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EFFECT OF CHLORIDE ON SINTERING OF Pt/Al_2O_3 CATALYSTS

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Reduced Pt/Al_2O_3 catalysts with different chloride contents were treated at different temperatures under oxygen flow. TPR and TPD studies of oxidized species show that at low Cl/Pt atomic ratio ($\leqslant 1$) PtO_2 is formed at low temperature (400–500 K) and is totally decomposed (900 K) yielding reduced metallic Pt and inducing metal sintering. At high Cl/Pt atomic ratio ($\geqslant 6$) formation of stable (up to 1000 K) platinum oxichloride avoids metal sintering.

Keywords: Platinum, alumina, oxichloride, oxidation, sintering

1. Introduction

Transition metal catalysts are particularly sensitive to catalyst deactivation during a prolonged operation. The main causes can be sintering of the metal or poisoning by impurities adsorption as formation of surface residues, like coke, by side reactions.

Treatments by oxygen are generally used to regenerate such fouled catalysts, although the nature of the oxidized species formed is far from known. So 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. The existence of four different species containing Pt(IV) was detected by Lieske et al. [7]: two surface oxides $\alpha(PtO_2)$, $\beta(PtO_2)$ are halogen free and two chloride containing complexes $[Pt^{4+}(OH)_xCl_y]$ and $[Pt^{4+}O_xCl_y]$. Wagstaff and Prins [1] proposed the formation of two platinum oxides by reoxidation of reduced platinum but at low temperature PtO would be formed. By ESCA measurements Escard et al. [8] pointed out Pt(IV) species with low quantities of Pt(II). Although the effect of gas atmosphere and temperature on the dispersion have been studied in details [9], other variables are suspected to play an important part in the nature of platinum species under oxygen atmosphere which can be formed not only during catalysts regeneration but also in oxidative process (for example automotive exhaust gas treatment).

The purpose of this work is to define the role of chloride during treatment by oxygen of platinum supported catalysts. The main techniques used, Temperature Programmed Reduction (TPR), Temperature Programmed Desorption (TPD) and selective chemisorption, allow to discuss the nature and the stability of formed species.

2. Experimental

1. MATERIALS

The support used was the Rhône Poulenc GFS 400-Al_2O_3 (surface area 210 m^2/g) previously treated under air flow at 923 K. Three series of Pt/Al_2O_3 catalysts were studied. Two catalysts (series A and B) of different metal loading (0.6 and 6%) were prepared by impregnation of the support with the appropriate quantity of H_2PtCl_6 solutions. Two non chlorided Pt/Al_2O_3 catalysts (series C and D) loaded at 6% and 0.6% in Pt were prepared from $Pt(NH_3)_2(NO_2)_2$.

The alumina powder was immersed in distilled water before addition of platinum salt. After 24 hours of digestion, the solution is evaporated and the catalyst dried in air at 393 K. All catalysts were calcined in oxygen at 723 K for 2 hours and reduced in hydrogen flow for 2 h at 673 K.

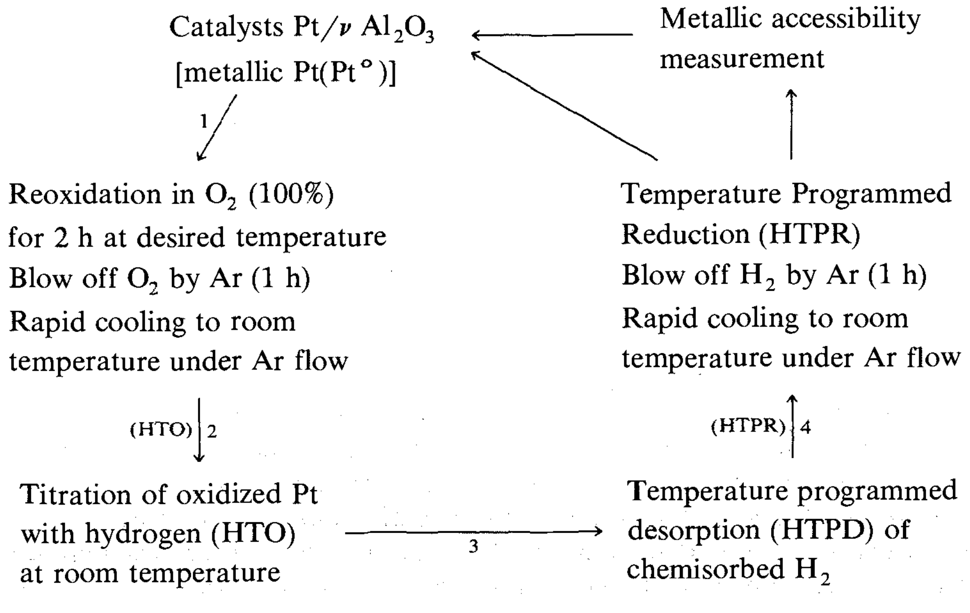
Platinum and chloride contents were determined by the ICP technique. The metallic accessibilities were calculated:

- either by volumetric titration of preadsorbed hydrogen by oxygen (OT)
- or by volumetric titration of preadsorbed oxygen by hydrogen (HT)

The stoichiometries used are H/Pt = O/Pt = 1.

