A temperature programmed reduction study of Pt on Al2O3 and TiO2

Citation for published version (APA):

DOI:
10.1016/0166-9834(84)80104-9

Document status and date:
Published: 01/01/1984

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 22. Dec. 2020
A TEMPERATURE PROGRAMMED REDUCTION STUDY OF Pt ON Al₂O₃ and TiO₂

T. HUIZINGA, J. VAN GRONDELLE and R. PRINS

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

aPresent address: Koninklijke/Shell Laboratorium, Badhuisweg 3, Amsterdam.
bTo whom correspondence should be addressed.

(Received 9 December 1983, accepted 10 February 1984)

ABSTRACT

The reducibility of platinum on γ-Al₂O₃ and TiO₂ was studied with the aid of temperature programmed reduction. The reduction peak temperature was found to be dependent on the temperature of the primary oxidation after impregnation and drying. The higher the oxidation temperature the lower the TPR peak temperature and the higher the H₂ consumption. During the oxidation small PtO₂ particles were formed which were more easily reduced than the original isolated Pt²⁺ ions. For Pt/Al₂O₃ no decomposition of PtO₂ was observed up to 750 K, while bulk PtO₂ decomposed around 600 K. This demonstrated that there is a substantial interaction between PtO₂ and Al₂O₃. For PtO₂ supported on TiO₂ and SiO₂ this interaction is much weaker and on these supports PtO₂ decomposed at lower temperatures than on Al₂O₃.

Reduction of passivated catalysts, with H/Pt < 0.8 in the metallic state, took place even at 223 K. After passivation these catalysts consist of a metal core surrounded by a metal oxide skin. Due to the presence of the metallic core, H₂ can be dissociatively chemisorbed at low temperatures and induce reduction of the oxide layer. The implications of this for the O₂-H₂ titration method are discussed. Reduction of Pt/TiO₂ led to metal assisted reduction of the support. Below 500 K only a small part of the support is (reversibly) reduced in the near vicinity of the metal particles. Above 500 K further metal assisted reduction of the TiO₂ support takes place, probably promoted by increased ion mobility.

INTRODUCTION

Reduction is an important activation step in the preparation of supported metal catalysts and methods which enable the study of this reduction are therefore of great value in the characterization of the catalysts. Temperature Programmed Reduction (TPR) is such a technique. In TPR hydrogen is continuously led over the catalyst while the temperature is raised linearly with time. By measuring the consumption of hydrogen (due to the reduction of species in the catalyst) as a function of the applied temperature a so-called reduction profile is obtained. One of the first studies in which TPR was used as a characterization technique was performed by Robertson et al. on the reduction of Cu-Ni/SiO₂ catalysts [1,2]. They affirmed complete reduction of the metals and were able to identify alloying. Later studies of Wagstaff and Prins confirmed the power of the use of TPR in the
characterization of bimetallic Pt-Re/Al₂O₃ and Pt-Ir/Al₂O₃ reforming catalysts [3,4]. For Pt-Re/Al₂O₃ they concluded that intimate contact between the two metals was achieved after reduction of catalysts calcined in air at 798 K. Calcination in air of reduced samples above 473 K caused segregation of platinum oxide and rhenium oxide.

In recent years more articles about TPR have been published and recently even a review article appeared [5]. All this indicates that there is a growing interest in the use of TPR to characterize supported catalysts and to study their behaviour under reductive and oxidative conditions.

In this publication the reducibility of monometallic Pt supported on both γ-Al₂O₃ and TiO₂ as studied by the TPR technique will be discussed and especially the influence of drying, calcination and passivation.

EXPERIMENTAL

Catalysts

The supports used were γ-Al₂O₃ (Akzo 000-1.5 E, S.A. 195 m²g⁻¹, P.V. 0.6 cm³ g⁻¹) and TiO₂ (anatase, Tioxide CLDD 1367, S.A.20 m² g⁻¹, P.V. 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 the supports and stirring was continued for 6 hours. Subsequently the water was evaporated by slowly heating to 363 K at reduced
Apparatus and procedure

