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Reactions of Platinum in Oxygen- and Hydrogen-Treated $Pt/\gamma\text{-}Al_2O_3$ Catalysts

I. Temperature-Programmed Reduction, Adsorption, and Redispersion of Platinum

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$Pt/\gamma\text{-}Al_2O_3$ catalysts with and without chloride were treated at different temperatures in oxygen or hydrogen and were studied by temperature-programmed reduction and by hydrogen adsorption. Two surface oxides, α- and β-$[PtO_2]_s$, and two chloride-containing surface complexes, $[Pt^{IV}(OH)_xCl_y]_s$ and $[Pt^{IV}O_xCl_y]_s$, could be found and a comprehensive scheme of surface reactions is proposed. Redispersion of Pt in oxygen is possible only in the presence of chloride and is connected with the formation of $[Pt^{IV}O_xCl_y]_s$. A model for the redispersion is proposed.

INTRODUCTION

Dispersed platinum on alumina is an extensively used catalyst, especially in the reforming process. Treatments in oxygen and in hydrogen are established procedures in the activation of fresh catalysts as well as in the regeneration of deactivated catalysts. Although it is generally accepted that during the oxygen treatment oxidized platinum is formed, relatively little is known about the nature of the oxidized species. Pt : O ratios ranging from 1 : 1 (*1*) to 1 : 2 (*1–5*) and even up to 1 : 3.7 (*6*) have been found under different conditions.

It is well known that supported Pt can be redispersed by oxygen or air treatments between 400 and 550°C (*5, 7–10, 14*) whereas at higher temperatures sintering occurs. Numerous attempts have been made to explain redispersion either by molecular migration or by crystallite migration models (*8–15*). Different oxidic species on the surface of the alumina are assumed in these models, but no direct experimental evidence has been given and in none of these models has the crucial role of chloride in the alumina been taken into account.

In the present work Pt/Al_2O_3 catalysts with and without chloride have been treated at different temperatures in oxygen and investigated by temperature-programmed reduction (TPR) and by hydrogen adsorption measurements. Four different oxidized platinum species could be observed, and two of them are halogen containing. On the basis of the formation and decomposition of these species a new model of redispersion is proposed, a halogen-containing species playing the crucial role.

EXPERIMENTAL

Materials

Three alumina-supported Pt catalysts (A, B, and C) were used. Catalyst A, 0.5 wt% Pt on γ-alumina (Condea), contained highly dispersed Pt and chloride. The chloride content after calcination at 500°C in O_2 amounted to 1.5 wt%. Catalyst B, 0.5 wt% Pt on γ-alumina, contained highly dispersed Pt but was chloride-free. Catalyst C, 1.0 wt% Pt on γ-alumina, contained dispersed and crystalline Pt and was chloride-free. The γ-alumina of catalysts B and C was of

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similar high purity and surface area (190 m^2/g) to the Condea alumina. Catalyst A was prepared by impregnating Condea γ-alumina with a solution of H_2PtCl_6 in dilute hydrochloric acid and dried at 120°C. Catalyst B was prepared by impregnating γ-alumina with a solution of the Pt–π-methylallyl complex in pentane according to Ryndin (*16*). Catalyst C was prepared by impregnation of γ-Al_2O_3 with a solution of $H_2Pt(OH)_6$ in conc HNO_3 dissolved in methanol. The carrier had been impregnated before with 0.5 wt% KOH. After drying the catalyst was calcined in air for 1 h at 400°C and reduced for 1 h at 500°C.

The gases used in this study were taken from tanks and purified. Argon: oxygen traces were removed by Leuna catalyst 4492 at 100°C (Cu on Mg silicate). Hydrogen and hydrogen/argon mixture: oxygen traces were removed by Leuna catalyst 7748 (Pd on alumina). Oxygen as well as argon and hydrogen were dried by a molecular sieve.

Temperature-Programmed Reduction

The TPR equipment used in this study was similar to that described by Robertson *et al.* (*17*). The samples could be heated in a quartz tube reactor up to 800°C with a constant heating rate. The hydrogen concentration at the outlet of the reactor was measured by a catharometer connected with a recorder.

