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

II. Ultraviolet–Visible Studies, Sintering of Platinum, and Soluble Platinum

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$Pt/\gamma\text{-}Al_2O_3$ catalysts treated in oxygen between 100 and 600°C and in hydrogen at 500°C were studied by uv–vis reflectance spectroscopy. The formation of different oxidized Pt surface species previously indicated by TPR studies [H. Lieske, G. Lietz, H. Spindler, and J. Völter, *J. Catal.* **81**, 8 (1983)] was confirmed by characteristic uv–vis spectra. The results are used as the basis for a model describing the types of surface reactions and details of the platinum surface species formed in oxygen and in hydrogen, and for a model of the sintering in oxygen. The amount of soluble platinum was found to correspond with the amount of highly dispersed platinum. Hence, only surface platinum atoms are soluble.

INTRODUCTION

Oxygen and hydrogen treatments are essential procedures in the activation and regeneration of alumina-supported platinum, which is a well-known and extensively used catalyst for industrial hydrocarbon conversions. Although it is generally accepted that interesting catalytic factors such as the redispersion of platinum (*2–4*) and the formation of the so-called soluble platinum (*3, 5, 6*) are connected with an oxidation of the platinum, little is known about the details of oxidized platinum surface species. In Part I (*1*) TPR studies of oxygen treated $Pt/\gamma\text{-}Al_2O_3$ are reported. The existence of four different oxidized species, all of them containing Pt(IV), could be detected. Anticipating the results of the present paper, the species were denoted from the beginning with the formula $\alpha\text{-}[PtO_2]_s$, $\beta\text{-}[PtO_2]_s$, $[Pt^{IV}(OH)_xCl_y]_s$, and $[Pt^{IV}O_xCl_y]_s$. The index "s" indicates complex formation with an alumina surface site. In this work the existence and the nature of these surface complexes have been verified by an independent method, namely uv–vis reflectance spectroscopy. This method is especially sensitive to variations in the surface layers, but in the literature only few examples concerning supported metal catalysts could be found (*7, 8*).

Details of the spectra after particular chemical treatments have enabled models to be drawn up to describe the platinum surface species and their reactions. The formation of crystalline Pt at high temperatures was studied by X rays. Together with the previous TPR investigations (*1*) the results are used to draw up a model for the sintering in oxygen.

The nature of the surface platinum species must be connected with the solubility of platinum. Soluble platinum has been proposed to be either (i) dispersed Pt on the Al_2O_3 surface, becoming soluble in nonoxidizing agents after contact with oxygen (*9*), or (ii) special platinum–alumina complexes, containing ionic platinum, unreducible in hydrogen (*5, 6*). In order to clarify the relations between oxidized and soluble platinum, the formation of soluble platinum was

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studied as a function of the pretreatment in oxygen at different temperatures.

EXPERIMENTAL

Materials

Catalysts A and B, both containing 0.5 wt% Pt on γ-Al_2O_3 (Condea), were prepared from H_2PtCl_6 and $Pt(C_4H_7)_2$, respectively. These catalysts were used in the TPR studies of Part I, where further details of the preparation were described (*1*).

Catalyst D with 0.1 wt% Pt on SiO_2 (Aerosil) was prepared by impregnation of SiO_2 with an aqueous solution of H_2PtCl_6 and subsequent drying at 120°C for 2 h and calcination in flowing oxygen at 500°C for 2 h. $PtO_2 \cdot H_2O$ was prepared following Adams (*10*). $PtCl_2$ and K_2PtCl_4 were commercial p.a. products.

Procedures

The powdered samples used for uv–vis reflectance spectroscopy were calcined and reoxidized in an oxygen stream flowing at 6.0 liters/h; the time of treatment was 1 h. The samples were reduced *in situ* in the cuvette for 1 h at 500°C in a hydrogen stream flowing at 3.0 liters/h. The reference standard in the spectrometer, Pt-free γ-Al_2O_3 (Condea), was always treated in the same way as the samples. For catalyst D the standard was SiO_2 (Aerosil).

A Beckman spectrophotometer, DK-2A, was used for the uv–vis reflectance spectroscopy in the range between 200 and 1500 nm.

