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Influence of Chlorine on the Activity and Stability of Pt/Al_2O_3 Catalysts in the Complete Oxidation of Toluene

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In this paper we discuss the effect of chlorine, added either as a part of the platinum precursor salt or after the noble metal impregnation, on the catalytic activity of Pt/Al_2O_3 for complete oxidation of toluene. Three different chlorinated and nonchlorinated platinum precursor salts have been used for the preparation of the catalysts. Characterisation of the catalysts has been carried out by N_2 adsorption, NH_3 TPD, TPR, HREM, and CO adsorption under oxidising conditions followed by DRIFTS. The catalytic activity has been studied by toluene ignition curves and additional stability tests have been carried out under isothermal conditions. The inhibitory effect of chlorine has been proved and assigned to the formation of oxychlorided platinum species. A model of chlorine mobility, responsible for the observed stability trends, is also proposed.

Key Words: **chlorine mobility; supported platinum catalysts; complete toluene oxidation; catalytic stability.**

1. INTRODUCTION

Supported platinum catalysts are widely used for catalytic incineration of volatile organic compounds (VOCs), in the environmental control of effluent gases (1). Chlorinated platinum precursors have been used for the preparation of these catalysts, due to the great knowledge acquired in the preparation of hydrogenation and reforming catalysts. However, the use of chlorinated platinum precursors for complete oxidation reactions has resulted in several problems due to the reported inhibition effect and its elimination during the reaction itself (2–8). H_2O is one of the products of the complete oxidation reactions, which can react with the chlorine atoms present on the catalyst, eliminating them in the gas stream (5, 7, 8). As a result, chlorine is a reversible poison, the effects of which cannot be completely eliminated after pretreatment in H_2 (3, 8).

The inhibitory effects of chlorine have been attributed to several causes. On one hand, the use of chlorinated precursors can lead to high metal dispersions, which can produce the complete oxidation of the noble metal under oxidising conditions, and consequently to a lower catalytic activity (9, 10). On the other hand, a partial blockage of platinum particles by chlorine has also been suggested, decreasing their ability to chemisorb (6, 10–12). Finally, the formation of oxychlorinated species resulting from the chemical interaction of platinum with chlorine would lead to a less active oxidation site (3, 5, 11).

A deeper knowledge of the inhibition mechanism of the oxidative catalytic activity requires a better knowledge of the chlorine location on the catalyst. Several locations have been described for chlorine in supported catalysts: on the support, in the interior of the platinum particles, and on the surface of the platinum particles. Cant *et al.* and Stencel *et al.* postulate that the reduction of the catalysts decreases the chlorine concentration on the surface of platinum particles, and increases it in the interior of the particles and on the support (8, 13). The admittance of the oxidant reaction flow will produce the movement of the chlorine to the platinum particle surface again (13), and a $H_2 + H_2O$ treatment will favour definitive chlorine elimination from the catalyst (8, 11).

The aim of this paper is to understand the chlorine effect and its mobility during the complete oxidation of toluene on Pt/Al_2O_3 catalysts. To this end, we have prepared different Pt/Al_2O_3 catalysts with chlorinated and nonchlorinated precursors. Additionally, chlorine has been added to a Pt/Al_2O_3 catalyst prepared initially from a nonchlorinated precursor. The previous characterisation of the catalysts has included the measurement of structural properties, such as the surface area or the pore volume by N_2 adsorption, the surface acidity by NH_3 TPD, Pt reducibility by TPR, the noble metal dispersion by H_2 chemisorption, and the study of the platinum surface under oxidant conditions by CO adsorption followed by DRIFTS. The catalytic tests have been done by following the ignition curves of toluene over the different catalysts. Furthermore, stability tests at constant temperature have been carried out to see the influence of chlorine on the stability of the catalysts. The analysis of the reaction products has been carried out with an online GC, a CO_2 detector, and a mass spectrometer.

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2. EXPERIMENTAL

Two of the Pt/Al_2O_3 catalysts were prepared by incipient wetness impregnation of γ-Al_2O_3 (Spheralite 250, Procatalyse; 100–200 μm particle size fraction) with aqueous solutions of $(Pt(NH_3)_4)(OH)_2$ (Johnson Matthey, Alfa) and $(NH_4)_2PtCl_4$ (Johnson Matthey, Alfa). The catalysts were dried at 393 K for 16 h and calcined at 773 K for 2 h in air. On the other hand, Al_2O_3 was also impregnated with $(NH_4)_2PtCl_6$ (Johnson Matthey, Alfa) by the wet impregnation method: 10 g of Al_2O_3 was stirred in 100 ml of bidistilled water containing the hexachloroplatinic salt for 14 h at room temperature, in a rotary evaporator. Afterward, the temperature was raised to 338 K and the vacuum was connected until all the liquid was evaporated. The obtained solid was calcined at 773 K for 2 h. The catalyst prepared from the nonchlorinated precursor will be called Pt_{NH_3}/Al_2O_3, and the ones prepared from the chlorinated platinum salts will be called Pt_{Cl_4}/Al_2O_3 and Pt_{Cl_6}/Al_2O_3. The Pt loading was 1% by weight in the three cases.