The gas used in TPR was a mixture of 5 vol% H_2 in Ar, and the oxidizing gas was pure oxygen. The gas leaving the reactor was dried in a cold trap. The standard heating rate amounted to 8°C/min. The gas flow rate of the TPR gas was 1500 ml h^{-1} (STP). Normally the catalyst samples weighed 1 g. Generally the TPR starting temperature was -30°C. With experiments where no TPR signals below 100°C were expected the TPR was started at room temperature. The procedure for a normal TPR measurement consisted of the following steps. (1) The fresh catalyst sample was calcined in O_2 for 1 h at the desired temperature, cooled to 100°C in O_2, switched from O_2 to Ar, cooled to the start temperature, and switched from Ar to the H_2/Ar mixture. (2) After reaching the zero line of the recorder, TPR was carried out in the H_2/Ar mixture up to the desired temperature. In the case of reoxidation experiments the procedure was continued by (3) a 1-h isothermal treatment at 500°C in H_2/Ar, cooling to room temperature, switching from H_2/Ar to Ar, and after 5 min switching from Ar to O_2; (4) reoxidation in O_2 at the desired temperature for 1 h, cooling in O_2 to 100°C, switching from O_2 to Ar, cooling to TPR starting temperature, and switching to H_2/Ar; (5) TPR according to step 2.

The catharometer was quantitatively calibrated. Therefore, it was possible to determine the hydrogen consumption from the TPR peak areas with an accuracy of $\pm 5\%$. From the hydrogen consumption the average valence of Pt could be calculated.

In the evaluation of the TPR spectra the peak intensity was corrected for the amount of hydrogen adsorbed on the reduced Pt. The adsorbed hydrogen causes a negative peak behind the reduction peak (Figs. 2a, b and 4a, b). The area of this negative peak was subtracted from the area of the reduction peak. This correction was necessary only in the case of low temperature TPR peaks ($\leq$100°C).

Hydrogen Chemisorption

Hydrogen chemisorption was measured by means of a dynamic pulse apparatus with catharometric detection. The catalyst samples previously investigated by TPR were placed in the chemisorption reactor and treated at 500°C for 1 h in H_2 and subsequently for 1 h in Ar (1 ml/s). After cooling to 0°C H_2 was pulsed into the Ar stream (pulse volume 0.233 ml).

From the amount of hydrogen consumed H/Pt values were calculated as a measure for the average Pt dispersion of the catalyst samples. In the case of dispersed catalyst samples H/Pt values of $\approx$1.1 were found.

Such results are not unusual with extremely dispersed Pt.

RESULTS

The formation of oxidized Pt species during treatments in oxygen at different temperatures has been studied by TPR. The same problem, but investigated by uv–vis reflectance spectroscopy, is treated in Part II of this series (*18*). The results of both studies are used to propose formulas for Pt surface species. In order to make it easier to survey, these formulas will be used from the very beginning, and detailed proofs will be furnished later on in Part I and in Part II. Reaction paths (r), connecting the different species, are summarized in Fig. 7 and are cited in brackets at the appropriate places.

Catalyst A: Pt_{disp}, Chloride-Containing

The first TPR experiments were performed with a fresh catalyst only once calcined in oxygen. The results are shown in Fig. 1. After calcination at 300°C (reaction path r1 in Fig. 7) the maximum rate of reduction, indicated by the peak in TPR curve a, is observed at 260°C (Fig. 7, r12). This species will be denoted by $[Pt^{IV}(OH)_xCl_y]_s$. Calcination at higher temperatures of 500 to 600°C (Fig. 7, r2) results in a species with a higher reduction temperature of 290°C (curve b and Fig. 7, r11), called $[Pt^{IV}O_xCl_y]_s$. The distinction between $[Pt^{IV}(OH)_xCl_y]_s$ and $[Pt^{IV}O_xCl_y]_s$ is based not only on the relatively small difference of the reduction temperatures, but especially on clearly different uv–vis spectra (*18*). The hydrogen consumption for the reduction of $[Pt^{IV}O_xCl_y]_s$ corresponds to the reduction from Pt^{4+} to Pt^0 (change of valence 4.06).

