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Reduction of Pt/Al_2O_3 Catalysts: Effect of Hydrogen and of Water and Hydrochloric Acid Vapor on the Accessibility of Platinum

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The direct reduction by hydrogen, without precalcination, of Pt/Al_2O_3 activated by H_2PtCl_6 was studied on several series of catalysts with different metal and chloride loadings. It appears that H_2O acts as a kinetic inhibitor of the reduction reaction but can also induce platinum sintering. HCl has no kinetic effect on the reduction but is able to increase the metallic accessibility. The higher the hydrogen pressure, the lower the platinum dispersion. The extent to which the metal is accessible is considered to be resultant of two parallel reactions, namely polymerization and reduction of partly reduced Pt^{2+} complexes. © 1992 Academic Press, Inc.

INTRODUCTION

Dispersion of platinum in supported catalysts is particularly sensitive to activation pretreatment (*1–9*). Thus, such catalysts are well dispersed when they are activated by calcination before reduction, whereas the metal accessibility decreases when the precursor is reduced directly without calcination. As water is known to induce metal sintering, several authors explained this phenomenon by assuming that the drying of the precursor before the reduction is a prominent variable for the final dispersion of the metal (*1–6*).

In the case of a platinum chloride as precursor, the reduction leads to the production of hydrochloric acid which can desorb from the support. The amount of hydrochloric acid desorbed, for a given support, depends on the metal loading. Thus, a catalyst with a low platinum loading (and therefore with a low amount of chloride introduced as H_2PtCl_6) will maintain the totality of chloride at the surface of the alumina, whereas a catalyst with a high platinum chloride loading will lead, after saturation of the support, to a chloride desorption as HCl during the reduction. Under such conditions chloride is able to increase metallic dispersion.

The purpose of this work is to study the reduction of Pt/Al_2O_3 catalyst without preliminary calcination in order to define the conjoint effects of water and hydrochloric acid on the metal accessibility. The accessibility was evaluated by selective chemisorption of hydrogen taking into account that chemisorption of gases requires the availability of adsorption sites on the crystallites (which may be covered and hence prevent chemisorption, even though the dispersion is high).

EXPERIMENTAL

Two $Pt/\gamma\text{-}Al_2O_3$ samples, with Pt loadings of 0.6 and 6 wt%, respectively, were prepared by impregnation of a γ-alumina powder support with the appropriate quantity of chloroplatinic acid solution. The mixtures were evaporated and dried in air at 393 K. The alumina carrier was Rhône Poulenc GFS 400 (210 $m^2\ g^{-1}$) and was previously heated at 923 K.

Pt and Cl contents of the solid samples were determined by analysis carried out respectively by inductive coupling plasma (ICP) and ionic chromatography.

To study the effect of produced water and chloride on dispersion, a reactor with three superimposed catalyst beds was used.

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The accessibilities of Pt/Al_2O_3 catalysts, reduced under hydrogen flow at 623 K for 2 h, were determined by the surface gas titration method introduced by Benson and Boudart (stoichiometries H/Pt = O/Pt = 1) (*9*). The volumetric technique method was used for chemisorption measurements. The irreversible chemisorptions were evaluated by the double isotherm technique, i.e., the difference between the total adsorption (first isotherm) and the reversible adsorption (second isotherm) carried out after evacuation for 1 h at room temperature.

TPR measurements were made in a flow system similar to that described by Boer *et al.* (*10*) with temperatures ranging from 293 to 673 K. Nonreduced catalysts were submitted to a programmed temperature rise (2 to 6 $K \cdot min^{-1}$) while H_2/Ar (1/100) gas mixture was flowed over it. The rate of reduction was continuously measured by monitoring the composition of the reducing gas at the outlet of the reactor. Analysis was carried out by using a thermal conductivity detector.

Equipment for thermogravimetric analysis (TGA) was a Mettler TA 300 system allowing weight loss recording under N_2 flow with a rate of rise of temperature equal to 10 $K \cdot min^{-1}$.