Additionally, the Pt_{NH_3}/Al_2O_3 catalyst was doped with chlorine from NH_4Cl salt (Fluka puriss, p.a.). The addition was carried out with a dry incipient wetness impregnation of the desired amount of chlorine, i.e., 1.6% by weight. After the chlorine impregnation, the catalyst was dried at 393 K for 16 h and calcined at 773 K for 2 h in air again.

The BET specific surface areas were measured by nitrogen adsorption at 77 K using an automatic volumetric apparatus (Micromeritics ASAP 2000). Samples had been previously degassed for 8 h at 473 K and 10^{-3} Torr. Pt dispersion was measured by HREM (Jeol, JEM 2000EX).

In order to analyse the change of the acidic properties of the Al_2O_3 after the impregnation of platinum from different salts, NH_3 TPD experiments were carried out. NH_3 (Alphagaz, 99.96%) was adsorbed at 373 K and the desorption was carried out in He (Air Liquide, 99.999%) with a temperature ramp of 10 K/min (Micromeritics Pulse Chemisorb 2700).

On the other hand, temperature-programmed reductions (TPR) of the catalyst were carried out in the same apparatus. The samples were pretreated in Ar (Air Liquide, 99.999%) at 373 K before the reduction to desorb H_2O. The reduction started at 298 K, and it was carried out in a reducing flow of 1.5% H_2 (Air Liquide, 99.999%) in Ar with a heating rate of 10 K/min. The calibration of the amount of H_2 consumed during the TPR experiments was carried out with CuO.

The IR spectra of CO adsorbed on transition metals are very sensitive to the oxidation state of the metal. Therefore, the adsorption of CO was carried out in order to elucidate the superficial oxidation state of platinum in the oxidising atmosphere of the reaction. The adsorption was followed by DRIFTS. The spectra were obtained by using a controlled-temperature-and-environment diffuse reflectance DRIFTS chamber (SPECTRA TECH 0030-005) with ZnSe windows in a Nicolet Protégé 460 infrared spectrometer with KBr optics and DTGS detector. The Pt/Al_2O_3 catalysts were subjected to a H_2 (Praxair, 99.999%) (50 cm^3/min) pretreatment at 573 K for 60 min. The sample was then cooled to room temperature in He (Praxair, 99.999%) and a mixture of 10% CO (Air Liquide, 99.9%) in He was passed through the sample. After the spectrum of CO adsorbed on Pt under an inert atmosphere was recorded, He was substituted by air (Air Liquide, 99.999%) and the temperature was raised to 573 K at 2.5 K/min. The spectra were treated using as background the spectrum of the sample at different temperatures without CO. The spectrum of CO gas was substracted as well. As a result, the presented spectra will only correspond to the adsorbed species.

Toluene complete oxidation reactions were carried out in a tubular fixed-bed reactor at atmospheric pressure. Mass flow controllers (Brooks 5850TR) were used to prepare the feed mixture. He (Air Liquide, 99.999%) was bubbled through two thermostated and pressurised saturators containing toluene (Fluka, puriss. p.a.). This stream was further mixed with O_2/He (Praxair, 99.999%; 21% O_2 and 79% He) in order to set the feed stream composition at 225 ppmv (parts per million by volume) of toluene and passed through the catalyst placed on the top of a carborundum bed. This configuration was designed to premix and preheat the stream entering the reactor, to obtain a homogeneous temperature, measured by a thermocouple placed just at the beginning of the catalyst bed. The reactor was surrounded by an electrical furnace equipped with a temperature programmer. Toluene oxidation over Pt/Al_2O_3 was carried out at a W/Q_{A0} ratio of 1.7 ($g_{catalyst}$ min/$cm^3_{toluene\,NPT}$), with 200 mg of catalyst and a total gas flow rate of 510 cm^3/min (GHSV 9700 h^{-1}). The ignition curves were constructed by following both the VOC disappearance and the CO_2 appearance at a controlled heating rate of 2.5 K/min. Analyses were done by online gas chromatography (GC, Hewlett Packard 6890, TR-WAX 30-m column) with use of a thermal conductivity detector (TCD). The CO_2 concentration was continuously monitored by means of an IR analyser (Digital Control Systems Model 300). The catalysts were treated under 100 cm^3_{air}/min of either O_2/He or H_2 at 573 K for 1 h before reaction, and then cooled in air to the starting reaction temperature. The effects of diffusion limitations have been studied by carrying out calculations of the Thiele modulus (internal diffusion). To have insignificant internal diffusion effects, the effectiveness factor (η) has to exceed 0.95 (14). In terms of the dimensionless Thiele modulus Φ, which contains only observable quantities, it has to be $\leq$1.0 for first-order reactions or $\leq$6.0 for zero-order reactions. Complete oxidation of toluene is supposed to be between 0 and 1 order of reaction in toluene, so we chose the most exigent case (first-order kinetics) to prove the diffusion limitations effects.

