Influence of the nature of the platinum precursor on the surface properties and catalytic activity of alumina-supported catalysts

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Received 21 August 1995; accepted 30 November 1995

The influence of the nature of the metal precursor – platinum acetylacetonates and chloroplatinic acid – on the surface properties and catalytic activity of Pt/Al_2O_3 catalysts is reported. The obtained results indicate that the catalysts prepared by the organometallic route present higher metal dispersion and lower acidity compared with those prepared from H_2PtCl_6. On the other hand, XPS results showed that the state of platinum is essentially Pt^0 in the catalysts obtained from $Pt(acac)_2$ while in the solids prepared by impregnation of H_2PtCl_6 there exists an important contribution of $Pt^{\delta+}$ species which plays a positive role in the hydrogenation of toluene. An additional hydrogen spillover due to the presence of more acidic support is also suggested as an explanation of the observed catalytic results.

Keywords: catalysts; platinum; alumina; acetylacetonates; chemisorption; hydrogenation

1. Introduction

The use of organometallic complexes as precursors of supported metal catalysts provides an important way to prepare highly dispersed and selective catalysts [1,2]. However, due to the high price of organometallic compounds and to the difficulty of preparing large amounts of catalysts, such a preparation route is still not very common. Among potential organometallic complexes, the acetylacetonate family is easy to prepare and presents a rather good stability under laboratory atmosphere. Palladium acetylacetonates have been used, for example, to prepare interesting alumina-supported palladium samples [3,4]. As in other preparations, the metal loading, the calcination and reduction temperatures seem critical to obtain small metal particles.

Although the preceding way for preparing supported metal catalysts is known, systematic comparison between the properties of catalysts prepared by this new route and those prepared through inorganic salt impregnation is not always documented.

In the present paper, Pt/alumina catalysts, with different metal loadings, are prepared using both platinum acetylacetonate and hexachloroplatinic acid as precursors. The reduced catalysts were characterized by hydrogen chemisorption, temperature programmed reduction (TPR), surface acidity measurements through thermal desorption of *t*-butylamine, and X-ray photoelectron spectroscopy (XPS). In addition, the catalysts were used in the hydrogenation of toluene, a structure insensitive reaction according to Boudart's classification.

2. Experimental

2.1. Materials

The alumina used in this study was supplied by Girdler (T-126). Specific surface area and pore volume were respectively 188 m^2/g and 0.39 cm^3/g.

Platinum acetylacetonate ($Pt(C_5H_7O_2)_2$ – 97% purity) was obtained from Aldrich and hexachloroplatinic acid (H_2PtCl_6 – 40 wt% platinum) from Merck.

The catalysts were prepared by impregnation of alumina, either with a toluene solution (acetylacetonate – 10 mg/g of catalyst) or with an aqueous solution (chloroplatinic acid – 5 ml/g of catalyst) at room temperature. The obtained solids were first dried at 393 K, then calcined in oxygen flow at 573 K. Finally, the solids were reduced in hydrogen flow (50 cm^3/min) at 773 K.

2.2. Characterization

The adsorption measurements were carried out in a greaseless volumetric system. The specific surface area was evaluated by nitrogen adsorption at 77 K and the metallic area (and dispersion) from hydrogen adsorption isotherms at 298 K.

TPR experiments were carried out in a conventional flow system, using TCD for monitoring hydrogen consumption. The reducing gas was a mixture of 5% hydrogen in argon and the heating rate was 6 K/min. TPO experiments used a mixture of 1% oxygen in helium (40 cm^3/min) as the reacting gas and a quadrupole mass analyzer (Balzers QMS 200) to follow oxygen consumption and product formation.

TPD of *t*-butylamine was carried out in a flow system, with the concentration of the base being monitored by TCD. The adsorption of the base was performed at room temperature by flowing 60 cm^3/min of argon saturated at 293 K by *t*-butylamine. Then, under the same flow of pure argon, the temperature was raised to 323 K to desorb the physically adsorbed fraction of the base. Finally, the temperature was lowered to room temperature, the TCD signal equilibrated and the temperature linearly increased up to 873 K (8 K/min).