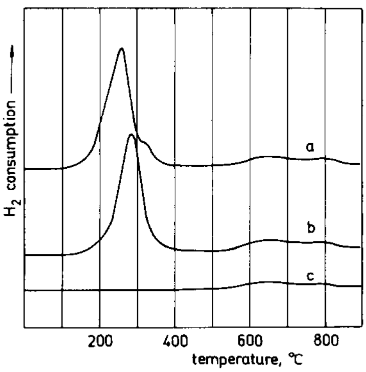

FIG. 1. TPR curves of catalyst A (chloride-containing), only calcined 1 h in O_2 (a) at 300°C and (b) at 500°C, (c) carrier calcined 1 h at 500°C in O_2.

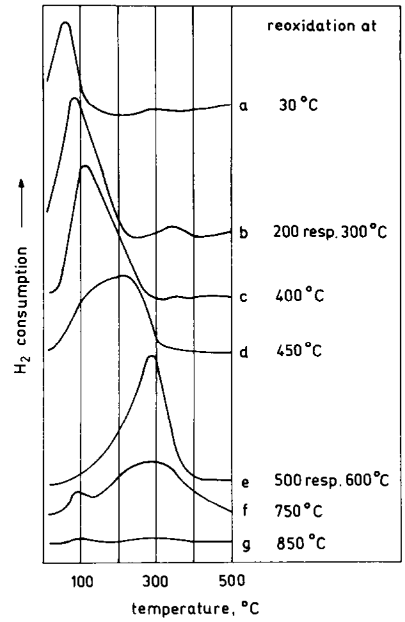

FIG. 2. Selected TPR curves of catalyst A (chloride-containing), reoxidized at different temperatures.

In the second series of experiments, shown in Fig. 2, reoxidized catalysts were used. These had been calcined at 500°C and reduced at 500°C. After reoxidation between 200 and 400°C (Fig. 7, r6) a TPR peak appears near 100°C (curves a–c), caused by reduction of a surface species, termed α-$[PtO_2]_s$ (Fig. 7, r10). This peak is followed by a negative peak (curves a and b), attributed to the desorption of hydrogen.

The small peak at 350°C in curve b, seen more distinctly in Fig. 4b, which appears only after reoxidation between 100 and 350°C, is not caused by reduction of Pt. Its intensity depends on the amount of carrier and not on the amount of Pt (*19*).

In a narrow temperature range at about 450°C (curve d) a significant shift of the TPR peak towards higher temperatures occurs. After reoxidation at 500 or 600°C (curve e) the TPR signal appears at the same maximum temperature and with the same shape and intensity as the signal observed with the sample only once calcined at 500°C (Fig. 1b). Therefore, one must assume that the same species $[Pt^{IV}O_xCl_y]_s$ has been formed (Fig. 7, r5).

From Fig. 3 it can be seen that the dispersion of catalyst A, characterized by the hydrogen adsorption, is very high (H/Pt = 1.12) and almost independent of oxygen treatments at temperatures up to 600°C. Hence, the drastic change of the TPR signal between the reoxidation temperatures of 400 and 450°C cannot be due to a change in dispersion, but must be caused by a change in the surface chemistry of the catalyst.

Moreover, Fig. 3 shows the change of the average valence of the Pt during the TPR in dependence on the reoxidation temperature. By an additional TPR experiment we could show that the formation of $[Pt^{IV}O_xCl_y]_s$ (Fig. 7, r5) also proceeds if the catalyst, reoxidized at 300°C, is subsequently treated in Ar between 500 and 600°C. This proves the existence of two species, α-$[PtO_2]_s$ and $[Pt^{IV}O_xCl_y]_s$ with the same oxidation state of Pt^{4+}.

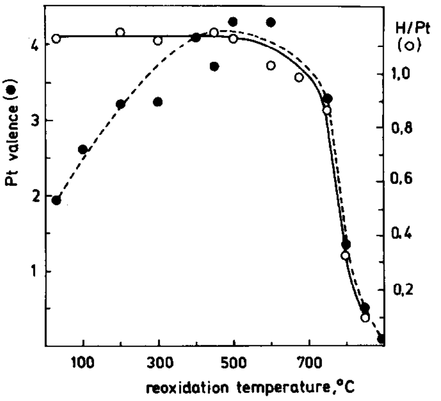

FIG. 3. Hydrogen chemisorption (dispersion) (○) and valence state (●) of Pt as a function of the reoxidation temperature of catalyst A.

