143</td>
<td>0.16</td>
<td>314.40 314.40</td>
<td>71.20 71.20</td>
</tr>
</tbody>
</table>

$^a$ RIS = rereduced in situ.

$^b$ Untreated samples.

$^c$ Pt foil.
that the Pt 4f lines can be measured as well. This is important because the 4f lines are much narrower than the 4d lines. We observe, however, that both the 4f and 4d levels behave identically. In table 2 the binding energy values are also given for samples reduced in situ at temperatures high enough to cause the so-called strong metal-support interaction (SMSI). This SMSI state is characterized by its anomalous hydrogen and carbon monoxide chemisorption

Fig. 3. Pt 4d_{5/2} binding energy of Pt/TiO_2 catalysts as a function of dispersion: (×) re-reduced in situ at 523 K; (○) re-reduced in situ at 823 K; (□) points for Pt/Al_2O_3.

Fig. 4. Pt 4f_{7/2} binding energy of Pt/TiO_2 catalysts as a function of dispersion: (×) re-reduced in situ at 523 K; (○) re-reduced in situ at 823 K; (□) extrapolated curve for Pt/Al_2O_3.
behaviour: When TiO$_2$ supported 4d and 5d group-VIII-metals are reduced at high temperatures (773 K) they lose their ability to chemisorb H$_2$ or CO, although the metal particle size has not changed [12]. In figs. 3 and 4 the Pt 4d$_{5/2}$ and Pt 4f$_{7/2}$ binding energies are plotted as a function of the dispersion. As in case of Pt/Al$_2$O$_3$ there is a decrease of binding energy with decrease in dispersion. With prereduction temperatures above 1015 K ((H/M)$_i$ < 0.27), however, a slight increase is found. Again no variation in the spin–orbit coupling of both the doublets, nor in the linewidths was found. For comparison the 4d$_{5/2}$ line of Pt/Al$_2$O$_3$ has been replotted in fig. 3, while in fig. 4 a Pt 4f line is plotted which is calculated from the Pt/Al$_2$O$_3$ 4d results and the Pt/TiO$_2$ 4f–4d energy difference. If the core levels feel the same innerpotential (as illustrated for Pt/TiO$_2$) then this line is the one to be expected for the Pt 4f$_{7/2}$ electron binding energies in Pt/Al$_2$O$_3$. From the data it is obvious that the binding energies of all reduced Pt/TiO$_2$ samples are slightly higher than those of corresponding Pt/Al$_2$O$_3$ samples taken at the same dispersion. No pronounced differences are observed between the high- and low-temperature reduced Pt/TiO$_2$ samples. This means that particles with the same size, as deduced from hydrogen chemisorption, have nearly equal binding energies, irrespective of the heat treatment. Thus the electronic configuration of the small particles should be almost the same after the low- and high-temperature reduction treatment. Changing the support (at the same dispersion) does not alter the platinum binding energies substantially. For the 4d energies a shift of 0.2–0.3 eV is found, whereas for the Pt 4f a shift of 0.1–0.2 eV is observed. In all cases the binding energies of the Pt/TiO$_2$ samples are higher than those of the Pt/Al$_2$O$_3$ samples.

The increase of the binding energies at low (H/M)$_i$ values is due to a phase transition of the support. X-ray diffraction studies demonstrated that after treatment in hydrogen above 1015 K the anatase has been transformed to the energetically more favourable rutile structure. For these samples temperature programmed reduction studies demonstrated that the metal particles are encapsulated in the final rutile structure and shielded from gases [28]. As a result the (H/M)$_i$ values decrease. From the observed increase in binding energies it is inferred that during encapsulation a concurrent spalling of the metal particles occurs.

Our XPS results demonstrate that in all cases the binding energies of the Pt/TiO$_2$ samples are higher than those of the Pt/Al$_2$O$_3$ samples and that there are no pronounced differences between the Pt/TiO$_2$ samples reduced at high- or low-temperature. These results suggest that the charge on the platinum atoms in Pt/TiO$_2$ samples is not very much different from that on platinum atoms in Pt/Al$_2$O$_3$ samples. If differences do exist at all, our results indicate that the charge is more positive for the platinum atoms in Pt/TiO$_2$ than in Pt/Al$_2$O$_3$.

This conclusion is in contradiction with two recent claims in the literature,
but it is in good agreement with recent studies of the intensity of Pt white lines. We will first discuss the results apparently contradicting our results and conclusions.