XPS experiments were performed in a Fisons Escalab 200R spectrometer with a hemispherical analyzer operated in the constant path energy mode. Unmonochromatized Mg Kα X-ray radiation ($h\nu = 1253.6$ eV) at 10 mA and 12 kV was used as the excitation source. The setup was fitted with a high pressure reaction cell to carry out pretreatment at high temperature. The samples were pressed in the form of thin smooth wafers and placed in the high pressure cell. They were reduced in hydrogen at 773 K for 1/2 h. They were then transferred to the analysis chamber without contact with air. The C 1s line, at a binding energy of 284.9 eV, was used as an internal standard. The intensity of various XPS peaks was determined using S-shaped background subtraction and integration of peak areas. The Pt/Al atomic surface ratio was estimated from the integrated intensities of Pt 4d and Al 2p, using the sensitivity factors of Wagner et al. [5].

For catalytic evaluation, toluene was hydrogenated in a fixed-bed microcatalytic reactor working at atmospheric pressure. A H_2/toluene = 112 (molar ratio) mixture was flowed (30 cm^3/min) through the catalytic bed. The reaction temperature was in the range 313–358 K. Only 0.025 g catalyst was used so as to keep conversion at low level and to avoid mass and heat transfer limitations. The gas phase analysis was carried out on line by gas chromatography.

3. Results and discussion

3.1. Hydrogen chemisorption

In table 1, the H/Pt atomic ratios derived from hydrogen uptakes at 298 K and estimated Pt particle sizes are given. The method of Benson and Boudart [6] and Wilson and Hall [7], in which a linear portion of the isotherm between 40 and 240 Torr is extrapolated to zero pressure, has been used to obtain the hydrogen uptake. The particle size (d) was calculated by the equation $d = 5/S\rho$ [8], assuming that the hydrogen is essentially adsorbed by platinum atoms with a stoichiometry H/Pt = 1. In this equation S represents the metal surface area and ρ the metal specific weight. This equation is obtained assuming that the metal particles are of cubic shape; one face of the cube remains in contact with the support and therefore it does not chemisorb hydrogen. The values of particle sizes reported in table 1 may be underestimated by about 20% with respect to spherical shape.

Table 1
H/Pt ratios and particle size in Pt/Al_2O_3 catalysts

Catalysts [a]	H/Pt	Particle size, d (nm)
1 wt% Pt/Al_2O_3 (A)	0.43	2.0
2 wt% Pt/Al_2O_3 (A)	0.42	2.0
1 wt% Pt/Al_2O_3 (B)	0.55	1.6
2 wt% Pt/Al_2O_3 (B)	0.71	1.2
1 wt% Pt/Al_2O_3 (B*)	0.53	1.6
2 wt% Pt/Al_2O_3 (B*)	0.69	1.2

[a] A: ex H_2PtCl_6; B: ex $Pt(acac)_2$; * calc. 693 K.

The values obtained for H/Pt ratios (metal dispersion) are the expected ones. The Pt/alumina catalysts prepared by impregnation with the inorganic salt have the same dispersion. The catalysts prepared from the organometallic complex lead to higher dispersion. A model of fixation of platinum acetylacetonate [8] on the support can be summarized as follows:

$$\exists\!-\!OH + Pt(acac)_2 \longrightarrow \exists\!-\!O\!-\!Pt(acac) + acac\!-\!H$$

At higher Pt loading, the introduction of the complex is not only due to anchorage and exchange, but also to simple impregnation. This latter may lead, as reported in table 1, to an increase of metal dispersion, probably through molecular migration of the complex or a fraction of it, before decomposition to metallic state.

In addition, in table 1 the calcination temperature, 573 or 673 K, does not affect significantly the metal dispersion. This means that the factors which induce the metal dispersion take place during the low temperature part of the calcination.