The reversibility of reduction and reoxidation of $[Pt^{IV}O_xCl_y]_s$, as predicted by the cycle of the reaction paths 11, 6, and 5 in Fig. 7 has been checked in a special experiment. After seven cycles of reduction and reoxidation at 500°C the halogen content of the sample (1.5 wt%) as well as the high Pt dispersion (1.1) and the high Pt valence (+4) remained constant. Obviously, the chloride ions remain on the alumina after the reduction to metallic Pt and are available for each following formation of $[Pt^{IV}O_xCl_y]_s$ from α-$[PtO_2]_s$.

The redispersion was checked with another sample. This sample was pretreated in oxygen at 800°C until the low dispersion of 0.41 was reached. After an oxygen treatment of 11 h at 550°C the dispersion had increased to 0.60 H/Pt.

At reoxidation temperatures above 700°C (Figs. 2f and g) a strong decrease of the TPR peak intensity is observed. At 850 and 900°C no reducible surface species are detectable. The amounts of adsorbed hydrogen decrease parallel to the average Pt valence (Fig. 3). As will be shown in Part II (*18*), metallic platinum is formed (Fig. 7, r3).

Catalyst B: Pt_{disp}, Chloride-Free

With catalyst B only reoxidation experiments have been made. The samples were dried in Ar at 160°C and then reduced in hydrogen at 500°C for 1 h. Reoxidation and TPR were carried out *in situ*. Catalyst B had nearly the same dispersion as catalyst A (H/Pt = 1.10, Fig. 5). The peaks at temperatures near 100°C in the TPR curves a–c in Fig. 4 show that in the case of a chloride-free catalyst during oxidation at low temperatures α-$[PtO_2]_s$ is also formed (Fig. 7, r6). This has been confirmed by uv–vis spectroscopy (*18*). Thus it is proved that this species really is a chloride-free one.

Contrary to catalyst A, catalyst B still contains α-$[PtO_2]_s$ even after reoxidation at 500 or 550°C (Fig. 4c). However, an HCl treatment of this sample (1 ml 0.5 *N* HCl/g catalyst; 20°C) followed by drying and O_2

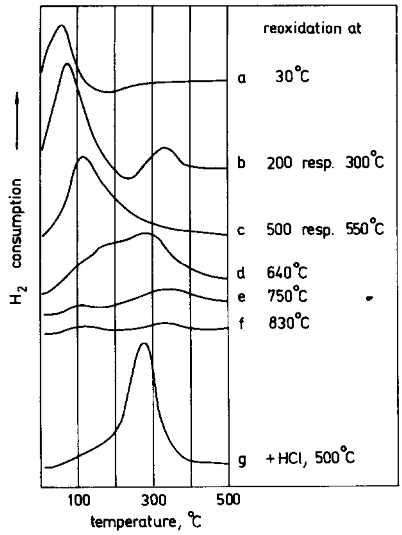

FIG. 4. Selected TPR curves of catalyst B (chloride-free), reoxidized at different temperatures, with curve g after addition of HCl.

treatment at 500°C (1 h) causes a dramatic shift of the TPR peak (Figs. 4c, g). The shape and temperature of the new peak are identical with the peak of the $[Pt^{IV}O_xCl_y]_s$ species observed in the chloride-containing catalyst A (Fig. 2e). We therefore conclude that this species is formed and that this is a chloride-containing species (Fig. 7, r5). Further support for the chloride content will be given below.

Above 550°C (Fig. 4d) also with the chloride-free catalyst B a further species is formed, termed β-$[PtO_2]_s$ (Fig. 7, r7). Its TPR signal appears in a wider temperature range and is less characteristic. Its uv–vis spectrum is quite different from that of $[Pt^{IV}O_xCl_y]_s$ (*18*). A repeated reduction and reoxidation corresponding to the cycle of pathways 9, 6, and 7 in Fig. 7 is also possible with catalyst B.

In Fig. 5 is demonstrated that after reoxidation at 200–600°C catalyst B mainly contains Pt^{4+} as with catalyst A. At higher temperatures (Figs. 4e, f) also with catalyst B the average valence and the dispersion of Pt strongly decrease. However, a comparison of the values at 750°C in Figs. 3 and 5 shows that this decrease proceeds at distinctly lower temperatures with catalyst B.