Determination of Crystalline and Soluble Platinum

Crystalline and soluble Pt were determined as a function of thermal treatment in oxygen in the range from 200 to 900°C. After these pretreatments the Pt content of the samples was measured once more. Only in the case of chlorine-containing samples and with temperatures of 800°C and higher was some loss of Pt observed. For 800 and 900°C treatments the Pt content decreased from 0.56 to 0.45 and 0.36 wt%, respectively. This loss was taken into account when calculating the values of crystalline and soluble Pt.

The amount of crystalline platinum was determined by X-ray analysis using the Pt (311) reflection (*11*). A catalyst sample with 2.3 wt% Pt annealed at 800°C in oxygen was used as a standard for completely crystallized platinum. The amount of soluble platinum was determined by dissolving the powdered catalysts in H_2SO_4 (25%) and determining platinum with a spectrophotometer (*3*).

RESULTS AND DISCUSSION

Surface Complexes of Oxidized and Reduced Pt

$[PtCl_6]_s^{2-}$. The surface complex, denoted $[PtCl_6]_s^{2-}$, is obtained after impregnating γ-Al_2O_3 with a H_2PtCl_6/HCl mixture and drying at 120°C (catalyst A). We propose that a chemical reaction takes place during the impregnation. The anion $[PtCl_6]^{2-}$ is adsorbed on a positively charged Al site by a ligand exchange of OH^- or Cl^- for $[PtCl_6]^{2-}$ and this surface fixation of the complex is preserved after drying at 120°C with only very slight distortion of the complex.

This thesis is supported by the following experiments. The uv–vis spectrum of the $[PtCl_6]_s^{2-}$ species is shown in Fig. 1, curve 1. Three absorption bands are seen at 275, 353, and 450 nm (36 364, 28 329, and 22 222 cm^{-1}). Nearly the same bands are known from the spectrum of H_2PtCl_6 in aqueous solution (*12*) with d–d transition bands at 353 and 450 nm and a charge transfer (CT) band resulting from an electron transfer from chlorine to platinum at 262 nm. Schematic diagrams of the spectra are shown in Fig. 2, where it can be seen that in comparison to the complex in solution the d–d bands in the surface complex are unchanged. The CT band is shifted a little to higher wavelengths, from 262 to 275 nm. This shift is regarded as a distinct hint of some chemical interaction with the surface

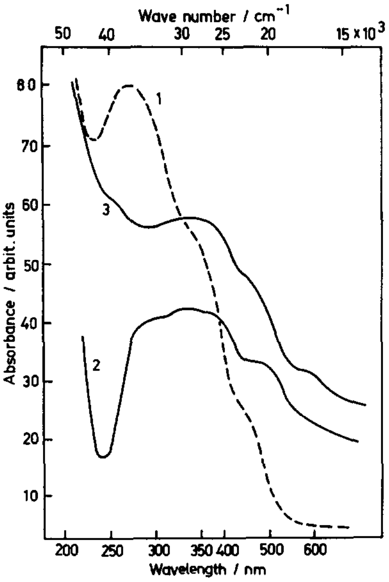

FIG. 1. Uv–vis spectra of catalyst A after pretreatment in oxygen at 120°C: $[PtCl_6]_s^{2-}$ (curve 1), at 300°C: $[Pt(OH)_xCl_y]_s$ (curve 2), and at 500°C: $[PtO_xCl_y]_s$ (curve 3).

site "s." The unchanged d–d bands suggest that the octahedral complex with the six Cl^- ligands is preserved.

A surface interaction can be explained as a reaction with OH^- groups of the alumina. This is in accordance with observations that the impregnation of γ-Al_2O_3 with $[PtCl_6]^{2-}$ (*13*) and with $[PtCl_6]^{2-}$ and HCl (*14*) reaches a saturation value and this value of 10^{14} sites/cm^2 is of the same order of magnitude as the OH^- group density (*15*). The proposed surface interaction is an anion exchange between $[PtCl_6]^{2-}$ and OH^-, or Cl^- in the presence of HCl. The absence of amphoteric OH^- groups on silica could explain the well known experience that $[PtCl_6]^{2-}$ is adsorbed much better on Al_2O_3 than on SiO_2.