2. PROCEDURE

The catalysts samples previously reduced were treated according to the following sequence:



The different steps (reoxidation, TPR, TPD and titrations) were carried out in situ.

The temperature programmed reduction was performed in an apparatus previously described [10] and according to [11] we took care to conduct successful TPR experiments. The catalyst sample (50 mg 6% Pt/Al_2O_3 or 500 mg 0.6% Pt/Al_2O_3) was inserted into a quartz tube and heated at a rate of 6 K/min under a flow of 1% H_2/Ar (Alphagaz Research Grade). The flow rate was 1,500 ml h^{-1} (S.T.P.). The gas flow outcoming from the reactor was dried over magnesium perchlorate before introduction on the thermal conductivity cell.

The average oxidation state of Pt after oxygen treatment (step 1) can be calculated from the hydrogen consumption (Q_H) given by the following equation:

$$Q_H = (\mathrm{HTO}) + (\mathrm{HTPR}) - (\mathrm{HTPD})$$

Step 2 (HTO) = quantity of hydrogen atoms consumed at room temperature by treatment of platinum catalysts partially oxidized during step 1. (HTO can be hydrogen irreversibly adsorbed on non oxidized Pt atoms or hydrogen consumed in order to reduce, at room temperature, a part of the oxidized platinum atoms.)

Step 3 (HTPD) = quantity of hydrogen atoms irreversibly adsorbed at room temperature after step 2.

Step 4 (HTPR) = quantity of hydrogen atoms consumed during temperature programmed reduction of oxidized platinum atoms (non reducible atoms at room temperature after step 2).

The average oxidation of Pt after step 1 can be calculated by the ratio Q_H over the total number of Pt atoms introduced in the sample ($Q_H/Pt_{total} = H/Pt$).

3. Results

The three series of Pt/Al_2O_3 catalysts were characterized by their accessibilities and chloride contents (table 1). It appears that the metallic accessibilities are

Table 1
Characteristics of the different Pt/Al_2O_3 catalysts.

Catalysts	Chloride content after reduction (%)	Cl/Pt	Platinum accessibility	
			OT	HT
A 0.6% Pt/Al_2O_3 ex H_2PtCl_6	0.65	5.9	53	60
B 6% Pt/Al_2O_3 ex H_2PtCl_6	1.3	1.2	50	58
C 6% Pt/Al_2O_3 ex $Pt(NH_3)_2(NO_2)_2$	0.0	0	48	57
D 0.6% Pt/Al_2O_3 ex $Pt(NH_3)_2(NO_2)_2$	0.0	0	50	59

almost the same for the different catalysts under consideration. On the other hand the chloride loading and therefore, the ratio Cl/Pt after reduction, varies from 5.9 for A to 1.2 for B and 0 for C and D catalysts. The different prereduced catalysts were oxidized at different temperatures under a pure oxygen flow according to the step 1. Such oxidized catalysts went through the different hydrogen treatment previously described. A further analysis of chloride content after one cycle on 0.6% Pt/Al_2O_3 (Cl/Pt = 5.9) showed that no chloride is eliminated.

1. EFFECT OF THE TEMPERATURE OF REOXIDATION ON THE PLATINUM OXIDATION STATE

The different catalysts with various Cl/Pt contents were oxidized at various temperatures (step 1). The state of oxidation of platinum induced by such treatment was evaluated according to the previously described steps. Fig. 1 gives the evolution of the oxidation state of platinum as a function of the temperature of treatment. It is worth noting that the oxidation degree changes according to temperature. As the metallic accessibilities of the three catalysts under consideration are almost the same, the differences between the three curves (fig. 1) could be