Catalyst C: Pt_{cryst}, Chloride-Free

The relations between dispersion, redispersion, oxidation, and chloride content have been examined with the halogen-free catalyst C, containing mainly crystalline platinum beside little dispersed platinum.

The results are shown in Fig. 6. Before the experiments the sample was reoxidized at 600°C for 1 h and reduced at 500°C. Treatment in oxygen at 600°C causes a decrease in dispersion (Fig. 6a). (The sintering occurs on catalyst C at a somewhat lower temperature than on catalyst B; this is probably caused by the small alkali content of catalyst C.) Further oxygen treatments between 400 and 550°C are without influence both on the Pt valence and on the dispersion (Fig. 6a). As can be seen from the peaks in Fig. 6b, 1) the product of these treatments is a mixture of α-$[PtO_2]_s$ and β-$[PtO_2]_s$.

After the reduced sample was wetted with 0.5 N HCl and reoxidized at 600°C a considerable increase in the average dispersion was observed and this has been connected to a proportional increase of the average Pt valence. The corresponding TPR

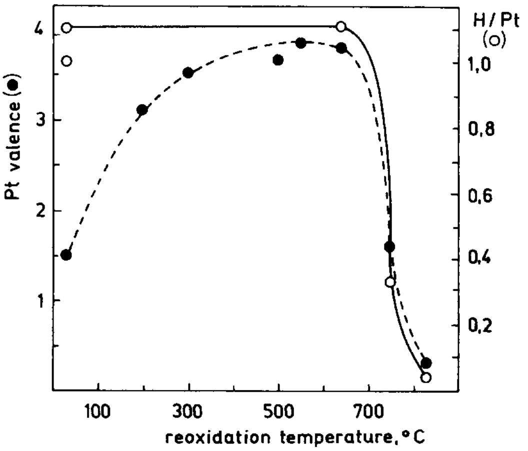

FIG. 5. Hydrogen chemisorption (dispersion) (○) and valence state (●) of Pt as a function of the reoxidation temperature of catalyst B.

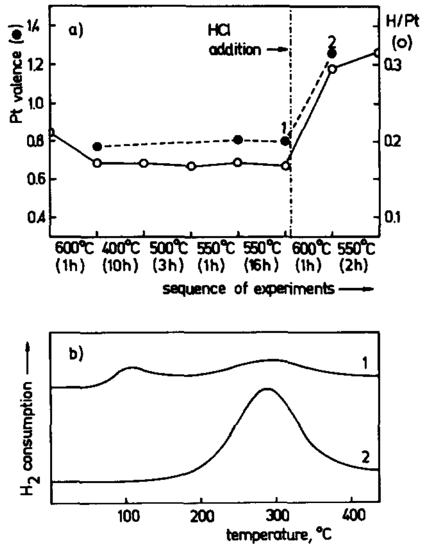

FIG. 6. Sintering and redispersion with one sample of catalyst C (chloride-free). (a) Dispersion (H_2 chemisorption) (O), valence state (●) as a function of the temperature of reoxidation and of HCl addition. (b) TPR curves of this sample at points 1 and 2, indicated in a, before (1) and after (2) HCl addition.

curve (Fig. 6b, 2) proves that this redispersing oxidation is directly connected with the formation of $[Pt^{IV}O_xCl_y]_s$. Further treatment of the chlorinated sample at 550°C leads to a slow, but distinct further redispersion.

The problem of whether a redispersion of Pt on a chloride-free catalyst is possible or not has repeatedly been checked. For example, the catalyst B was heavily sintered in oxygen. The resulting dispersion of H/Pt = 0.12 could not be increased by an oxygen treatment of 5 h at 550°C; only after HCl addition was it possible.

DISCUSSION

Oxidized Species

Four different oxidized surface complexes can be distinguished from the TPR studies: α-$[PtO_2]_s$ and β-$[PtO_2]_s$ are halogen-free, whereas $[Pt^{IV}(OH)_xCl_y]_s$ and $[Pt^{IV}O_xCl_y]_s$ include chloride. The valence of Pt is +4 in all the surface complexes. The number of ligands x and y can vary. The index s symbolizes a surface complex, stabilized by some interaction with the alumina. The identity of these species is confirmed by uv–vis spectroscopy (*18*).