The TPR apparatus used was very similar to the one that has recently been described in detail by Boer et al. [6]. A schematic drawing of the apparatus is presented in Figure 1. The apparatus consisted of a pneumatic circuit for preparing 5% H₂ in Ar and 5% O₂ in He, a reactor section comprising a quartz tube placed in a silver block oven with electrical heaters and a supply of liquid nitrogen coolant, and a thermal conductivity detector (TCD) of the diffusion type which was maintained in a cabinet at a constant temperature of 307 K. TCD's are very sensitive in detecting small changes in the concentrations of H₂ in Ar or O₂ in He, because of the differences in thermal conductivities between the active (H₂ or O₂) and inert gases (Ar and He). The gases used were all purified over molecular sieves for the removal of water and over a BTS column for the removal of traces of oxygen. Since water is formed during reduction of the supported oxides by hydrogen, the gas coming from the reactor was dried over magnesium perchlorate before entering the thermal conductivity cell. The heating rate during all TPR measurements was 5 K min⁻¹ (as in most other TPR studies) and the gas flow rate
300 ml h\(^{-1}\) (STP). For switching of the various gas streams to the reactor a universal programming unit was installed. This, in combination with a LN 1300 temperature controller, makes it possible to perform various treatments like oxidation, reduction or desorption in desired sequences. An often used sequence during TPR will be described in more detail (cf. Figure 2).

The TPR was started with a switch from pure argon to the 5% H\(_2\)/Ar mixture during an isothermal period at 223 K. During this switch a strong signal was detected by the thermal conductivity detector due to the displacement of argon by the 5% H\(_2\)/Ar mixture. This artificial hydrogen consumption peak lasted for a few minutes (1st switch peak). In some cases, however, a real hydrogen consumption might take place even at 223 K. For these cases a procedure was developed to discriminate between artificial and real hydrogen consumption during the switch peak. After the first switch peak the actual TPR run was initiated by starting the temperature ramp. The TPR was ended with an isothermal period at the final temperature. Thereafter the temperature was brought back to the starting temperature (223 K) under the flowing H\(_2\)/Ar mixture. At this temperature the H\(_2\)/Ar mixture was replaced by argon, resulting in a negative TCD signal. Since the metal catalyst had now been reduced and was covered by strongly bound chemisorbed hydrogen no real hydrogen consumption was expected when the argon was once more replaced by the 5% H\(_2\)/Ar mixture. This means that the resulting 2nd switch peak was due solely to the displacement of the argon by the H\(_2\)/Ar mixture and that consequently the artificial switch peak was known. The difference in apparent hydrogen consumption between the second and first switch peaks was due to the real hydrogen consumption at 223 K (cf. Figure 2). In subsequent figures this real hydrogen consumption at 223 K will be indicated by a block at the isothermal period at 223 K. Note again that in our TPR runs the lowest temperature used was 223 K.

RESULTS AND DISCUSSION

\[ \text{Pt/Al}_2\text{O}_3 \]

The reduction profile of 5% Pt/Al\(_2\)O\(_3\), prepared via a combined ion exchange and wet impregnation of the \(\gamma\)-Al\(_2\)O\(_3\) with Pt(NH\(_3\))\(_4\)(OH)\(_2\), is presented in Figure 3a. The total hydrogen consumption, expressed as the amount of dihydrogen consumed per metal atom (H\(_2\)/M value) is indicated in the figures. Unless otherwise specified, this value is calculated for the entire TPR run, including real consumption at 223 K and desorption at higher temperatures. (Note that during reduction hydrogen is also chemisorbed, which increases the H\(_2\)/M value. This chemisorbed hydrogen is desorbed again at higher temperatures and shows up in the TPR profiles as a negative TCD signal). The uncertainty in the H\(_2\)/M values is estimated to be 10%.

The H\(_2\)/M value in Figure 3a indicates that the average oxidation state of the platinum before reduction is 2.6. The reduction peak is asymmetric and broad, indicating that various reducible platinum species are present. This became more
FIGURE 3 TPR profiles of Pt/Al₂O₃ catalysts. a dried at 473 K, b oxidised at 473 K, c oxidised at 573 K, d oxidised at 773 K, e reduced at 773 K and oxidised at 673 K, f reduced at 908 K and passivated. The numbers under the TPR profiles represent the net total hydrogen consumptions (H₂/M values, see text). Note that the lowest temperature used is 223 K and that the part of the abscissa to the left of the 223 K mark represents an isothermal period at that temperature. The TPR run is ended with another isothermal period at the highest temperature.
FIGURE 4 TPO profile of Pt/Al₂O₃ reduced at 773 K.

clear when the dry sample was preoxidized. In Figures 3b, 3c and d the influence of progressively higher calcination temperatures is illustrated. In all cases the final oxidation temperature was maintained for 1 hour. The TPR profiles show a shift of the reduction peak towards lower temperatures and also an increase in the H₂/M values from 1.6 to 2.2. This means that during the oxidative treatment Pt⁴⁺ species are formed, probably in the form of small oxide particles which are more easily reduced than the isolated Pt²⁺ ions originally present in the ion exchanged and dried sample. After calcination at 773 K the TPR profile has a peak at about 330 K, which is close to the value observed by Lieske et al. in the TPR of a chlorine free Pt/Al₂O₃ catalyst [7]. These authors assigned this peak to the reduction of PtO₂ particles on the basis of a comparison between their TPR and UV-VIS results [7,8].