$$\Phi = R^2\left(-\frac{1}{V_c}\frac{dn}{dt}\right)\frac{1}{D_{\text{eff}}\, c_s} \qquad \text{and}$$

$$D_{\text{eff}} = 19400 \times \frac{\theta^2}{\tau S_g \rho_p}\sqrt{\frac{T}{M}}.$$

We have calculated Φ for 480 and 580 K, temperatures at which the curves are between 80% and 100% conversion. The value of Φ was found to be 0.68 for 480 K, and $\Phi = 0.94$ for 580 K. So we have considered that diffusion limitation effects could not influence the highest part of the ignition curves, because the Φ value was found to be less than 1. This result is consistent with the small particle size used in this study (100–200 μm). Additionally, experiments carried out with different linear velocities at constant w/F_{A0} have shown insignificant external diffusion.

The stability of the oxidation activity of Pt/Al_2O_3 catalysts during the reaction was also measured. These experiments were carried out in the same reactor equipment described above, but once the pretreatment of the catalyst was finished, the catalyst was cooled to the temperature at which the reaction was going to take place. The toluene/synthetic air mixture was stabilised outside the reactor and it was passed through it once the analysis was started. The oven was kept at constant temperature, and the bed inlet temperature and the conversion were monitored as a function of time. Additionally, a mass spectrometer (Omnistar, Balzers Instruments) was used to analyse online the reaction products of the stability test.

3. RESULTS AND DISCUSSION

As can be seen in Table 1, the properties of Al_2O_3 did not change considerably when platinum was impregnated from different precursor salts. The specific surface area decreased slightly when platinum was impregnated, but the total pore volume did not change appreciably.

TABLE 1

Specific Surface Area (S_{BET} m^2/g), Pore Volume (V_p), and the Quantification of the Amount of NH_3 Desorbed from Al_2O_3 and Pt/Al_2O_3 Catalysts per Square Meter in the 373 K to 773 K Range

	Catalyst			
	Al_2O_3	Pt_{NH_3}/Al_2O_3	Pt_{Cl_4}/Al_2O_3	Pt_{Cl_6}/Al_2O_3
S_{BET} (m^2/g)	257	224	219	229
V_p (ml/g)	0.42	0.41	0.42	0.40
NH_3 molecules/m^2	9.5×10^{17}	9.8×10^{17}	11×10^{17}	12×10^{17}

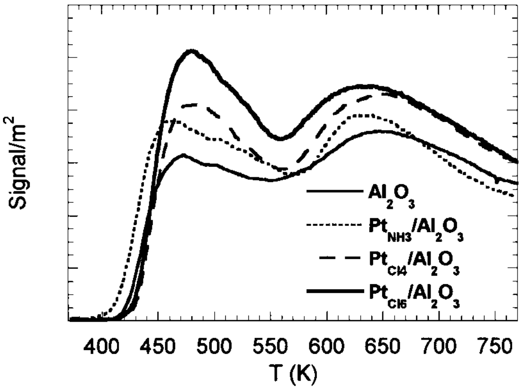

FIG. 1. Temperature-programmed NH_3 desorption curves over Al_2O_3 (narrow line), Pt_{NH_3}/Al_2O_3 (dotted line), Pt_{Cl_4}/Al_2O_3 (dashed line), and Pt_{Cl_6}/Al_2O_3 (thick line).

The results obtained from the TPD of NH_3 are plotted in Fig. 1, and the quantification of the amount of NH_3 desorbed per square meter is shown in Table 1. As can be observed, the impregnation of Al_2O_3 with $(Pt(NH_3)_4)(OH)_2$ does not vary the superficial acidity considerably. However, the impregnation with the chlorinated salts resulted in a slight increase of the NH_3 desorbed from the surface, corresponding to an increase of the acidic centres on the surface. This fact has been attributed to the possible deposition of chlorides on the support, producing a more electrophilic support and consequently a more acidic catalyst (6, 7, 15).

Figure 2 shows the temperature-programmed reduction (TPR) curves for the different Pt/Al_2O_3 samples. Pt_{NH_3}/Al_2O_3 presents a reduction maximum at 528 K, while the chlorinated species Pt_{Cl_4}/Al_2O_3 and Pt_{Cl_6}/Al_2O_3 present their maxima at 558 K, some 30 K later. Another feature to be noted is the presence of a shoulder at 603 K for Pt_{NH_3}/Al_2O_3 and at 643 K for Pt_{Cl_4}/Al_2O_3, that is not present for Pt_{Cl_6}/Al_2O_3.