$[Pt^{IV}(OH)_xCl_y]_s$. The treatment of catalyst A containing $[PtCl_6]_s^{2-}$ in oxygen at 300°C causes a transformation into a new species $[Pt^{IV}(OH)_xCl_y]_s$, previously detected in TPR experiments (*1*). The existence of this species is confirmed by the uv–vis spectra shown in Figs. 1 and 2. Four bands can be distinguished. The band at 285 nm (35 088 cm^{-1}) is in the range of CT transitions involving Pt, whilst the bands at 335, 375, and 475 nm (29 851, 26 667, and 21 053 cm^{-1}) indicate d–d transitions.

This new species is formed from $[PtCl_6]^{2-}$ and the spectra seem to be comparable (Fig. 2) with the exception that a new band is observed. This could be caused by a splitting of the 350-nm band into bands at 335 and 375 nm. It is known that with an unchanged coordination of the complex a splitting is caused by a substitution of ligands (*16*). We take this as an indication that in the surface reaction chloride is partly substituted by another ligand.

From the chemistry of the H_2PtCl_6 solutions it is known that in nonacidic solutions a hydrolytic ligand exchange according to

$$[PtCl_6]_s^{2-} + xH_2O \rightarrow [Pt(OH)_xCl_y]_s^{2-} + xH^+ + xCl^- \quad (1)$$

easily occurs, and $[PtCl_5(OH)]^{2-}$ and $[PtCl_4(OH)_2]^{2-}$ can be identified (*17*). We found in additional experiments with γ-Al_2O_3 in HCl-free H_2PtCl_6 solutions that after 24 h four Cl^- ions from the $[PtCl_6]^{2-}$ are

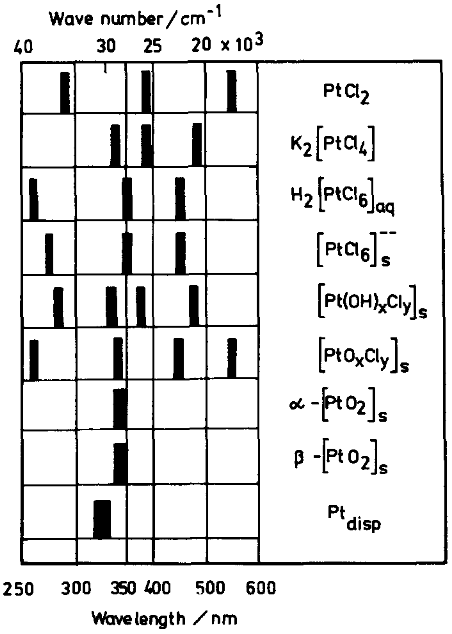

FIG. 2. Scheme of the observed uv–vis bands of the investigated Pt species.

exchanged, whereas HCl inhibits the exchange.

During pretreatment in oxygen at 300°C water is present from the dehydration of the alumina and the H^+ formed can be neutralized by OH surface groups. These conditions are in favor of a Cl^- ligand substitution according to Eq. (1). Formation of $PtCl_2$, as concluded by Escard *et al.* (*18*) from ESCA experiments, and of $[PtCl_4]^{2-}$ must be excluded. TPR experiments (*1*) proved a Pt valence of +4. Moreover the uv–vis spectra of $PtCl_2$ and K_2PtCl_4, both observed in mechanical mixtures with γ-Al_2O_3, are quite different from that of $[Pt(OH)_xCl_y]_s$ (Fig. 2).

Thus, the uv–vis results suggest that a ligand exchange takes place. The chemistry of the $[PtCl_6]^{2-}$ anion and of the alumina surface argues for a ligand exchange Cl^- against OH^-. Therefore, we propose the surface species hydroxochloroplatinum $[Pt^{IV}(OH)_xCl_y]_s$, with variable amounts of ligands x and y. In closer analogy to the known hydrolytic exchange in solution, this species could be a hydroxochloroplatinate $[Pt^{IV}(OH)_xCl_y]^{2-}$.

$[Pt^{IV}O_xCl_y]_s$. According to TPR experiments (*1*) treatment of the catalyst containing $[Pt^{IV}(OH)_xCl_y]_s$ at 500°C in oxygen or argon results in a new surface species with Pt(IV), denoted $[Pt^{IV}O_xCl_y]_s$. The existence of this species has now been confirmed by a specific uv–vis spectrum, as can be seen in Figs. 1 and 2.