Recently Fung [29] performed XPS measurements for Pt/TiO₂. A Pt/TiO₂ sample was prepared by depositing 75 nm of TiO₂ on a stainless-steel foil, followed by vapour deposition of a “one atom” thick platinum layer on top of the oxide. After transportation to the XPS apparatus (no reduction treatment is mentioned) the resulting platinum film had a 4f₁/₂ binding energy of 72.7 eV. We believe that this value is due to a platinum oxide, whereas Fung ascribes it to metallic platinum which is able to chemisorb hydrogen. Reduction in situ at 623 K decreased the binding energy to 71.1 eV. Further reduction at 873 K did not result in any shift. According to Fung platinum is unable to chemisorb hydrogen when only the low binding energy peak is observed. The shift from 72.7 to 71.1 eV was thought to be due to electron transfer from the support to the metal. The reported values are, however, above the values for Pt foil and can therefore without further proof hardly be taken as evidence for negatively charged platinum atoms. Furthermore, from the work of Tauster [12] it is known that after reduction at 623 K still hydrogen chemisorption occurs, which makes the conclusions of Fung even more questionable. Also with Pt/TiO₂ prepared from Degussa P25 TiO₂ powder Fung observed two peaks at 72.5 and 71.1 eV after reduction at 423 K (in situ?) and 473 K. Further reduction at 823 K resulted in a single 4f₁/₂ peak at 71.1 eV. Again Fung ascribed the high energy level to platinum which is still able to chemisorb hydrogen, while the low 4f₁/₂ level was supposed to be due to platinum in the SMSI state. From our TPR studies [30] it follows that after treatment with hydrogen at 423 or 473 K the reduction is not complete, which means that indeed two platinum species can be present: an oxidic form and a metallic one.

Other XPS studies on the SMSI behaviour were performed by Chung and co-workers [31–34]. The authors studied the platinum–SrTiO₃(100) interface and the nickel–rutile (100) and (110) interface. They prepared their supports (e.g. SrTiO₃ and TiO₂) from single crystals which were reduced in vacuum at 723 and 673 K, respectively. Subsequently they deposited various layer thicknesses of Pt and Ni on the crystals, but never reduced the supported metals at elevated temperatures, although high temperature reduction is generally believed to be the prerequisite for the induction of SMSI properties. For “monolayer” coverages of Pt and Ni they concluded from the chemical shifts of the core-levels after taking into account the effects of relaxation that charge transfer of 0.6 electron had occurred from SrTiO₃ to Pt, and 0.13 electron from TiO₂(110) to Ni. For Ni/TiO₂ they concluded also that the charge per nickel atom falls off rapidly from 0.15 at the interface to essentially zero for atoms at a few layers distance from the interface.
Their conclusions were based on the validity of the following expressions for the energy shifts:

\[ \Delta BE = \Delta E - \Delta R + \Delta E_{\text{bending}}, \]
\[ \Delta KE = -\Delta E + 3\Delta R + \Delta E_{\text{bending}}. \]

In these formulae \( \Delta BE \) is the shift in XPS binding energy, \( \Delta E \) is the chemical shift due to changes in the initial state charge distribution, \( \Delta R \) the relaxation shift, \( \Delta E_{\text{bending}} \) the band bending shift and \( \Delta KE \) is the kinetic energy shift of an Auger line. In the derivation of these formulae it is assumed that the final state two-hole relaxation energy is \( 2\Delta R \). However, Thomas [35] has recently pointed out that especially for small metal particles or isolated atoms this is certainly not a valid approximation and corrections up to 3 eV are necessary. With such correction terms even a reversed charge transfer from the metal to the support may be derived from the data discussed by Chung and co-workers. We therefore believe that neither the XPS study of Fung nor the XPS studies of Chung et al. constitute proof for the hypothesis that metal particles on TiO\(_2\) in the SMSI state are negatively charged.

This conclusion can further be justified by the results of a X-ray absorption edge study [36]. From the area of the \( L_{\text{III}} \) and \( L_{\text{II}} \) absorption edges in Pt/TiO\(_2\) (a measure for the total number of d holes) it was concluded that a small positive charge is present on the platinum atoms and that this charge was only slightly more positive than that in platinum atoms in Pt/Al\(_2\)O\(_3\). This observation is in full agreement with our findings of higher 4f\(_{7/2}\) binding energies in Pt/TiO\(_2\).