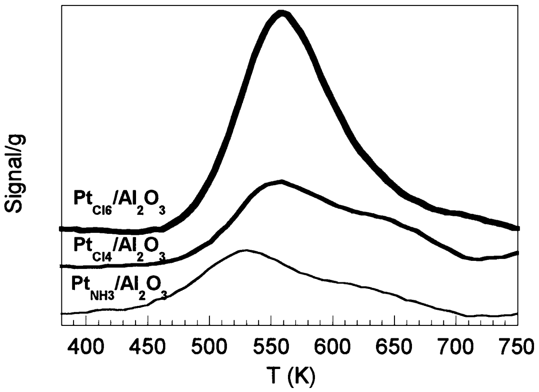

FIG. 2. Temperature-programmed reduction of the Pt/Al_2O_3 catalysts prepared from different platinum precursors: Pt_{NH_3}/Al_2O_3, Pt_{Cl_4}/Al_2O_3, and Pt_{Cl_6}/Al_2O_3, as indicated in the figure.

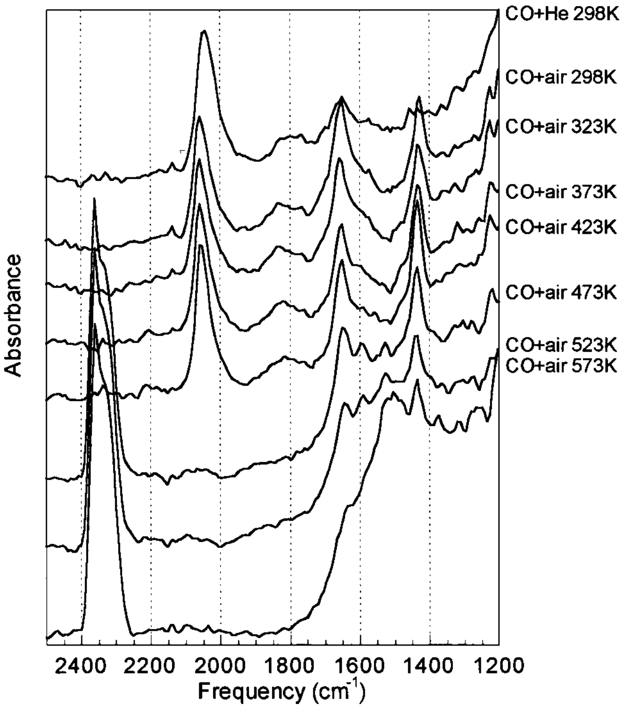

FIG. 3. DRIFTS spectra of CO adsorption on Pt_{NH_3}/Al_2O_3 under inert and oxidising conditions at increasing temperatures.

The position of the reduction curve maxima can give us some insights on the Pt species present in the catalyst. The use of chlorinated precursors has produced the increment of 30 K in the reduction maxima. Marceau *et al.* have indicated the formation of oxichlorinated platinum species, PtO_xCl_y, when calcining at 773 K platinum catalysts prepared from chlorinated salts (6). Those species will be reduced at 563 K. Hwang and Yeh add that dispersed PtO_xCl_y species posses a higher reduction temperature around 623 K (16). So, we can conclude that at least part of the chlorine present in Pt_{Cl_4}/Al_2O_3 and Pt_{Cl_6}/Al_2O_3 catalyst will be forming oxichlorinated species, which would be more difficult to reduce.

DRIFTS spectra of CO adsorbed on the different Pt/Al_2O_3 catalysts have been presented in Figs. 3–5. Figure 3 shows the spectra obtained on Pt_{NH_3}/Al_2O_3 reduced at 573 K, after the adsorption of CO in He at 298 K and in air at increasing temperatures from 298 to 573 K. The adsorption of CO in He produces a main adsorption peak at 2044 cm^{-1}, corresponding to CO adsorbed linearly on Pt^0, and a small band at 2137 cm^{-1} due to CO adsorbed on Pt^+ (17–19). So, the Pt is mainly reduced on the surface of the platinum particles. There is also a broad band centred at 1800 cm^{-1}, due to bridged CO. De La Cruz and Sheppard suggest that the CO appearing at that position is bonded in a multiple way, probably with a triple coordination to (111) surfaces of the noble metal (20). Furthermore, there is a band at 1650 cm^{-1}, attributed to bicarbonate species (17, 21–23), formed by the interaction of CO with the Pt and the surface hydroxyl groups of the Al_2O_3. When the oxidant flow is added to the chamber, the peak due to Pt^0–CO is shifted to 2060 cm^{-1}. This movement of bands can be seen as a "slight oxidation" of the platinum when introducing air into the chamber at room temperature. The band due to bridge-bonded CO is centred at 1828 cm^{-1}. This new position of the bridged CO band is attributed to CO doubly bonded to open (100) or (110) surfaces (20). On the other hand, at 298 K, new and more intense bicarbonate bands appear at 1650 cm^{-1}, 1428 cm^{-1}, and 1230 cm^{-1}. When the temperature is raised under CO/air, the three adsorbed species remain on the surface until 423 K, i.e., Pt^0–CO, Pt–CO–Pt, and bicarbonates, together with a small Pt^+–CO band. However, from 473 K on there is no more CO adsorbed on the Pt, and it is completely oxidised to CO_2, as can be seen by the doublet centred at 2349 cm^{-1}. At 473 K, the bands at 1650 cm^{-1} and 1230 cm^{-1} start to decrease, and new bands around 1585 cm^{-1} and 1525 cm^{-1} appear. These bands have been attributed to carbonates, as a product of bicarbonate oxidation (17, 18, 24).