Instead of the expected decomposition of PtO₂/Al₂O₃ (PtO₂ decomposes in Pt and O₂ above 623 K at 100 kPa O₂ [9]) after calcination at 773 K a high H₂/M value is observed which is indicative for fully oxidized platinum. Apparently, the small platinum oxide particles formed on Al₂O₃ are stabilized by the support surface. We have confirmed this conclusion by performing a temperature programmed oxidation
FIGURE 5 Model for passivated metal-on-support particles: metal oxide skin on a metal core.

(TPO) of a reduced Pt/Al₂O₃ catalyst. As can be seen from Figure 4 up to 750 K the metal takes up O₂, while above 750 K the resulting PtO₂ decomposes as follows from the negative TPO peak due to O₂ evolution. The decomposition temperature of PtO₂ on Al₂O₃ at 5 kPa O₂ is thus about 100 degrees higher than that of pure PtO₂ at 100 kPa O₂. From this temperature difference and the heat of formation of PtO₂ (25 kcal mol⁻¹) the heat of formation of small PtO₂ particles on Al₂O₃ can be calculated if it is assumed that the entropy of formation is completely determined by the oxygen gas in the reaction PtO₂ ⇌ Pt + O₂. The result is 35.6 kcal mol⁻¹, indicating that the interaction energy between PtO₂ and Al₂O₃ is in the order of 10 kcal mol⁻¹. Furthermore it can be calculated that the decomposition temperature of pure PtO₂ under 0.05 atm O₂ (as in the TPO experiment) is equal to 550 K, while the decomposition temperature of PtO₂ on Al₂O₃ under 0.2 atm O₂ is 790 K. The latter value confirms that during our calcination in air at atmospheric pressure and 773 K the platinum particles are completely oxidized, but shows at the same time that the temperature margin was slim.

In agreement with the observed stabilisation of small PtO₂ particles on the Al₂O₃ surface, Yao et al. [10] found two reduction peaks in their TPR study of Pt/Al₂O₃ samples prepared from H₂PtCl₆ and calcined at 673 and 773 K. Samples which were prepared by the ion-exchange method and which contained low amounts of platinum exhibited a reduction peak at high temperature, while samples with high amounts of platinum also showed a peak at lower temperature. The high temperature peak was ascribed to platinum oxide in interaction with the γ-Al₂O₃ surface and the lower temperature peak to large bulk like PtO₂ particles.

In Figure 3e the TPR profile is shown for a sample which had been reduced at 773 K and subsequently oxidized at 673 K (a so-called second TPR profile was measured after having performed a first TPR measurement, followed by a TPO measurement).
A single peak at 318 K, with a $H_2/M$ value of 2.1 is now observed. This second reduction profile is independent of the pretreatments, provided that the step preceding the TPR run is an oxidation at 673 K. The value of 2.1 for $H_2/Pt$ indicates that during this TPR PtO$_2$ is reduced to metallic platinum. The reduction peak temperature is lower than that of a sample which was directly oxidized at 573 K, although the $H_2/Pt$ values are about equal. This indicates that although the oxidation state of the platinum oxides is approximately the same, the reducibility of the oxides is different, most probably due to differences in their structure. We assume that the oxides formed during oxidation of previously reduced systems consist of larger oxidic agglomerates, as we suggested before on the basis of ESR results [11]. The directly oxidized samples contain isolated Pt$^{4+}$ ions or Pt$^{4+}$ ions in badly developed small oxide particles. It is normally assumed that the first step in the reduction process involves dissociation of hydrogen. Most probably this step will be facilitated if two hydrogen adsorption sites are close to each other. This situation will be more frequently found in the larger dense metal-oxide particles and for this reason they are more easily reduced.