The same spectrum and therefore the same species is obtained by thermal treatment at 500°C, if a chloride-free catalyst containing only α-$[PtO_2]_s$ is treated with HCl (*1*). The two ways of synthesis can be represented by

$$\alpha\text{-}[PtO_2]_s + 2Cl^- \rightarrow [PtO_2Cl_2]_s^{2-}, \quad (2)$$

$$[Pt(OH)_4Cl_2]_s^{2-} \rightarrow [PtO_2Cl_2]_s^{2-} + 2H_2O. \quad (3)$$

This would mean that the thermal treatment causes in one case [Eq. (2)] an addition of chloride, and in the other case [Eq. (3)] a dehydration, incorporating a transformation of OH^- ligands to O^{2-} ligands and water.

In the uv–vis spectrum of this species four bands are observed (Figs. 1 and 2) with maxima at 260, 340, 450, and 550 nm (38 462, 29 412, 22 222, and 18 182 cm^{-1}). The band at 260 nm corresponds well with the CT transition Cl → Pt in $[PtCl_6]^{2-}$ in aqueous solution. This strongly supports the proposal that this surface species really contains chloride. The assumed four-ligand complex $[Pt^{IV}O_2Cl_2]_s^{2-}$ has a lower symmetry than the octahedral $[PtCl_6]^{2-}$. As a rule lowering of symmetry causes a splitting of the d–d bands (*16*). In comparison with the spectrum of $[PtCl_6]^{2-}$ an additional band is observed in the new species.

Therefore, the uv–vis species and the chemical reactivity are consistent with the assumption of a $[Pt^{IV}O_2Cl_2]_s^{2-}$ surface species. The less sophisticated, more general proposal is $[Pt^{IV}O_xCl_y]_s$.

It should be mentioned that the spectrum of this species is only obtainable with dried catalysts. After access of water vapour only one broad band at about 325 nm appears. After drying at 300°C the four-band spectrum reappears. This means that on the surface complex water can be reversibly coordinated.

Pt_{disp}. The reduction at 500°C in hydrogen converts $[PtO_xCl_y]_s$ into highly dispersed metallic platinum, Pt_{disp}, with a hydrogen adsorption of 1.1 H/Pt (*1*). This species gives a characteristic broad absorption band at 325 nm (30 769 cm^{-1}) in the range of charge transfer transitions involving Pt (Fig. 3). The same band is seen with dispersed platinum obtained by reduction of α-$[PtO_2]_s$ or β-$[PtO_2]_s$ surface species present in chloride-free catalysts. However, this band is absent in the spectra from Pt–Mohr (*19*), which was mechanically mixed with γ-Al_2O_3, and in the spectrum of reduced Pt on silica (catalyst D) (Fig. 4, curves 5 and 6).

The observed absorption band should indicate an interaction of the dispersed platinum with the alumina. We propose the for-

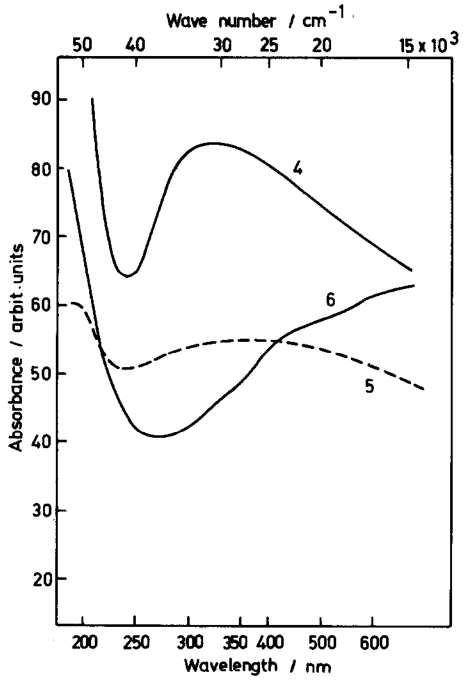

FIG. 3. uv–vis spectra of reduced platinum on alumina (curve 4 Pt_{disp}), on silica (curve 5), and on unsupported Pt–Mohr (curve 6).

mation of a molecular charge-transfer complex between oxidizing sites of the alumina and molecular dispersed Pt. The formation of such a molecular complex with a slight admixture of an ionic state of electron-deficient Pt and of acidic alumina sites, has been suggested by Figueras *et al.* (*20*).