Figure 4 shows the spectra obtained upon the adsorption of CO in an inert atmosphere and in oxidant atmosphere at increasing temperatures over Pt_{Cl_4}/Al_2O_3 reduced at 573 K. The spectrum of CO adsorption in He at 298 K presents a high peak at 2052 cm^{-1} due to the linear adsorption of CO over Pt^0, and a small peak at 2129 cm^{-1} due to the linear adsorption of CO over Pt^+. Furthermore, there are two bands

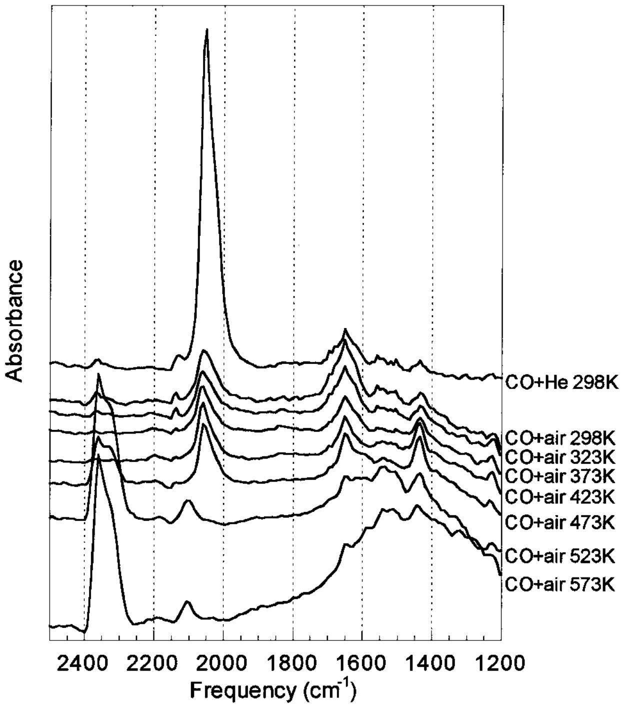

FIG. 4. DRIFTS spectra of CO adsorption on Pt_{Cl_4}/Al_2O_3 under inert and oxidising conditions at increasing temperatures.

at 1648 cm^{-1} and 1434 cm^{-1}, which have been attributed to bicarbonate species. When the He flow is changed by an air flow at 298 K, the spectrum changes slightly. The peak at 2052 cm^{-1} decreases and shifts to 2057 cm^{-1} and the one at 2129 cm^{-1} shifts to 2137 cm^{-1}. The bands due to the bicarbonate species increase and a new one appears at 1222 cm^{-1}. When the temperature is increased under the CO/air flow, the peak due to linear Pt^{+}–CO disappears and the Pt^{0}–CO peak is maintained until 473 K. Above that temperature, the only CO species adsorbed linearly is the one producing a peak at 2102 cm^{-1}. At 473 K the CO$_2$ doublet centred at 2349 cm^{-1} starts to grow. Furthermore, from 523 K the bands at 1648 cm^{-1} and 1222 cm^{-1} due to bicarbonates decrease, and new bands around 1500 cm^{-1} start to appear.

DRIFTS spectra of CO adsorption on Pt$_{Cl_6}$/Al$_2$O$_3$ reduced at 573 K are depicted in Fig. 5. Under inert conditions, there is a main peak at 2054 cm^{-1}, corresponding to linear Pt^{0}–CO, a small peak at 2133 cm^{-1} (Pt^{+}–CO), and a band centred at 1636 cm^{-1} corresponding to bicarbonates. When air is added to the CO flow, the Pt^{0}–CO peak shifts to 2064 cm^{-1}, with a shoulder at lower frequencies. A new band corresponding to the bicarbonate species appears at 1443 cm^{-1}. In any case, the amount of bicarbonate species present is less than in the other two catalysts. When the temperature is raised in the oxidant atmosphere, the peak corresponding to Pt^{0}–CO shifts to higher frequencies, reaching 2082 cm^{-1} at 523 K when it is just a shoulder of the peak appearing at 2114 cm^{-1}. It can be said that the platinum present on the surface of the particles in Pt$_{Cl_6}$/Al$_2$O$_3$ is mainly oxidised (Pt^{+}) in an oxidant atmosphere above 523 K, even if it has been previously reduced at 573 K. At 523 K the bicarbonates start to convert in carbonates, as can be seen from the disappearance of the band at 1635 cm^{-1} and the appearance of a new band at 1521 cm^{-1}. The complete oxidation of CO to CO$_2$ starts gradually at 473 K and becomes more pronounced above 523 K.