3.2. TPR results

In fig. 1, the TPR curves for the Pt/alumina catalysts are displayed. For the catalysts prepared from chloroplatinic acid, the profiles are similar although they show differences in intensity according to metal loading. They present a peak centered at 470 K and a small peak at 635 K. The low temperature peak compares well with the one reported by Huizinga et al. [9] for a 5 wt% Pt/alumina catalyst; it can be due to the reduction of PtO_2 par-

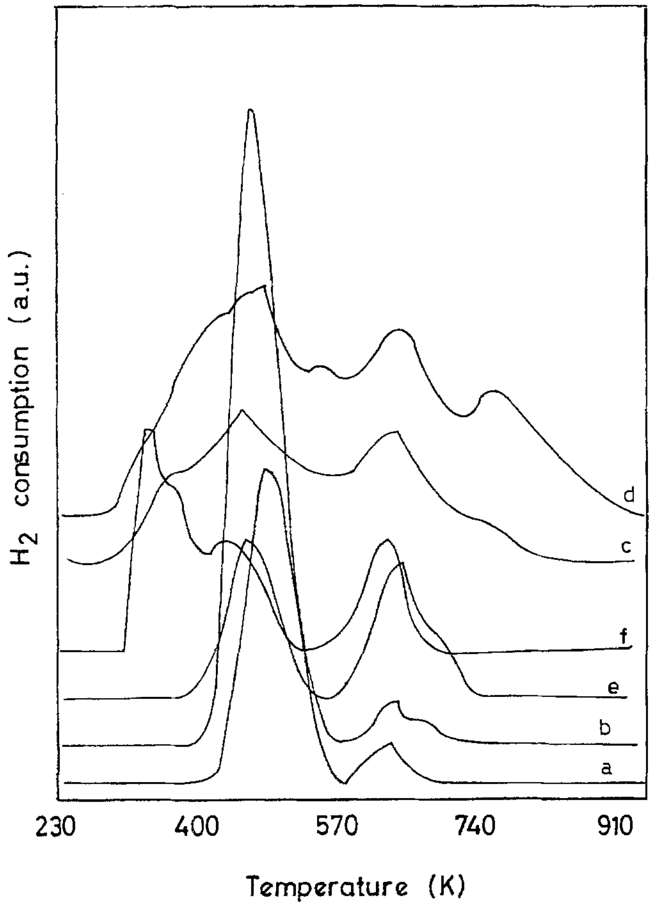

Fig. 1. Temperature programmed reduction profiles for various Pt/γ-Al_2O_3 catalysts. (a) 1 wt% Pt (A), (b) 2 wt% Pt (A), (c) 1 wt% Pt (B), (d) 2 wt% Pt (B), (e) 1 wt% Pt (B*), (f) 2 wt% Pt (B*). (A: ex H_2PtCl_6; B: ex $Pt(acac)_2$; * calcined at 673 K.)

ticles. The small peak at 635 K may be attributed to the reduction of platinum oxide strongly interacting with the carrier.

The TPR profiles of the catalysts obtained from acetylacetonate are more complex, showing hydrogen uptake at lower temperatures. This behaviour is clearer for the 2 wt% Pt/alumina catalyst, which displayed its main peak at about 340 K, a temperature observed for the reduction of unsupported PtO_2 [10,11]. This suggests the presence of different types of "supported species–support" interaction depending on the platinum precursor. Another possibility is that, in the case of the catalyst prepared via organometallic route, the complex is not fully decomposed after the 573 K calcination, and that during the TPR experiment a partial hydrogenation of the carboneous fragments occurs, increasing the hydrogen uptake. When these samples are calcined at 673 K, previous to TPR run, the profiles present two peaks with comparable intensity, the low temperature one centered at 470 K and the second at 670 K, in better agreement with the observations in the case of catalysts prepared from inorganic platinum salt.

In order to add more evidence to this explanation, a TPO experiment was considered. In the catalyst prepared from H_2PtCl_6, only water vapor and a very small amount of CO_2 were detected, with CO_2 being due to desorption of adsorbed species on the alumina. In the catalysts prepared through platinum acetylacetonate, a number of different products was detected. The main evolved products, as followed by quadrupole mass spectroscopic analysis, are presented in fig. 2. Among these products/fragments, H_2O, CO_2, CO, CH_3CO, HCOH and even H_2 were observed. These results suggest that a calcination temperature of 573 K was not enough to produce a complete decomposition of the organic part of the metal precursor or a total elimination of the organic fragments attached to the alumina. This fact will be discussed later, since it also affects the catalytic results.