RESULTS

Reducibility of Platinum

The temperature-programmed reduction (TPR) of Pt/Al_2O_3 catalysts, without preliminary calcination, was studied on precursors with different metal loadings and hence with variable amounts of chloride.

Effect of the metal loading. Figure 1 presents the TPR curves of two samples of alumina impregnated with different amounts of H_2PtCl_6.

An increase of the platinum loading induces a decrease in the temperature of the maximum of the TPR peak and hence an increase of the rate of the reduction reaction. On the other hand an increasing heating rate of reduction goes in parallel with a higher temperature for the TPR peak. Thus the higher the rate of rise of temperature, the lower the rate of reduction (Table 1).

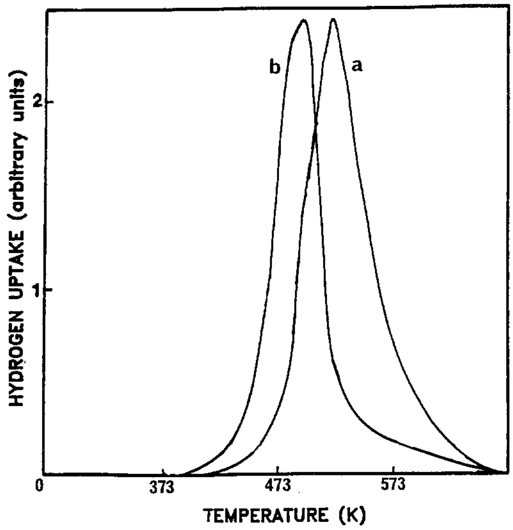

FIG. 1. TPR curves of Pt/Al_2O_3 catalysts. (a) 0.6 wt% Pt/Al_2O_3. (b) 6 wt% Pt/Al_2O_3.

Integration of the TPR peak areas of Fig. 1 enables one to determine the oxidation degree of deposited platinum, which was equal to 4, whatever the metal loading was. (The oxidation degree of 0.6 wt% Pt/Al_2O_3 was found to be 4.0 ± 0.1 while that of a 6 wt% Pt/Al_2O_3 was 3.9 ± 0.1.)

Effect of chloride. The hydrochloric acid content of the gas phase during the reduction varies with the H_2PtCl_6 loading of the impregnated precursor. For the 0.6 wt% Pt/Al_2O_3 catalyst the chloride content is equal to 0.65 wt% before or after reduction while for the 6 wt% Pt/Al_2O_3 catalyst, the chloride content is 6.55 wt% before reduction and 1.20 wt% after reduction. Thus, after reduction with a low metal loading (0.6 wt% Pt) all chloride introduced during impregnation remains absorbed on the catalyst. Accordingly, in this case, the HCl pressure in the gas phase during the reduction will be negligible. On the other hand, for a catalyst with a high metal loading (6 wt% Pt), a large amount of hydrochloric acid desorbs during the reduction. Figure 2 shows the variation of the HCl desorption versus

TABLE 1

Effects of Metal Loading and of Heating Rate on the Temperature Corresponding to the Maximum of the TPR Peak

Catalyst	Heating rate ($K \cdot min^{-1}$)	Temperature of maximum of TPR peak ± 5 K
0.6 wt% Pt/Al_2O_3	2	519
	6	554
6 wt% Pt/Al_2O_3	2	492
	6	533

temperature compared with the hydrogen consumption during the reduction. It appears that hydrochloric acid is desorbed as soon as it is formed.

A sample of 0.6 wt% Pt/Al_2O_3 was loaded with 6 wt% in chloride by hydrochloric acid addition during impregnation. Figure 3 allows the comparison of the TPR curves for two samples of catalysts with significantly different initial chloride contents. The similarity between the two curves demonstrates that the effect of hydrochloric acid on the rate of platinum reduction is negligible.