In Figure 3f the reduction profile is given for a Pt/Al$_2$O$_3$ sample which has been reduced at 908 K and subsequently passivated. In the passivation step oxygen is slowly admitted to a stream of nitrogen which was used to replace the hydrogen from the reduction step. Now hydrogen consumption is observed at 223 K and the total $H_2/M$ value is 1.3. The consumption of hydrogen at 223 K in the "switch" peak accounts for 0.6 and the reduction peak at 269 K (including the desorption peaks above 373 K) accounts for a $H_2/M$ value of 0.7.

It is interesting to compare the results of Wagstaff and Prins [3] with the present results. After reduction and a one hour reoxidation these authors [3] found that the temperature at which the rereduction took place in TPR, depended upon the temperature of reoxidation. For the hydrogen consumption they reported $H_2/M$ values of 1, if the oxidation temperature had not exceeded 673 K. As can be seen from their reduction profiles, reduction began at 223 K. Oxidation at 773 K led to a $H_2/M$ value of 2 in their study. From the data presented here it follows that the $H_2/M$ values of reference 3 might have been underestimated, because in reference 3 a possible hydrogen consumption in the switch peak was not taken into account.

The results as presented in Figure 3f leave us with the question how to rationalize the low temperature reduction behaviour. During passivation the metal particles are covered by a layer of platinum oxide. The final situation will be as sketched in Figure 5, with a thin skin of platinum oxide surrounding the metal core which smothers further oxidation. Of course, the temperature of oxidation (passivation) will determine the thickness of the skin. However, as is well known in metallurgy, the small hydrogen molecules can diffuse through this oxide layer and as long as metallic platinum is present, hydrogen will be dissociated and reduction
will proceed without any inhibition. When the oxide layer becomes thicker, the layer will be more dense, diffusion of hydrogen will be slowed down and the reduction peak temperature will be increased. This is consistent with our results and with the results described in reference 3.

Recently Nandi et al. published two articles on the characterization of Pt and Pd on SiO$_2$ [12,13]. Their results are very similar to ours, although obtained with other techniques and with another support. From X-ray diffraction (XRD) and Extended X-ray Absorption Fine Structure (EXAFS) measurements they concluded that Pt and Pd in well dispersed Pt/SiO$_2$ and Pd/SiO$_2$ catalysts, (H/M)$_{\text{irrev}}$ > 0.8, are completely transformed into metal oxides when exposed to oxygen at room temperature. With less well dispersed systems lattice parameters identical to that of the metal still showed up in XRD (for H/M < 0.65) as well as metal-metal distances in EXAFS (for H/M < 0.8). These results confirm our conclusions obtained from TPR measurements that passivation of well dispersed metals on a support leads to a complete transformation of the metal particles into oxide particles, while the admission of oxygen to bigger metal particles only leads to a skin of metal oxide on top of a metal kernel.

The ease of the reduction of passivated samples is already employed in the hydrogen-oxygen titration method as described by Benson and Boudart [14]. However, in this method it is assumed that only surface platinum atoms are able to chemisorb oxygen atoms (O/Pt$_s$ = 1). After admission of hydrogen, water is formed and hydrogen is chemisorbed, which increases the normal H/Pt$_s$ stoichiometry from 1 in the clean metal to 3 in the samples which were previously covered by oxygen. From the results presented here it follows that small changes in the temperature of both oxygen and hydrogen chemisorption strongly alter the observed stoichiometries. Because of the connection between time and temperature in kinetics, also the duration of the oxygen adsorption will have an influence. Furthermore, the metal particle size can also influence normally accepted stoichiometries, as became clear from the work of Uchijima et al. [15] and Kobayashi et al. [16]. We conclude that it is rather dangerous to use the hydrogen-oxygen titration method for the measurement of metal surface area, unless great care is taken to standardize the method for every other metal.

Pt/TiO$_2$

The TPR profiles for various Pt/TiO$_2$ samples are presented in Figure 6. The dried Pt(NH$_3$)$_4$(OH)$_2$/TiO$_2$ sample (Figure 6a) exhibits in its TPR profile a reduction peak at 428 K with shoulders at 470 and 583 K. Some reduction is observed above this temperature. The total hydrogen consumption over the entire temperature range corresponds to a H$_2$/M value of 3.1, which is much too high to account for reduction of platinum species only. Although during reduction NH$_3$ will be removed from the catalyst this alone cannot explain the enhanced hydrogen consumption.
FIGURE 6 TPR profiles of Pt/TiO$_2$ catalysts. a dried at 423 K, b oxidised at 673 K, c bare TiO$_2$ support dried at 423 K, d reduced at 818 K, passivated, e reduced at 818 K, oxidised at 673 K. For further details see caption to Figure 3.
From XPS measurements we conclude that the N/Pt ratio decreased from about 3 before reduction to zero afterwards. However, the thermal conductivity of NH$_3$ does not differ much from that of Ar (0.22 versus 0.17 mW cm$^{-1}$ K$^{-1}$) while that of H$_2$ is much higher (1.75). This means that apart from a small contribution due to desorption of NH$_3$ the main part of the high hydrogen consumption observed must be caused by reduction of the support.