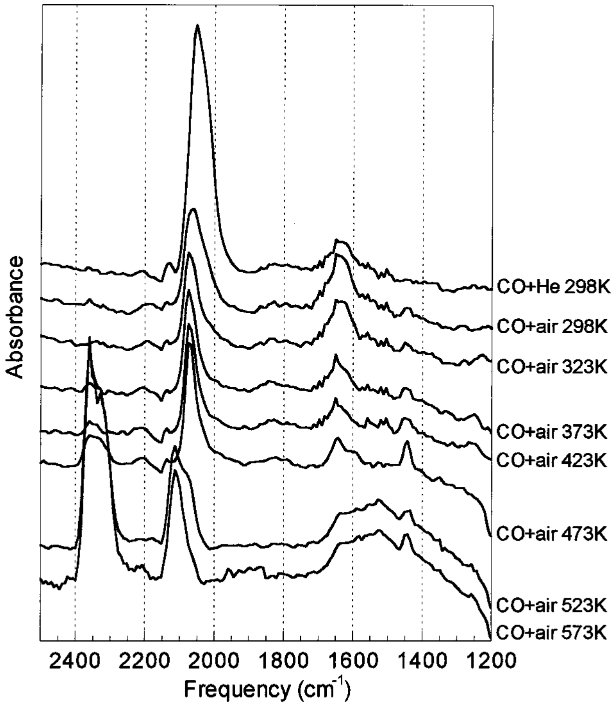

FIG. 5. DRIFTS spectra of CO adsorption on Pt$_{Cl_6}$/Al$_2$O$_3$ under inert and oxidising conditions at increasing temperatures.

The results obtained on the effect of the platinum precursor salt on the CO adsorption spectra can be summarised in the following way. The catalyst prepared with the nonchlorinated salt, Pt$_{NH_3}$/Al$_2$O$_3$, has two main differences from the other two catalysts. On one hand, it does not present any linearly adsorbed CO peak above 473 K and all the CO is oxidised to CO$_2$ above that temperature, showing that this catalyst is the most active of the three for the complete oxidation of CO. On the other hand, it is the only catalyst to present bridge-bonded CO. The presence of bridge-bonded CO has been attributed either to a less rough platinum surface or to a higher electronic density on the platinum due to a more alkaline character of the support (25, 26). The nonaddition of chlorine to this catalyst, which has been used in catalysis to increase the electrophilic character of the Al$_2$O$_3$ (6, 7, 15), makes this support less acidic. In this way, the catalysts prepared with a nonchlorinated platinum salt will posses platinum with a higher electronic density.

The Pt$_{Cl_6}$/Al$_2$O$_3$ catalyst can also be differentiated by the longer persistence of the 2114 cm^{-1} peak, indicating the oxidation of platinum at high temperatures in this catalyst, and the lower CO oxidation activity. Grbic *et al.* (27) have indicated that while just a layer of chemisorbed oxygen is formed over big platinum particles, a layer of platinum oxide is formed over small platinum particles. In our case, Pt$_{Cl_6}$/Al$_2$O$_3$ is the catalyst having the smallest platinum particles, so the oxidation of those particles will be favoured. Furthermore, the amount of bicarbonates or carbonates presumably on the support is lower in this catalyst, probably due to the deposition of chlorine species on the support in the preparation step. Thus, the precursor salt varies the surface properties of the catalyst for the CO adsorption under oxidizing conditions.

Catalytic Tests

The toluene ignition curves obtained after the reduction at 573 K of the Pt/Al$_2$O$_3$ catalysts prepared from the different precursor salts are shown in Fig. 6. Pt$_{NH_3}$/Al$_2$O$_3$ is the most active catalyst for toluene complete oxidation, having a T_{50} of 470 K. Both chlorinated catalysts have similar T_{50} (503 K in the case of Pt$_{Cl_4}$/Al$_2$O$_3$ and 512 K in the case of Pt$_{Cl_6}$/Al$_2$O$_3$), but differ in the T_{90}, or the temperature at which the 90% conversion is reached, Pt$_{Cl_4}$/Al$_2$O$_3$ having lower T_{90} (532 K) than Pt$_{Cl_6}$/Al$_2$O$_3$ (552 K). The difference in catalytic activity cannot be due to a big dispersion

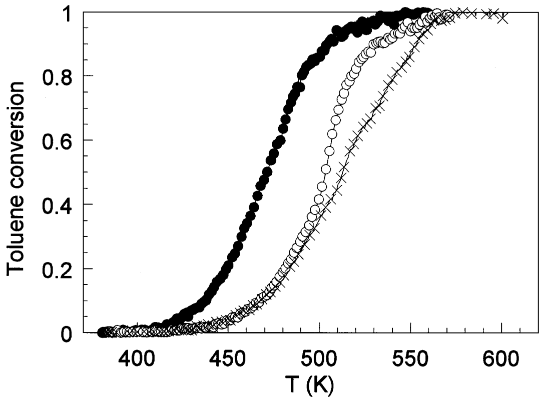

FIG. 6. Ignition curves of toluene complete oxidation over Pt/Al$_2$O$_3$ reduced at 573 K and prepared from different platinum precursors: (●) Pt_{NH_3}/Al_2O_3, (○) Pt_{Cl_4}/Al_2O_3, and (×) Pt_{Cl_6}/Al_2O_3.