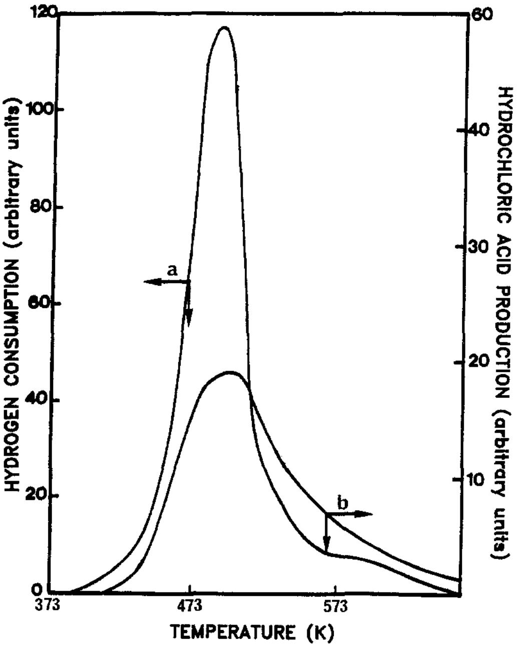

FIG. 2. Comparison of H_2 consumption (a) and hydrochloric acid production (b) during reduction of 6 wt% Pt/Al_2O_3 catalyst.

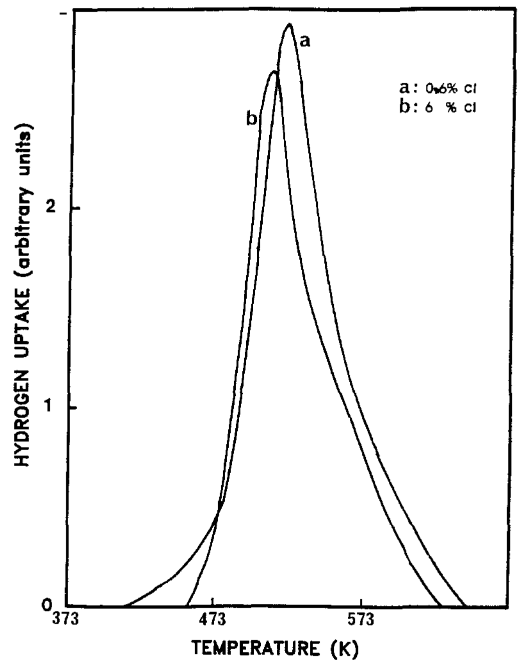

FIG. 3. Effect of chloride content on the TPR curves of 0.6 wt% Pt/Al_2O_3 catalysts. (a) 0.6 wt% in Cl^-. (b) 6 wt% in Cl^-.

Effect of the Operating Conditions on Platinum Accessibility

The different parameters studied were the height of the catalyst bed, the heating rate, and the hydrogen partial pressure used during reduction.

Height of the catalyst bed. Different amounts of a 6 wt% Pt/Al_2O_3 catalyst, from 1 to 9 g, were directly reduced in the same reactor. Figure 4 indicates that the metallic dispersion decreases when the catalyst weight and hence the height of the catalyst bed increases.

Heating rate. This study was carried out in a glass flow reactor with three superimposed catalyst beds. The results recorded in Table 2 for catalyst beds of 1 g of 6 wt%

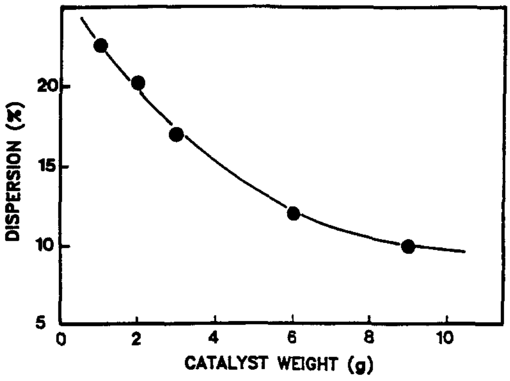

FIG. 4. Effect of the weight of reduced Pt/Al_2O_3 samples on the accessibility of Pt.