The data in the literature concerning oxidized Pt species are scarce and contradictory. The oxidation state +4 was found by several authors (*1–3*). An influence of chloride (*2, 4*) or the formation of chloride-containing surface complexes (*20, 21*) was only assumed. A first hint of two oxidized phases after reoxidation is given by Wagstaff and Prins (*1*), but they interpret one phase as a Pt(II) species. Foger and Jaeger (*22*) could not find any reoxidized Pt species by TPR. Ushakov *et al.* (*23*) interpret their X-ray data by the formation of platinum–alumina spinels at 500°C. This would mean that Pt(II) is formed. Escard *et al.* (*20*) derived from ESCA experiments that Pt(IV) is accompanied by perceptible amounts of $PtCl_2$.

Our data prove that highly dispersed platinum is completely oxidized to the valence state +4 by oxygen treatment between 400 and 600°C. This is independent of whether the catalyst is chloride-containing (Fig. 3) or chloride-free (Fig. 5).

All the observed surface species are summarized in a comprehensive scheme of reaction paths, indicating the conditions of formation and transformation of the species. This scheme is shown in Fig. 7. Reaction paths (r) in oxygen are shown by full lines, together with a temperature of treatment. These temperatures are selected examples from the experiments. Temperature ranges, as far as they were investigated, are mentioned below.

To a certain extent the temperatures depend on the nature of the alumina and on the concentration of the Pt. In this scheme not all the possible, but only the investigated reactions are included. Reactions in hydrogen are shown by dotted lines, together with the temperatures of the maximum rate of the TPR.

After the usual impregnation with H_2PtCl_6 the platinate is transformed by a

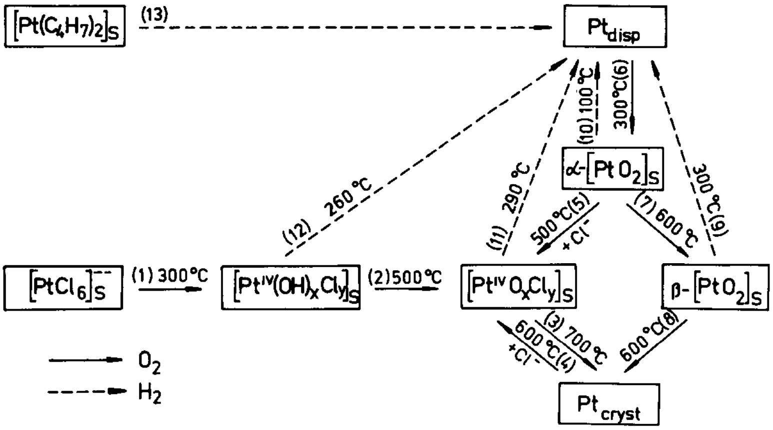

FIG. 7. Reaction pathways of supported Pt species in oxygen (———→) and hydrogen (----→) at different temperatures. +Cl⁻ indicates reaction with chloride, present in the catalyst or added.

first oxygen treatment at about 300°C into $[Pt^{IV}(OH)_xCl_y]_s$ and at higher temperatures between 450 and 600°C into $[Pt^{IV}O_xCl_y]_s$ (r1 and 2). Reduction of this surface complex results in highly dispersed platinum, Pt_{disp} (r11). Slight reoxidation between 200 and 400°C gives mainly the halogen-free α-$[PtO_2]_s$, as well as a possible lower oxide and/or residual Pt_{disp} (r6). At higher temperatures between 450 and 600°C the chloride from the alumina or added chloride reacts and $[Pt^{IV}O_xCl_y]_s$ is formed (r5). This product of reoxidation is identical with the product of the first oxygen treatment (r1 and 2). The cycle of reduction (r11) and reoxidation (r6 and 5) can be repeated very often. In oxygen at temperatures above 700°C the surface complex decomposes and crystalline Pt is formed (r3). This process of sintering will be proved and discussed in part II (*18*). The reverse process (r4), a redispersion with formation of $[Pt^{IV}O_xCl_y]_s$, is possible only in halogen-containing catalysts. This will be discussed in the next section.