3.3. Rh/Al\(_2\)O\(_3\) and Rh/TiO\(_2\)

The results for Rh/Al\(_2\)O\(_3\) are presented in table 3. Again as in the Pt/Al\(_2\)O\(_3\) case, a continuous decrease is found in binding energy with increasing particle size (fig. 5). It seems that the maximum relaxation shift for platinum and rhodium does not exceed 0.5 eV, assuming that maximum dispersions have been reached indeed. Note, however, that the increase in binding energies for Pt/Al\(_2\)O\(_3\) starts at lower (H/M)\(_1\) values than for the Rh/Al\(_2\)O\(_3\) samples. How can this be explained? Without any further information on the metal particle size, obtained via other methods like transmission electron microscopy it seems precarious to answer this question definitively, but some speculations can be put forward. The maximum dispersion values of Rh/Al\(_2\)O\(_3\) and Pt/Al\(_2\)O\(_3\) differ by almost a factor of two, although the total numbers of metal atoms per square nanometer Al\(_2\)O\(_3\) surface area do not differ much. This means that either the metal–support interactions in Rh/Al\(_2\)O\(_3\) are different from those in Pt/Al\(_2\)O\(_3\) or the structure of supported rhodium is completely different from that of supported platinum. The first explanation
does not seem very likely in view of our ESR results [16]. These measurements demonstrated that in both cases positively charged ions are present at the metal–support interface, which is an indication for comparable metal–support interactions. The second explanation is more likely. The observed (H/M) values of supported rhodium exceed 1, which means that multiple hydrogen chemisorption takes place. Also other workers often report high H/Rh values [36]. The occurrence of multiple hydrogen chemisorption precludes the calculation of the correct number of surface atoms and consequently the H/M value cannot be directly related to the metal particle size. If for example the structure of supported rhodium is much more open than that of platinum, with many

Table 3
Hydrogen chemisorption data and binding energies of Rh/AI₂O₃ catalysts with different dispersions obtained by sintering at varying temperature

<table>
<thead>
<tr>
<th>Rh (wt%)</th>
<th>Prereduction temperature (K)</th>
<th>Dispersion (H/M)</th>
<th>$E_b$, Rh 3d₅/₂ reduced in situ 573 K (eV)</th>
</tr>
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<tbody>
<tr>
<td>2.3</td>
<td>473</td>
<td>1.70</td>
<td>307.45</td>
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<tr>
<td>2.3</td>
<td>773</td>
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<td>307.35</td>
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<td>2.3</td>
<td>873</td>
<td>1.33</td>
<td>307.25</td>
</tr>
<tr>
<td>2.3</td>
<td>973</td>
<td>1.23</td>
<td>307.20</td>
</tr>
<tr>
<td>2.3</td>
<td>1073</td>
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<td>307.10</td>
</tr>
<tr>
<td>0.5 a)</td>
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</tr>
<tr>
<td>Rh foil</td>
<td>–</td>
<td>–</td>
<td>307.00 b)</td>
</tr>
</tbody>
</table>

a) Support used was γ-Al₂O₃ from Martinswerk.
b) Literature value [14].
Table 4
Hydrogen chemisorption data and binding energies of Rh/TiO₂ catalysts with different dispersions obtained by sintering at varying temperature and by a variation in metal loading.

<table>
<thead>
<tr>
<th>Rh (wt%)</th>
<th>Prereduction temperature (K)</th>
<th>Dispersion (H/M)</th>
<th>$E_b$ Rh 3d₅/₂ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>RIS 483 K</td>
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<tr>
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<td>3.2</td>
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<td>0.17</td>
<td>307.70</td>
</tr>
<tr>
<td>3.2</td>
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<td>307.40</td>
</tr>
<tr>
<td>8.1</td>
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<tr>
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<tr>
<td>0.3</td>
<td>773</td>
<td>1.41</td>
<td>307.25</td>
</tr>
</tbody>
</table>

Crystal stacking faults and defects, then a different chemisorption behaviour could result. In that case higher H/M values will be observed for the rhodium catalyst due to the large number of highly coordinatively unsaturated atoms, while the particle sizes of the Rh and Pt catalysts are comparable. This will result in a higher H/M value for Rh than for Pt at comparable binding energies. As already stated above, further independent measurements on the particle size and shape are necessary to solve this question.

The results for the various TiO₂ supported rhodium samples are presented in table 4. As explained in the experimental section two series of Rh/TiO₂ catalysts were prepared. First of all a series in which the dispersion is varied by changing the metal content. All samples were prereduced at 773 K and passivated at room temperature prior to reduction in the preparation chamber.

![Figure 6](image-url)

Fig. 6. Rh 3d₅/₂ binding energy of Rh/TiO₂ catalysts as a function of dispersion (varying metal content): (×) rereduced in situ at 483 K; (●) rereduced in situ at 823 K; (---) curve for Rh/Al₂O₃.
of the XPS apparatus. The results for this series of catalysts are given in fig. 6. The resemblance between the Rh/Al$_2$O$_3$ and Rh/TiO$_2$ results is obvious. Both kinds of systems reveal the same variations of the binding energy with dispersion. Supported metals with the same (H/M)$_t$ value have, within the accuracy of the measurements, the same binding energy. Changing the reduction temperature in the preparation chamber from 483 to 823 K did not result in significant differences in binding energies. Thus differences in electronic configuration between Rh/Al$_2$O$_3$, Rh/TiO$_2$ in a non-SMSI state and Rh/TiO$_2$ in the SMSI state are – at least as far as XPS is concerned – vanishingly small. As in the Pt case the results demonstrate that the charge on the rhodium atoms in Rh/TiO$_2$ is not much different from that of rhodium atoms in Rh/Al$_2$O$_3$. If charge is present, then it must be a small positive charge.