The surface acidity of the catalysts was evaluated from TPD of *t*-butylamine. The TPD profiles are rather complex due to the fact that, under the present experimental conditions, both physically and chemically adsorbed species coexist. Therefore, the amount of base

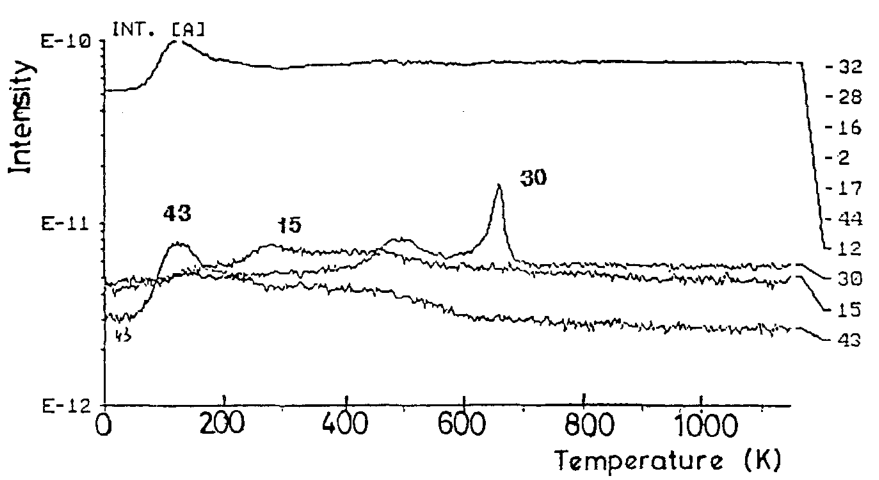

Fig. 2. Product evolution in TPO experiment. Catalyst: 2 wt% Pt/γ-Al_2O_3 (B).

Table 2
Surface acidity for Pt/Al_2O_3 catalysts

Catalysts [a]	D_1 (acid sites/g cat)	D_2 (acid sites/cm^2)
1% Pt/Al_2O_3 (A)	1.67×10^{20}	1.11×10^{14}
2% Pt/Al_2O_3 (A)	2.41×10^{20}	1.43×10^{14}
1% Pt/Al_2O_3 (B)	1.57×10^{20}	0.88×10^{14}
2% Pt/Al_2O_3 (B)	1.58×10^{20}	0.88×10^{14}

[a] A: ex H_2PtCl_6; B: ex $Pt(acac)_2$.

Table 3
Pt/Al and Cl/Al atomic surface ratios and binding energy for Pt 4d and Cl 2p in Pt/Al_2O_3 catalysts

Catalyst [a]	$(Pt/Al)_s$	$(Cl/Al)_s$	Binding energy BE (eV)	
			Pt $4d_{5/2}$	Cl $2p_{3/2}$
1% Pt/Al_2O_3 (A)	0.016	0.076	315.0	198.7
2% Pt/Al_2O_3 (A)	0.032	0.088	315.1	198.7
1% Pt/Al_2O_3 (B)	0.031	0.027	314.7	198.7
2% Pt/Al_2O_3 (B)	0.078	0.029	314.7	198.7

[a] A: ex H_2PtCl_6; B: ex $Pt(acac)_2$.

detected includes both contributions. However, for comparison, the total amount of *t*-butylamine is useful, even if it should be recalled that this measure is not directly linked to the number of acid sites. Table 2 summarizes the results.

The catalysts prepared from $Pt(acac)_2$ have lower acidity than those prepared from H_2PtCl_6. As expected, in that latter case, the acidity increases with the metal loading. This higher acidity may be attributed to the presence of chlorine in the precursor, which partially remains on the support, after calcination and reduction treatments.

3.3. *Physical characterization*

Table 3 displays the binding energies of Pt $4d_{5/2}$ and Cl $2p_{3/2}$ peaks as well as the Pt/Al and Pt/Cl atomic surface ratios of the studied catalysts. For the catalysts prepared from $Pt(acac)_2$ the BE of the $4d_{5/2}$ peak is 314.7 eV, corresponding to Pt^0. In the case of catalysts prepared with hexachloroplatinic acid, a shift in the binding energy is noted (315.0–315.1 eV), suggesting the presence of slightly oxidized platinum particles as may be expected due to the nature of the metal precursor. On the other hand, there is no change in the BE value of Cl $2p_{3/2}$.