Silica with its lower acidity in comparison with alumina should be less suited for the formation of the proposed Pt charge-transfer complex. This is in accordance with our experiments. As seen in Fig. 3, almost no absorption occurs at 325 nm.

The existence of small amounts of Pt in an electron-deficient state in reduced Pt on Al_2O_3 has been shown by ESCA (*21, 22*) and by EXAFS (*23*) experiments.

α-[PtO_2]$_s$ and β-[PtO_2]$_s$. The reoxidation of dispersed platinum, Pt_{disp}, at 300°C in oxygen results in the formation of α-[PtO_2]$_s$ and at higher temperatures in the case of a chloride-free catalyst (catalyst B) in the formation of β-[PtO_2]$_s$ (*1*). From both species the same spectrum is obtained with a broad absorption band at about 350 nm (28 571 cm^{-1}). This is shown in Fig. 4. The spectrum from bulk $PtO_2 \cdot H_2O$, mixed with γ-Al_2O_3 has a quite different maximum at 425 nm. Therefore, one must conclude that α- and β-[PtO_2]$_s$ really are surface complexes. TPR experiments indicated that the α- and β-oxides must be different species, both with Pt(IV) (*1*). The chemical explanation of this difference is still an open question. The terms α-[PtO_2]$_s$ and β-[PtO_2]$_s$ for our PtO_2 surface species are not related to the terms for different bulk modifications of PtO_2 used in the literature.

In additional experiments it could be observed that an oxygen treatment at room temperature of the Pt_{disp} caused no significant change of the uv–vis spectrum. From adsorption experiments it is known that at 0°C oxygen is adsorbed in the ratio 2 : 1 corresponding to Pt_2O_{ad} (*24*). The drastic change of this ratio up to 1 : 2 in α-[PtO_2]$_s$ at 300°C causes no detectable consequences

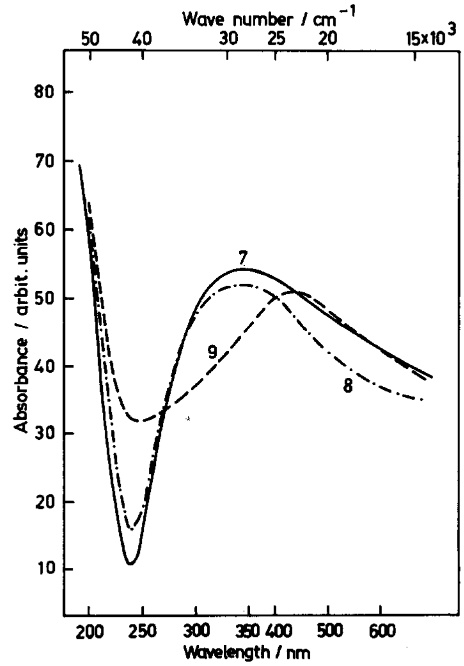

FIG. 4. uv–vis spectra of platinum oxides: α-[PtO_2]$_s$ (curve 7), β-[PtO_2]$_s$ (curve 8), and bulk $PtO_2 \cdot H_2O$ (curve 9).

in the spectrum. Always only one broad band at about 350 nm is seen.

It should be emphasized that the uv–vis spectra give a distinct difference between chloride-free and chloride-containing oxidized Pt species. The first ones give a one-band spectrum, the latter a four-band spectrum (Fig. 2). The appearance of four bands in the cases of $[Pt^{IV}(OH)_xCl_y]_s$ and $[Pt^{IV}O_xCl_y]_s$ is a further hint for the chloride content of these species.

Sintering of Platinum in Oxygen

X-Ray analysis. In Part I (*1*) it was suggested that the oxidized species decompose with formation of crystalline Pt. This has now been checked by X-ray analysis. The amount of crystalline platinum in catalyst A was determined as a function of the temperature of treatment in oxygen. The results are shown in Fig. 5b. The crystallinity was determined twice, once after the oxygen treatment and then again after a subsequent reduction in hydrogen at 500°C. The amount of crystalline platinum was the same in the oxidized and the reduced catalysts within an experimental error of ±5%. Below 700°C no crystalline platinum was found. In the range between 700 and 900°C the amount of crystalline platinum strongly increases. The particle size of the crystallites in the sample containing only 30% crystalline Pt (800°C) is already larger than 20 nm.