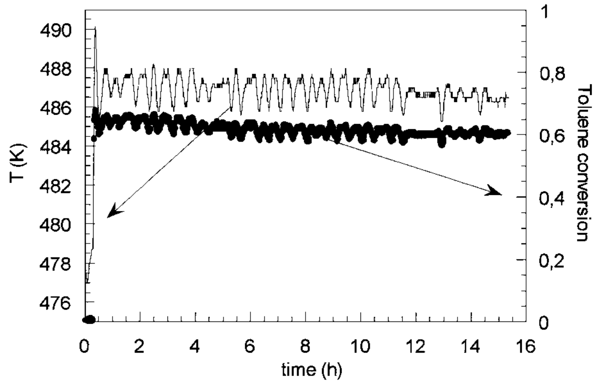

FIG. 8. Stability test of Pt_{NH_3}/Al_2O_3 in the toluene complete oxidation reaction. Temperature at the bed inlet (line) and toluene conversion followed by the CO_2 signal (●).

variation between the three samples. Preliminary dispersion measurements carried out by H_2 chemisorption showed high dispersion for all the samples. So the more chlorinated is the platinum precursor, the lower is the toluene oxidation activity.

In order to deepen our knowledge of the chlorine effect, the catalyst prepared with nonchlorinated salt was further impregnated with chlorine from NH_4Cl. Figure 7 presents the ignition curves of Pt_{NH_3}/Al_2O_3, the same catalyst impregnated with 0.8% and 1.6% Cl, and Pt_{Cl_4}/Al_2O_3 (maximum chlorine content, 0.73%) pretreated at 573 in H_2. The addition of 0.8% Cl did not vary significantly the activity of Pt_{NH_3}/Al_2O_3 catalyst. When 1.6% chlorine was added to Pt_{NH_3}/Al_2O_3, the activity showed differences from the undoped Pt_{NH_3}/Al_2O_3 starting above 30% conversion, its activity getting nearer to the Pt_{Cl_4}/Al_2O_3 one. The stability tests will help us to understand this behaviour.

Stability tests were carried out to study the evolution of the catalytic activity of the catalysts prepared from chlorinated and nonchlorinated platinum precursors, as a function of time.

Figure 8 depicts the evolution of the bed inlet temperature and conversion of toluene to CO_2 over Pt_{NH_3}/Al_2O_3 at an oven temperature of 463 K, for 15 h. As can be seen, the temperature oscillates by 2 K around the mean reactor internal value, and the conversion remains constant at 60% for the 15 h of the test. This leads us to believe that this sample has a high stability. In fact, if the ignition curves of the fresh Pt_{NH_3}/Al_2O_3 catalyst and that of the catalyst after 15 h of the stability test are measured, as can be observed in Fig. 9, it can be said that the activity has not changed after toluene is oxidised for 15 h.

The stability of the Pt_{NH_3}/Al_2O_3 catalyst doped with 1.6% chlorine has also been studied and it is presented in Fig. 10. The catalyst had been previously reduced at 573 K and the chosen oven temperature for the reaction was 466 K. As can be seen, the stability trend is very different from that for Pt_{NH_3}/Al_2O_3. When reactants are introduced

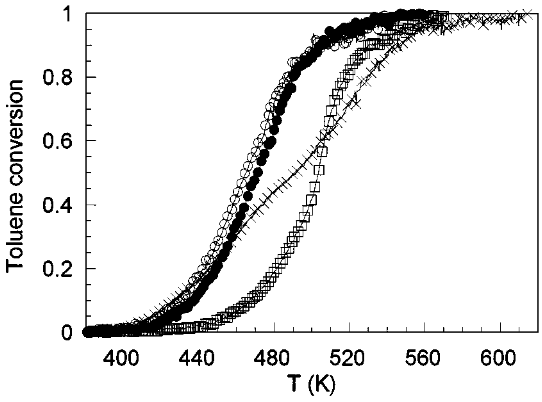

FIG. 7. Ignition curves of toluene complete oxidation over Pt/Al$_2$O$_3$ reduced at 573 K and prepared from different platinum precursors: (●) Pt_{NH_3}/Al_2O_3, (□) Pt_{Cl_4}/Al_2O_3, and Pt_{NH_3}/Al_2O_3 doped with different chlorine amounts, (○) 0.8% and (×) 1.6%.