TABLE 3

Effect of Hydrogen Partial Pressure on Platinum Accessibility

Catalyst (wt% Pt/Al_2O_3)	Heating rate ($K \cdot min^{-1}$)	H_2 pressure (bar)	Dispersion (%)
0.6	2	1	42
6	2	1	23
0.6	2	0.01	64
6	2	0.01	42
0.6	6	0.01	48
6	6	0.01	37

Pt/Al_2O_3 show that the lower the heating rate, the higher the metallic dispersion. On the other hand, the platinum dispersion decreases from the first catalyst bed to the last one. The higher the amount of reduced catalyst, and hence the higher the pressure of reduction products (H_2O or HCl), the lower the accessibility of the metal.

Hydrogen pressure. Table 3 enables one to compare the dispersion of Pt/Al_2O_3 catalysts reduced in a pure hydrogen flow with those reduced under 1% H_2–Ar mixture. For the same heating rate, a decrease of the hydrogen partial pressure induces an increase of the metal dispersion.

Effect of Water on Platinum Accessibility

The previous results showed that metallic dispersions are lowered by the products of direct reduction of impregnated chloroplatinic acid (mixture of water and hydrochloric acid vapor).

In order to differentiate the effect of water alone from that of the mixture of water and hydrochloric acid, the first catalyst bed, in the flow reactor with three superimposed beds, was replaced by pure alumina (without precursor) previously treated by water.

The results recorded in Table 4 indicate that the metal dispersion of the second bed is lower when only water desorbs from the first bed. This effect can be explained by assuming that hydrochloric acid, which comes from the platinum chloride reduction, partially hinders the deleterious effect of water on metal accessibility.

The TGA curve of alumina shows that the amount of water desorbed per unit of time is stable between 473 and 673 K, which is the same range of temperature as that of platinum reduction. Such water elimination allows one to define a partial pressure in the gas phase which will depend on hydrogen flow, heating rate, and alumina weight.

TABLE 2

Effect of Heating Rate on Platinum Accessibility (Three Superimposed Catalyst Beds)

Heating rate ($K \cdot min^{-1}$)	Catalyst bed	Quantity of catalyst (g)	Dispersion (%)
0.1	1st	1	38
	2nd	1	30
	3rd	1	30
6	1st	1	23
	2nd	1	16
	3rd	1	14
10	1st	1	22
	2nd	1	16
	3rd	1	14
6	1st	3	16
	2nd	3	8
	3rd	3	7

TABLE 4

Effect of Water on Platinum Accessibility

Reduction conditions	Dispersion (%)		
	1st bed	2nd bed	3rd bed
1 g of 6 wt% Pt/Al_2O_3 in each bed	23	16	14
1 g of Al_2O_3 in 1st bed and 1 g of 6 wt% Pt/Al_2O_3 in 2nd and 3rd beds	(Pure Al_2O_3)	8	8
6 g of Al_2O_3 in 1st bed and 1 g of 6 wt% Pt/Al_2O_3 in 2nd and 3rd beds	(Pure Al_2O_3)	8	8

Thus, an increase of the water partial pressure (6 or 1 g of alumina in the first bed (Table 4)) does not modify metal dispersion which comes down to a limiting value.

Effect of Hydrochloric Acid on Platinum Accessibility

The effect of the partial pressure of HCl during platinum reduction was studied by using two series of Pt/Al_2O_3 catalysts with different chloride loadings. In series A, catalysts with different metal loadings, chloride is introduced only by the H_2PtCl_6 precursor, while in series B the initial chloride content is increased by HCl addition during the impregnation step.

The results in Table 5 show that for a given metal loading, the higher the amount of chloride desorbed during reduction, the higher the dispersion of the metal.

DISCUSSION

The effects of steam or hydrochloric acid on supported metal catalysts have been extensively studied. It is well known that such compounds influence the dispersion of the metal crystallites in various ways, such as inducing or inhibiting sintering of prereduced Pt/Al_2O_3 catalysts (*11–16*). The purpose of the present work is to define the role of water and hydrochloric acid on the reaction of direct reduction of platinum introduced as H_2PtCl_6 on alumina.