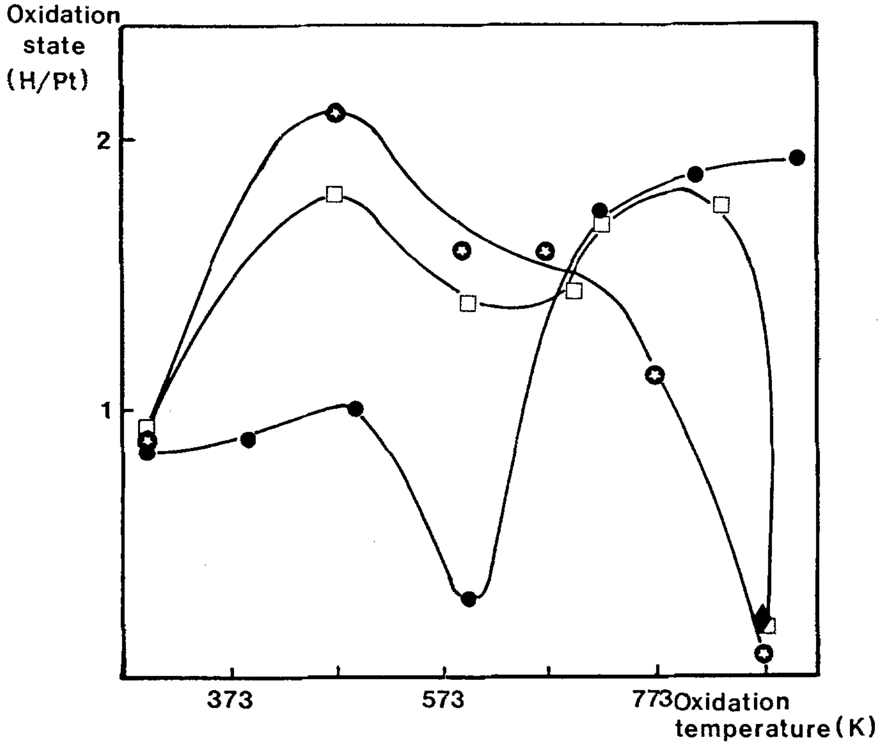


Fig. 1. Evolution of the platinum oxidation state versus oxidation temperature. ● 0.6% Pt/Al_2O_3 (Cl/Pt = 5.9), □ 6% Pt/Al_2O_3 (Cl/Pt = 1.2), ○ 6% Pt/Al_2O_3 (Cl/Pt = 0), ◆ 0.6% Pt/Al_2O_3 (Cl/Pt = 0).

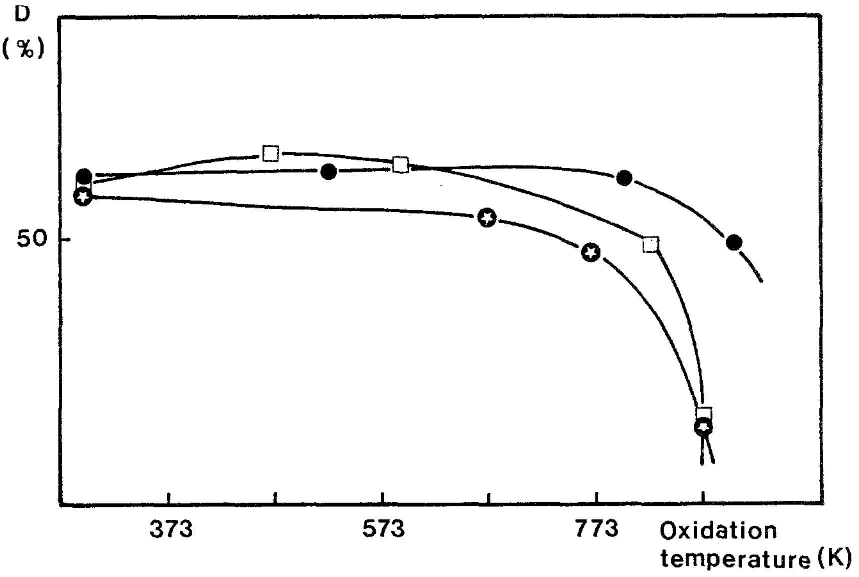


Fig. 2. Effect of the temperature of oxidation on the metallic accessibility (% D). ● 0.6% Pt/Al_2O_3 (Cl/Pt = 5.9), □ 6% Pt/Al_2O_3 (Cl/Pt = 1.2), ✪ 6% Pt/Al_2O_3 (Cl/Pt = 0).

due to the various Cl/Pt ratios. So at low temperatures (< 650 K), the higher the Cl/Pt ratio, the lower the platinum oxidation state.

At high temperatures reverse results are obtained. For example, at 873 K for low Cl/Pt ratios, platinum is in metallic state.