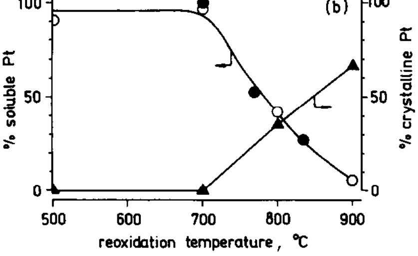

FIG. 5. (a) Dispersion (H/Pt) of catalyst A and valence per surface atom of catalyst A (●) and B (■), cited from Ref. (*1*), as a function of the temperature of oxygen treatment. (b) Content of soluble platinum from oxidized (●) and reduced (○) samples and content of crystalline platinum (▲) as a function of the temperature of oxygen treatment of catalyst A.

It should be mentioned that in catalysts containing more Pt (2.3 wt%), crystalline Pt can be detected already after treatments at lower temperatures (*25, 26*).

Species and bimodality of Pt in the sintering range. The X-ray analysis indicated an increasing amount of crystalline Pt at temperatures above 700°C. From TPR experiments it is known that in this range the oxidized Pt species $[PtO_xCl_y]_s$ in the case of Cl^--containing, and β-$[PtO_2]_s$ in the case of Cl^--free catalysts exist and that their amounts dramatically decrease (*1*). Thus it can be concluded that in the sintering range crystalline Pt and oxidized Pt species are coexisting. This means that there is a bimodal distribution of the Pt between relatively large crystals and molecular dispersed surface species.

This conclusion is supported by the following observations. (i) In Part I, Figs. 3, 5, and 6 a remarkable parallelism is observable between the average Pt valence and the average Pt dispersion (*1*). The ratio of these values, the valence per surface atom, is shown in Fig. 5a as a function of the reoxidation temperature; the dispersion is also included. It can be seen that the ratio is constant at about 4 : 1.

This means that in the range of high dispersion, below 700°C, as well as in the sintering range, above 700°C, only surface atoms are in an oxidized state. This is the oxidation state +4. (ii) The reduction temperature of the oxidized surface atoms is high and is the same in catalysts without crystalline Pt (highly dispersed) and catalysts with crystalline Pt; the TPR peaks do not change (*1*). Bulk PtO_2 without carrier stabilization from the alumina (*27*) as well as adsorbed oxygen on Pt are reduced at much lower temperatures. Hence, the reoxidized Pt atoms must be located directly on the alumina and not on the Pt crystallites.

The only explanation consistent with both the above conclusions is the coexistence of highly dispersed oxidized species and of crystalline Pt, which practically does not contribute to the average dispersion. Moreover, this bimodality is in line with the findings that the average particle size calculated from the hydrogen adsorption is relatively high (5 nm at 800°C), but is much lower than the size calculated from the X-ray diffraction (>20 nm). A similar bimodal distribution has been found by Dautzenberg and Wolters (*28*).

Several authors (*2, 29–31*) postulate the formation of bulk PtO_2 in their redispersion and sintering mechanisms. In this case no parallelism of average valence and average dispersion should be found and the ratio of valence and dispersion should exceed the value 4. Furthermore, the amount of crystalline Pt determined by X rays should be lower after oxygen than after hydrogen treatment. However, this is inconsistent with our experimental data.

Mechanism of sintering. From the observed changes in dispersion and valence the following model of sintering in oxygen is derived. The reason for the sintering is the thermal decomposition of the surface complexes $[PtO_xCl_y]_s$ or β-$[PtO_2]_s$. As a result of this decomposition Pt atoms or small clusters are formed. These species rapidly migrate on the surface of the alumina and via nucleation metallic crystallites are formed. These can grow by capturing further Pt atoms or clusters.

This mechanism involves the decomposition of molecular dispersed species and therefore is a molecular migration mechanism. This is in general accordance with several proposals in the literature (*2, 27, 28*), but is contrary to other models (*29, 32*).