An important statement is that $[Pt^{IV}O_xCl_y]_s$ is a chloride-containing surface complex. This is concluded from three independent observations: (i) This species is observed in the chloride-containing catalyst A (Fig. 2e), and is formed in a chloride-free catalyst only after HCl addition. (ii) The formation of this species is directly connected with a redispersion (Fig. 6). It could be asked whether chloride only catalyzes the formation of the dispersing surface species or whether it is a component of this species itself. From a thermodynamic point of view it is impossible that a catalyst at the same temperature (600°C) can reverse the direction from sintering to redispersion, as observed in the experiment (Fig. 6a). Therefore, chloride must have become a component of the dispersing species and consequently $[Pt^{IV}O_xCl_y]_s$ must contain chloride. (iii) The uv–vis spectra of H_2PtCl_6 and of the proposed chloride-containing surface species contain three or four absorption bands whereas spectra of the proposed α- and β-$[PtO_2]_s$ contain only one band (*18*).

Reduction of an appropriate halogen-free catalyst, prepared from a Pt–π-allyl complex, also gives highly dispersed Pt (r13). After oxidation between 200 and 550°C, α-$[PtO_2]_s$ is formed (r6). This oxide is converted at higher temperatures of about 600°C into β-$[PtO_2]_s$ (r7), or if chloride is added, into $[Pt^{IV}O_xCl_y]_s$ at 450 to 600°C (r5). The decomposition of β-$[PtO_2]_s$, connected with the formation of crystalline Pt, starts above 600°C (r8). The reverse reaction, the redispersing reoxidation of crystalline Pt, is impossible with chloride-free catalysts. It only becomes possible if chloride is added, according to r4.

Redispersion of Platinum

The physical process of redispersion of Pt in oxygen has attracted special interest because of its importance for the regeneration of the catalysts.

From Fig. 6 the following conclusions can be made. (i) There is no redispersion without oxidation of crystalline Pt and no oxidation without redispersion. Redispersion is accompanied by a proportional increase of the Pt oxidation state. This means that redispersion and oxidation of crystalline Pt are inseparably connected. (ii) This "redispersing oxidation" of crystalline Pt is impossible with chloride-free catalysts. (iii) The redispersing oxidation of crystalline Pt results in the formation of $[Pt^{IV}O_xCl_y]_s$. Hence, this oxidation product must be the dispersing species and consequently it must be mobile, i.e., it can migrate on the surface of the alumina.

The conclusion that $[Pt^{IV}O_xCl_y]_s$ is the redispersing species is supported by the fact that the temperature range where this species can be formed (Figs. 2d, e) is identical with the known temperatures of redispersion, approximately 500 to 600°C.

On the basis of the above conclusions and of previous adsorption data (*24, 25*), indicating that small amounts of oxygen remain adsorbed between 500 and 600°C, we propose a new model of redispersion. In a first step special localized surface atoms of the Pt crystallite can be oxidized by oxygen. In a second step these oxidized sites are attacked by chloride ions coming from the alumina surface. In this reaction $[Pt^{IV}O_xCl_y]_s$ is formed. This species is mobile and migrates on the surface of the alumina. As a result Pt is removed from the Pt crystallite and disperses on the carrier. In addition, $[Pt^{IV}O_xCl_y]_s$ may be trapped on appropriate centres of the alumina. As will be shown in Part II (*18*), $[Pt^{IV}O_xCl_y]_s$ could be a platinate anion. This could migrate in the same way as the chloride ions on the alumina.

The mechanisms of redispersion proposed in the literature can be divided into crystallite (*15*) and molecular migration (*10*) models. Our proposal with the formation and migration of an oxidized surface complex is a molecular migration mechanism.

In several mechanisms (*10, 13, 14*) only bulk and dispersed oxides were assumed, but no chloride-containing species. Special model catalysts were prepared without mentioning an influence of chloride (*9, 13*). Straguzzi *et al.* (*8*) suggests that chloride is not necessary for redispersion. Dautzenberg and Wolters (*12*) concluded that a redispersion by oxygen is totally impossible.

Although some participation of chloride during the redispersion has been indicated before (*5, 8*), its crucial role as a necessity has been largely overlooked.

Altogether, reactions of four new surface species have been shown by the TPR and by the adsorption measurements. In Part II the existence of these species will be confirmed by uv–vis spectra and proposals for the structure of these species will be derived. The close relation between oxidized Pt and the soluble platinum will also be shown and the problem of sintering in oxygen will be treated (*18*).

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