2. EFFECT OF THE TEMPERATURE OF REOXIDATION ON PLATINUM ACCESSIBILITY

Fig. 2 shows, for the different catalysts, the evolution of platinum accessibility as a function of the reoxidation temperature.

It appears that, for the 0.6 Pt/Al_2O_3 catalyst (Cl/Pt = 5.9), metal dispersions are only slighty modified at high temperatures (more than 900 K) when for low chloride contents catalysts an important sintering appears from 750 K.

Table 2
Temperature of total reduction of the various Pt/Al_2O_3 catalysts. Influence of the Cl/Pt atomic ratio.

Catalysts	0.6% Pt/Al_2O_3 Cl/Pt = 5.9	6% Pt/Al_2O_3 Cl/Pt = 1.2	6% Pt/Al_2O_3 Cl/Pt = 0
Temperature of reoxidation (K)	Temperature of total reduction (K)	Temperature of total reduction (K)	Temperature of total reduction (K)
673	508	440	423
800	648	510	473
900	748	non oxidized	non oxidized

3. EFFECT OF THE TEMPERATURE OF REOXIDATION ON THE TPR CURVES

The TPR technique gives not only the quantity of hydrogen consumed, and thus the degree of oxidation of the metal after calcination, but also information about species produced during calcination step, specially through analysis of reduction temperatures. Table 2 records the temperatures of total reduction of the various catalysts reoxidized at various temperatures. The comparison of catalysts with low and high Cl/Pt atomic ratios shows that during oxidation less reducible species can appear at high chloride contents. Finally oxidation at 900 K of low chloride contents catalysts yield reduced platinum.

4. Discussion

At room temperature the stoichiometry of oxygen adsorption on platinum was widely discussed. According to Benson and Boudart [12] one oxygen atom would be chemisorbed on one accessible platinum atom when for Mears and Hansford [13] only one oxygen atom could be adsorbed on two platinum atoms. The determination of the number of hydrogen atoms required for reduction of platinum oxidized at 300 K (fig. 1) shows that, whatever chloride or metal loadings there may be, the mean oxidation state of platinum (including all atoms: surface and bulk) is Pt^+, corresponding to Pt_2O. But by taking into account the metallic accessibility (50%), the surface stoichiometry of oxygen chemisorption is $O/Pt = 1$.

For higher oxidation temperatures ($300\text{ K} < T < 500\text{ K}$) the oxidation degree of platinum increases. The lower the Cl/Pt atomic ratio, the higher the oxidation state (fig. 1). It appears in this temperature range that chloride is able to lower the affinity of platinum for oxygen. Such result can be compared with the effect of chloride on the thioresistance of metallic catalysts [14]. As a matter of fact chloride is able to improve the acidity of the support and so to decrease the electronic density of supported platinum particles [15,16] which, then, would be less sensitive to adsorption of electrons acceptor compounds like sulfur or oxygen [14]. The same phenomenon can explain the very low oxidability of the 0.6 Pt/Al_2O_3 catalyst at 600 K.

At high oxidation temperatures ($T > 720$ K) chlorinated catalysts are more oxidizable than chloride free ones. Finally at around 900 K, in agreement with Huizinga et al. [17] platinum oxides are thermally destroyed yielding reduced metal. Such decomposition goes on a par with an important sintering of the metallic phase. If however the catalyst is highly loaded with chloride ($Cl/Pt \geqslant 6$), the oxidation state of platinum atoms (surface and bulk) is equal to $+2$. In the same conditions Lieske et al. [18,7] pointed out, during oxygen treatment of totally dispersed chlorinated Pt/Al_2O_3 catalysts, a total oxidation yielding Pt^{4+} species. The apparent difference with our results can be easily explained by taking into account that catalysts used in this work are only 50% dispersed. So, as proposed by Huizinga et al. [17], only accessible platinum atoms could be oxidized to Pt^{4+} creating an external passivating shell on the metallic particles and avoiding oxygen diffusion into the bulk of platinum.

Finally with regard to the chemical nature of the oxidized stable species produced at high temperature on the 0.6 Pt/Al_2O_3 catalyst, the effect of the Cl/Pt ratio on their formation allows to suppose that oxichlorides of platinum are produced. A previous work showed that such species are thermally stable and can be only reduced at high temperatures (table 2) [7,19].

In conclusion the surface state of platinum catalysts treated or working under oxygen flow is defined by the Cl/Pt atomic ratio. At low chloride content a decomposition of platinum oxides at high temperatures yielding reduced metallic catalyst is responsible for metal sintering. At high Cl/Pt atomic ratio, platinum oxichlorides are formed during oxygen treatment, such compounds are stable up to 1000 K [7,18] and impede platinum sintering.

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