Another possibility of sintering could be a gas phase transport by volatile Pt chlorides or carbonyls (*33*). The observed stronger sintering of the chloride-free catalyst B in comparison with the chloride-containing catalyst A (*1*) is an argument against a gas phase transport mechanism in the present case.

Soluble platinum. The formation of soluble platinum was examined in the chloride-containing catalyst A as a function of the temperature of the treatment in oxygen. After reduction at 500°C the catalysts were treated for 1 h in air at 100°C. This procedure has the same effect as a long time influence of air at room temperature. In accordance with previous findings (*34*) the platinum remains insoluble in reduced catalysts if an oxygen attack is excluded.

The results are shown in Fig. 5b. Within an experimental error of ±5% the solubility is the same in catalysts oxidized only and in catalysts subsequently reduced and reoxidized at 100°C. This means that the Pt valence state before the mild oxidation in air is without influence on the solubility. Up to pretreatment temperatures of 700°C practically 100% of the platinum is soluble. At higher temperatures the solubility decreases strongly, reaching practical insolubility at about 900°C.

This can be compared with the dispersion of Pt determined by hydrogen adsorption reported previously (*1*) and shown also in Fig. 5a. A distinct proportionality can be seen between dispersed platinum and soluble platinum. Moreover, the crystalline platinum can also be correlated. Soluble platinum was found to be amorphous, and with decreasing solubility above 700°C the amount of crystalline platinum increases to nearly the same extent.

All the correlations support the simple conclusion that soluble platinum is formed from surface atoms and only from surface atoms. These atoms become soluble if they are mildly or completely oxidized; the resulting oxidation state is without influence. By these conditions the nature of soluble platinum can be described.

The observed complete reduction of oxi-

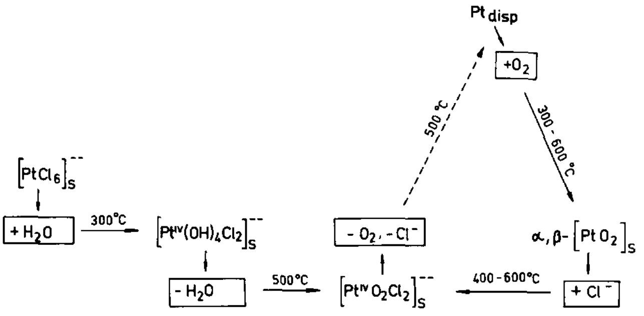

FIG. 6. Scheme of surface reactions of Pt/Al_2O_3 catalysts, caused by treatments in oxygen (——→) and hydrogen (- -→) at different temperatures.

dized Pt to dispersed Pt (*1*) excludes the possibility that soluble platinum is ionic platinum in special unreducible platinum alumina complexes, as proposed by McHenry *et al.* (*5*) and Bursian *et al.* (*6*).

Model of Surface Reactions

The results and conclusions with the exception of crystalline and soluble Pt can be summarized in the model of surface reactions shown in Fig. 6. This sequence of reactions corresponds with the usual procedure of catalyst preparation, viz., impregnation, calcination, and reduction and finally a reoxidation during regeneration treatments.

According to the model the $[PtCl_6]^{2-}$ anion is adsorbed on positively charged Al sites during the impregnation. The polar surface bond is maintained after drying at 120°C, and the surface complex is denoted as $[PtCl_6]_s^{2-}$. In oxygen at 300°C the Cl^- ligands are partly substituted by OH^-, forming $[Pt(OH)_4Cl_2]_s^{2-}$. At higher temperatures the OH^- ligands are transformed into O^{2-} and water, and $[PtO_2Cl_2]_s^{2-}$ results. The proposed number of Cl^-, OH^-, and O^{2-} ligands in these complexes gives one probable example of different possibilities with Pt(IV) only. By careful reduction from all oxidized surface species dispersed platinum, Pt_{disp}, is obtained. This forms a molecular charge-transfer complex with alumina. After reoxidation at 300°C α-$[PtO_2]_s$ is formed. At higher temperatures this species is transformed either into β-$[PtO_2]_s$ in the case of chloride-free catalysts or into $[PtO_2Cl_2]_s^{2-}$ in the case of chloride-containing catalysts. The formation of $[PtO_2Cl_2]_s^{2-}$ enables the redispersion to occur, whereas its thermal decomposition results in a sintering of the platinum.

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