For the second series of Rh/TiO$_2$ catalysts the dispersion was varied by changing the reduction temperature. Not that it is indeed possible to obtain large rhodium metal crystallites by reduction at elevated temperatures. It follows from the chemisorption results that particle growth can even occur when the Rh/TiO$_2$ samples are in the SMSI state. Apparently the metal–support interactions are not that strong that sintering via atomic migration or crystallite migration is completely inhibited. The results for this series of catalysts are illustrated in fig. 7. By way of comparison a part of the curve of fig. 6 is redrawn in this figure. As with platinum an increase is found for the binding energies at low (H/M)$_t$ values. When the samples are heated in hydrogen above 1015 K the anatase had completely transformed into the rutile structure. Again we assume that spalling of the metal particles during or following encapsulation in the final rutile structure is responsible for the higher binding energies on the one hand and for the low (H/M)$_t$ values on the other.

![Fig. 7. Rh 3d$_{5/2}$ binding energy of Rh/TiO$_2$ catalysts as a function of dispersion (varying prereduction temperature): (×) rereduced in situ at 483 K; (□) rereduced in situ at 823 K; (○) curve for Rh/TiO$_2$ with varying metal content.](image-url)
hand. From fig. 7 it also follows that the curve for the Rh/TiO$_2$ samples treated at different temperatures approaches the curve for samples with a varying metal content. This too indicates that when no phase transformation had taken place the two different series would have behaved similarly.

4. Conclusions

It has been shown for well-reduced platinum and rhodium catalysts supported on Al$_2$O$_3$ as well as on TiO$_2$ that the binding energy of metal core levels depends on the dispersion of the metal. This dependency mainly originates from a variation in the extra-atomic relaxation upon photoemission in various samples. Although the binding energies of Rh 3d electrons in Rh/Al$_2$O$_3$ and Rh/TiO$_2$ vary with dispersion, they are about equal at equal dispersion, indicating that the electronic configurations in both systems are almost the same. In Pt/TiO$_2$ the Pt 4f$_{7/2}$ and 4d$_{5/2}$ electrons even have a somewhat higher binding energy than those in Pt/Al$_2$O$_3$, although the dispersion dependencies in Pt/Al$_2$O$_3$ and Pt/TiO$_2$ are the same above $(H/M)_1 = 0.27$. In situ reduction at 823 K (the condition for bringing the metals in the SMSI state) did not alter the binding energy significantly. This leads to the conclusion that the electronic configurations in the SMSI and non-SMSI state are indistinguishable by XPS.

If the XPS results warrant a conclusion it must be that rhodium particles on TiO$_2$ have the same charge as those on Al$_2$O$_3$, while platinum particles on TiO$_2$ may have a somewhat higher positive charge. Other recent XPS studies, which claimed the opposite, must be disregarded.

Acknowledgements

We thank W.C. van der Vleuten for his technical assistance during the preparation of the heatable introduction rod. The present investigation has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Note added in proof

Very recently Mason published interesting experimental and theoretical results on supported metal particles prepared by sputtering [38]. His experimental results agree with ours in the sense that the core-level binding energies of the metal particles increase with decreasing particle size. In contrast to our
interpretation, however, Mason favours the initial state effect of s–d rehybridisation as the explanation. He agrees that extra-atomic relaxation can qualitatively explain the experimental results but argues that the effect is quantitatively too small. His arguments are rather weak, however. For instance, his own table II shows that XPS and XAS shifts do differ, thus demonstrating that screening is not complete for the small metal particles. Secondly, although the relation $\Delta \alpha = 2\Delta R$ for XPS and Auger shifts is indeed too simple (cf. the discussion in section 3.2), it does not necessarily mean that changes in screening with particle size are negligible. Furthermore, in his thermodynamic calculations he assumes a good conductivity for metal particles on carbon. The experimental results for metals supported on $\text{Al}_2\text{O}_3$, $\text{SiO}_2$ and $\text{C}$ are very similar and disprove his assumption. Metal particles on carbon either lie on a graphitic plane – the conductivity perpendicular to these planes is very small – or at defect or impurity sites. As a consequence the conductivity and screening will be small.

Although we fully agree that s–d rehybridisation takes place, at the moment we still have no reason to discard the final state–atomic relaxation effect as the main explanation for the increase in binding energies with decreasing particle size.

References