The Pt/Al atomic surface ratios present the expected trends. The catalysts prepared from the inorganic salt have comparable metal dispersions and the Pt/Al value for the 2 wt% Pt/alumina catalyst is twice the one shown by the catalyst with 1 wt% platinum loading. In the samples prepared with the organometallic compound, a change with the metal loading was observed, with the catalyst with the higher platinum content being more dispersed. The Pt/Al ratios are in line with this trend. Also, the catalysts prepared through the organometallic route are more dispersed than the catalyst prepared via the inorganic route, in agreement with the results of hydrogen chemisorption.

The results issued from the Cl/Al atomic surface ratios showed that the catalysts prepared from H_2PtCl_6 have higher Cl content than the catalysts prepared with the organometallic complex. In the former, a slight effect of the platinum loading can be observed; meanwhile, in the latter only a very small amount of chlorine was detected, at a similar level, whatever the platinum loading. This very small amount may be attributed to residual chlorine that remained on the alumina during the preparation of the support.

3.4. *Catalytic activity*

Toluene hydrogenation has been studied much less than benzene hydrogenation and few studies have involved platinum-based catalysts [12]. In a temperature range 333–373 K, it has been observed that the orders of reaction for toluene and hydrogen are near zero and varying between 0.7 and 1.0 respectively. The apparent activation energies are varying in a large range, as values from 6 to 17.5 kcal/mol have been reported [13–16].

The present toluene hydrogenation experiments were run under differential conditions. During a 2 h period on stream, the catalyst did not present any deactivation, methylcyclohexane being the sole detected product.

Table 4 lists the results of catalytic activity, expressed as toluene conversion and turnover frequency (TOF), at 333 K. The catalysts prepared from H_2PtCl_6 have higher TOF than those prepared with $Pt(acac)_2$ under the same reaction conditions. This behaviour can be explained taking into account the XPS results which suggest the presence of $Pt^{\delta+}$ species in the former catalyst. Such an explanation has been retained to explain similar

Table 4
Toluene conversion turnover number and activation energy in toluene hydrogenation on Pt/Al_2O_3 catalysts

Catalysts	mole/s/g × 10^7	$T = 333$ K		E_a (kcal/mol)
		X (%)	TON (s^{-1})	
1% Pt/Al_2O_3 (A)	3.83	5.22	2.0×10^{-3}	19.1
2% Pt/Al_2O_3 (A)	7.80	10.6	1.9×10^{-3}	19.0
1% Pt/Al_2O_3 (B)	2.91	3.95	8.2×10^{-3}	18.9
2% Pt/Al_2O_3 (B)	5.59	7.6	9.9×10^{-3}	16.3

behaviour with supported Pt [17] and Rh [18] catalysts. Alternatively, the lowest TOF noted in the case of catalysts prepared by the organometallic route could be related to the presence of some residual carbonaceous species, as suggested by TPR/TPO results, blocking sites for toluene adsorption without altering the hydrogen adsorption capacity. However, it has to be borne in mind that this explanation due to the electronic effect is essentially valid for a metal particle smaller than 1.5 nm. Therefore, taking into account that the metal particle may be underestimated as it was already mentioned, another possible explanation can be given. This is based on the fact that in the presence of more acidic supports (as it is produced from impregnation with H_2PtCl_6) an additional contribution to the overall activity may be obtained because of hydrogen spillover from the metal surface [12,19,20].

The values of TOF at 333 K are comparable with those reported previously for Pt catalysts [15]. The activation energy (19 kcal/mol) found in the present work is, however, close to the highest values yet reported.

4. Conclusions

The use of platinum acetylacetonate as a precursor for alumina-supported platinum catalyst provides an effective method to produce a highly dispersed metallic phase. The calcination conditions must, however, be studied with great detail in order to control or completely suppress residual carbonaceous species.

The catalysts prepared by impregnation of alumina with H_2PtCl_6 have a higher surface acidity than those prepared by the organometallic route. This is due to a high residual chlorine content, as shown by XPS.

From XPS results, it is also suggested that the state of platinum is essentially Pt^0 in the catalysts prepared via the organometallic route, while an important contribution of $Pt^{\delta+}$ species exists in the samples prepared with hexachloroplatinic acid. These species are suggested to play a positive role in hydrogenation of toluene.

Acknowledgement

The authors thank both CONICYT (Chile) and CNRS (France) for their financial help through a bilateral exchange programme.

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