To investigate this further, the dry sample was oxidized at 673 K to remove the NH$_3$ ligands. Now the reduction starts even at 223 K (Figure 6b). As has become clear from the results on passivated Pt/Al$_2$O$_3$ discussed in the foregoing, this low temperature hydrogen consumption is indicative of the presence of metallic Pt. Moreover, as stated above, oxidation of platinum oxide at temperatures above 623 K should lead to decomposition of PtO$_2$ into Pt and O$_2$, unless PtO$_2$ is stabilized by an interaction with the support. Because TiO$_2$ is a support with a completely different structure and with different chemical properties than Al$_2$O$_3$, the interaction between platinum oxides and TiO$_2$ might differ substantially from that between PtO$_2$ and Al$_2$O$_3$. To check this idea, temperature programmed oxidation measurements of reduced Pt/Al$_2$O$_3$, Pt/SiO$_2$ and Pt/TiO$_2$ have been performed. The resulting profiles are given in Figure 7. They show an uptake of oxygen due to oxidation of the Pt particles, followed by the evolution of O$_2$ due to the decomposition of PtO$_2$. The most interesting result is that PtO$_2$ on TiO$_2$ decomposes at a lower temperature than PtO$_2$ on Al$_2$O$_3$. Hence the indication for the presence of metallic platinum from the TPR profile (6b) is confirmed by the TPO experiments. In relation to these TPO results it is of importance to mention the results obtained by Attwood et al. [17] in a TPR study of Pt(NH$_3$)$_4$(OH)$_2$ supported on carbon fibre paper coated with pyrographite. These authors observed a reduction peak for the dried ion-exchanged catalyst at 469 K. When their catalyst was oxidized at 573 K in air, however, a reduction peak was observed at 217 K, while the H$_2$/Pt value had decreased. Attwood et al. pointed out that during oxidation of their system decomposition of surface groups on the carbon took place with a simultaneous formation of CO and CO$_2$ and they suggested that as a result of this part of the platinum oxide had been destabilized and reduced to the metallic state. We think that an alternative explanation may be that the interaction between PtO$_2$ and carbon is intrinsically weak and that PtO$_2$ had partly decomposed to Pt upon heating, as it also does on TiO$_2$ and SiO$_2$ and eventually also on Al$_2$O$_3$. The low decomposition temperature on carbon is consistent with this explanation.

Let us now return to the TPR profile of Figure 6b. The total H$_2$/M value for this profile is 3.1. From this value 2.3 is consumed up to 533 K and already 56% of this amount is consumed in the low temperature "switch peak." The high H$_2$/M value of 2.3 proves that support reduction is occurring, below 533 K, catalyzed by the platinum. It is somewhat difficult though, to assign a H$_2$/M value of 0.3 to the reduction of the support, since this would presume that 2.0 mol H$_2$ is needed...
FIGURE 7 TPO profiles of Pt/Al$_2$O$_3$, Pt/SiO$_2$ and Pt/TiO$_2$ after reduction at 773 K.
for the reduction of the platinum oxide, while the presence of the "switch peak" demonstrates that part of the platinum was not oxidic to start with. One could argue that this then means that (much) more than 0.3 mol H₂ is used in the reduction of the support below 533 K, but we prefer another explanation. At any moment during a TPR run the measured H₂ consumption is the result of the difference between a possible uptake of H₂ due to reduction and adsorption and a possible evolution of H₂ due to desorption. Keeping this in mind we feel that in Figure 6b the desorption of H₂ is underestimated. For instance, in independent TPD measurements we observed that the desorption of H₂ continued up to 650 K at least (compare also Figures 3e and 3f), whereas the TPR signal in Figure 6b crosses the baseline at 533 K. The reason for this must be that further reduction of the support starts even below 533 K. In view of all this, we believe that a more realistic interpretation of the TPR profile presented in Figure 6b is that about 1.6 mol H₂ is needed for the reduction of platinum oxide, about 0.3 mol H₂ for the reduction of TiO₂ below 500 K and about 1.2 mol H₂ for support reduction above 500 K. It is known from ESR and NMR measurements that indeed Ti³⁺ ions are formed when Pt/TiO₂ is reduced below about 500 K [18-20]. The value of 0.3 mol extra H₂ consumption per mol Pt obtained from the TPR results leads for our 4.2% Pt/TiO₂ sample to a Ti³⁺/Pt ratio of 0.6. From the ESR results for a 2% Pt/TiO₂ sample a Ti³⁺/Pt ratio of 0.3 was calculated [18]. Because of the large uncertainty in the value derived from the TPR results and because of the fact that there may have been more Ti³⁺ ions present than observed by ESR, we think that the agreement between the TPR and ESR values is reasonable. The small amount of support reduced below 500 K must be situated close to the metal particles since our ESR studies of Pt/TiO₂ showed that this support reduction could easily be reversed [18]. The same reversibility has been observed for Rh/TiO₂ by De Canio et al. [21] and by us [22].