In such experiments it stands to reason that modifications of the metal accessibility could be the result of two phenomena: the effect of H_2O or/and HCl before or during reduction of platinum ions; the effect of H_2O or/and HCl on the Pt atoms of a partly reduced metallic phase.

Regarding the second possibility, the migration of reduced platinum particles, the valid mechanism during sintering in hydrogen, is very slow at temperatures lower than 873 K (*13, 14*). Thus, during the reduction of platinum at low temperature, sintering of reduced platinum is not likely to occur.

In fact, the effects of water or hydrochloric acid displayed in this work could be in close relationship with chemical or kinetic modifications occurring before or during the reduction of platinum ions.

The Pt/Al_2O_3 catalysts studied were prepared by impregnation of alumina with aqueous solutions of chloroplatinic acid. Adsorption of H_2PtCl_6 on alumina has been widely studied (*17*). According to Anderson (*19*), activation of alumina occurs in parallel with a real ligand exchange yielding a surface platinum hydroxychloride. Bournonville (*20*) proposed that on γ-Al_2O_3 an anion exchange with surface hydroxyl groups oc-

TABLE 5

Effect of the Amount of Desorbed HCl during Reduction on the Accessibility (D) of Platinum

Series	Pt (wt%)	Cl (wt%) (before reduction)	Cl (wt%) (after reduction)	D %
A	0.45	0.5	0.5	42
	4.16	4.5	1.2	25
B	0.56	6.6	0.9	53
	4.62	11.0	0.9	38

curs, keeping $(PtCl_6)^{2-}$ in this form on the support.

Lieske *et al.* (*7, 8*) agree with this last assumption and consider that such deposited compounds will be stable up to 600 K. Hence, direct reduction of platinum catalysts, without previous calcination, involves this unmodified species. Meanwhile, if the absence of precalcination treatment leaves metal precursors in their initial states, a large amount of water is not eliminated from the catalyst. A thermogravimetric analysis has shown that the main part of that water is released between 500 and 700 K, which corresponds to the reduction temperature range (Fig. 1). Such steam emission is able to induce an important Pt dispersion decrease.

This phenomenon was often noted (*3, 6*) and could be due, when capillary condensation of water can occur, to the aquation of the adsorbed complex and/or to the dissolution of the metal precursor deposited on the support, which could therefore be dislodged from its site of exchange and then crystallize in large aggregates as soon as water is eliminated. The microporosity will play an important part in this phenomenon which, by precipitation from supersaturated solutions in the pores, yields formation of large particles at the mouths of the pores (*21, 22*). For slow rates of increasing temperature of reduction, the steam partial pressure remains low and so only very small pores are involved in the capillary condensation of water. However, at higher steam pressures (induced by a high rate of rise of the reduction temperature (Tables 2 and 3) or by an increasing weight of catalyst (Fig. 4), capillary condensation can occur in larger pores. Ultimately the whole porosity can be involved for a high enough steam pressure. As a result, the metallic dispersion will reach a lower limit (Tables 2 and 4) which will be independent of the water pressure during reduction and thus independent of the experimental conditions (temperature rise, weight of catalyst, hydrogen flow-rate, etc.).

On the other hand, increasing steam pressure induced by a higher rise of temperature during the reduction step brings about a lowering platinum accessibility (Table 2) and a lowering rate of reduction of the platinum salt by the hydrogen flow (Table 1). This result is unquestionable on 0.6 wt% Pt catalyst since no chloride, only water, is desorbed during reduction. This inhibiting effect of water on the rate of reduction may be of a kinetic nature but can be explained also by a modification of the chemical nature of the exchanged metallic salt. For instance, Michelot *et al.* (*21*) pointed out that the $(PtCl_6)^{2-}$ ion undergoes a slow hydrolysis at room temperature. Moreover, it is known that $(PtCl_6)^{2-}$ solution can be completely transformed into $(Pt(OH)_6)^{2-}$ in the presence of an excess of OH^- ions (*23*). The concentration of OH groups on the alumina support can be greatly increased by steam and so the exchanged $(PtCl_6)^{2-}$ ion could be transformed into a less reducible hydroxylated complex.