Above 533 K three small but broad reduction peaks are observed at progressively higher temperatures (573, 713 and 873 K). The total H₂/M value for these three peaks is 0.8. For pure TiO₂ samples no reduction at all is observed up to 673 K (Figure 6c) and only a small reduction peak is found at 840 K with an area of 24 µmol (254 mg TiO₂). The differences between Pt/TiO₂ and the bare support indicate that the high temperature reduction peaks in the Pt/TiO₂ samples can be explained in two ways. Either they are due to platinum species which are difficult to reduce or they are due to platinum assisted reduction of the support. Since also for Rh/TiO₂ these three high temperature reduction peaks are present in the TPR profiles [23], we conclude that also above 533 K metal assisted reduction of the TiO₂ support takes place. The occurrence of separate regions of metal assisted reducibility of TiO₂ points to the influence of ion mobility. Below 533 K only Ti⁴⁺ ions close to the metal particles at the surface of the TiO₂ are reduced, while at higher temperatures also other Ti⁴⁺ ions can be reduced. Increased mobility of the
Ti$^{3+}$ and OH$^-$ ions at higher temperature will be of importance in this.

The TPR profile of a sample which had been reduced at 818 K and subsequently passivated, is shown in Figure 6d. For this sample, most of the reduction takes place at 223 K. The H$_2$/M value of 0.4 indicates that not much of the platinum was oxidized, which can be understood when considering the rather low dispersion of this catalyst (H/M)$_t$ = 0.35. Of course in this case, where metallic platinum is present under the platinum oxide layer, the subsequent reduction will proceed easily. In the high temperature region not much reduction is observed, which means that the passivation step did not reverse the metal assisted reduction of the support.

The TPR profile of a Pt/TiO$_2$ sample reduced at 818 K and oxidized at 673 K, is given in Figure 6e. Not much difference between this profile and that of the directly oxidized sample (6b) is observed. The peak at 258 K for the reduced and oxidized sample is sharper, perhaps because the size distribution of platinum oxide particles formed upon oxidation after the reduction step is narrower than of particles formed during direct oxidation of the dry sample.

CONCLUSIONS

Oxidation of impregnated and doped Pt(NH$_3$)$_2$(OH)$_2$ on γ-Al$_2$O$_3$ and TiO$_2$ catalysts led to the formation of PtO$_2$ particles, which reduced at a much lower temperature than the originally present Pt$^{2+}$ ions. Although PtO$_2$ is known to decompose into Pt and O$_2$ above 600 K under 100 kPa O$_2$, PtO$_2$ on γ-Al$_2$O$_3$ was stable up to about 750 K. On the other hand, PtO$_2$ on TiO$_2$ and SiO$_2$ was found to be unstable at this temperature, demonstrating that PtO$_2$ particles have a much stronger interaction with γ-Al$_2$O$_3$ than with the other supports. Oxidation of a Pt/TiO$_2$ sample at 673 K even led to the formation of platinum particles with an outer oxide skin and a metal core. This was also the case, when the Pt catalysts were passivated. Also in that case the TPR showed the existence of a metal core and an outer platinum oxide skin. The present TPR study demonstrates that the reduction and oxidation behaviour of platinum on support catalysts is different from that of other noble metals because of the low stability of platinum oxide and of the influence of the support on this stability.

For Pt/TiO$_2$ catalysts a clear distinction could be made between a low temperature reduction of the TiO$_2$ support, which is reversible, and an irreversible high-temperature reduction above 500 K.

ACKNOWLEDGEMENTS

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).
REFERENCES

22 T. Huizenga and R. Prins, to be published.