In another way, water, during reduction by hydrogen, could induce an aquation of a partly reduced complex,

$$(PtCl_6)^{2-}/\text{support} + H_2 \rightarrow (PtCl_4)^{2-}/\text{support} + 2H^+$$

$$(PtCl_4)^{2-}/\text{support} + 2H_2O \rightarrow PtCl_2(H_2O)_2/\text{support} + 2Cl^-,$$

yielding a neutral complex which, as a consequence of this neutrality, could be more mobile on the alumina surface.

Such Pt^{2+} salts, due to their high propensity for sublimation, are often pointed out as the cause of platinum sintering. So, Pt^{4+} reduction by hydrogen can occur in two steps,

$$(PtX_6)^{2-} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (PtX_4)^{2-} + 2HX, \quad \text{where } X = \text{halide},$$

with respective rates

$$r_1 = k_1[(PtX_6)^{2-}](P_{H_2})$$

$$r_{-1} = k_{-1}[(PtX_4)^{2-}](HX)^2.$$

Assuming that both reactions are fast, one has at equilibrium

$$[(PtX_4)^{2-}] = \frac{k_1}{k_{-1}} \cdot \frac{[(PtX_6)^{2-}](P_{H_2})}{(HX)^2}. \quad (1)$$

Pt^{2+} salt could either polymerize or reduce to Pt^0 according to two competitive reactions,

$$n(PtX_4)^{2-} \xrightarrow{k_2} (PtX_4)_n^{2-} \xrightarrow{H_2} \text{large Pt particles},$$

where

$$r_2 = k_2[(PtX_4)^{2-}]^n, \quad (2)$$

and

$$(PtX_4)^{2-} + H_2 \xrightarrow{k_3} Pt^0 + 2HX + 2X^-,$$

where

$$r_3 = k_3[(PtX_4)^{2-}](P_{H_2}). \quad (3)$$

It is obvious that the higher the ratio r_3/r_2, the better the platinum accessibility.

From Eqs. (2) and (3)

$$r_3/r_2 = k_3/k_2[(PtX_4)^{2-}]^{1-n}(P_{H_2});$$

by including Eq. (1)

$$r_3/r_2 = k_3/k_2[k_1/k_{-1}]^{1-n} [(PtX_6)^{2-}]^{1-n}(P_{H_2})^{2-n}(P_{H_X})^{2n-2}.$$

For n higher than 2 (which corresponds to dimerization of $(PtX_4)^{2-}$) the higher the hydrogen pressure, the higher the $[PtX_4^{2-}]$ concentration on the surface, and the lower the platinum dispersion (Table 3).

On the other hand, the higher the HCl pressure during reduction, the higher the metallic accessibility (Table 5). It is worth noting that HCl in the proposed kinetics acts only in Eq. (1) and not in the rate-limiting steps (2) and (3). Thus, as is shown in Fig. 3, hydrochloric acid has no effect on the kinetics of platinum reduction but is able to modify the constant of the equilibrium (1) and thus, avoiding $(PtX_4)^{2-}$ species formation could improve the dispersion of platinum.

In conclusion, water, on the one hand, and hydrochloric acid produced during direct reduction by hydrogen of Pt/Al_2O_3 catalysts activated by hexachloroplatinic acid, on the other hand, have opposite effects on metal accessibility. Water not only acts as a kinetic inhibitor of the reduction reaction but also can induce platinum sintering. Hydrochloric acid has no kinetic effect on the reduction but is able to enhance the dispersion of the metal. Finally, increasing hydrogen pressure during reduction implies decreasing platinum accessibility.

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