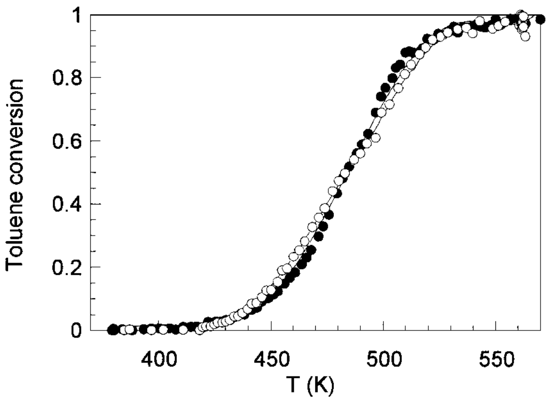

FIG. 9. Ignition curves of toluene complete oxidation over Pt_{NH_3}/Al_2O_3 pretreated in air at 300°C for 1 h (●) and after 15 h of stability test (○).

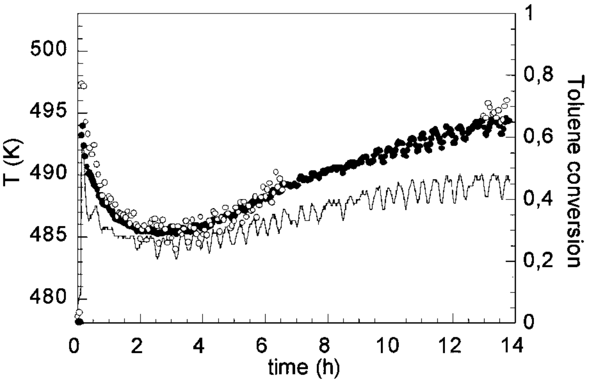

FIG. 10. Stability test of Pt_{NH_3}/Al_2O_3 doped with 1.6% of chlorine in the toluene complete oxidation reaction. Temperature at the bed inlet (line) and toluene conversion followed by the CO_2 signal (●) and toluene signal (○).

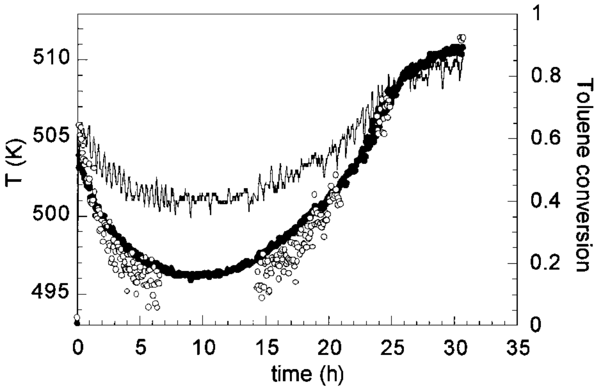

FIG. 12. Stability test of Pt_{Cl_4}/Al_2O_3 in the toluene complete oxidation reaction. Temperature at the bed inlet (line) and toluene conversion followed by the CO_2 signal (●) and toluene signal (○).

to the reactor, the bed inlet temperature suffers an increase of more than 10 K due to the exothermicity of the complete oxidation reaction. However, this initial activity decays to a minimum at 2.5 h of reaction, together with a temperature decrease of 7 K. From this time on, the activity and consequently the temperature increase again, until a plateau is reached around 13 h. Additionally, the ignition curves of fresh $Pt_{NH_3}/Al_2O_3 + 1.6\%Cl$, the catalyst after 2.5 h of reaction, and that after 14 h of reaction have been plotted (Fig. 11). The catalyst shows its lowest activity after 2.5 h of reaction, while it is most active after 14 h. In fact, the activity of the fresh catalyst varies between the activity of the other two, as was seen in Fig. 7, where the activity of $Pt_{NH_3}/Al_2O_3 + 1.6\%$ Cl moved from the activity of Pt_{NH_3}/Al_2O_3 to that of Pt_{Cl_4}/Al_2O_3.

Finally, the stability of a catalyst prepared from a chlorinated precursor, Pt_{Cl_4}/Al_2O_3, is shown in Fig. 12. The catalyst was reduced at 573 K before the test, and the oven temperature during reaction was 487 K. The trend of the activity is very similar to the one presented by $Pt_{NH_3}/Al_2O_3 +$ 1.6% Cl, having a minimum and a subsequent recovery of the activity. In this case the minimum of activity is only reached after 10 h of reaction, producing also a bed inlet temperature decrease of 5 K. From that time on, there is a conversion increase reaching 90% after 30 h of reaction, while the initial conversion was 55%. So the Pt_{Cl_4}/Al_2O_3 catalyst seems to have suffered an activation during the stability test, not observed in the $Pt_{NH_3}/Al_2O_3 + 1.6\%$ Cl catalyst. The ignition curves of the catalyst after stopping the stability reaction at different times confirm this hypothesis (Fig. 13). The T_{50} of the catalyst maintained under reaction conditions for 30 h is the lowest one and that of the catalyst after 10 h of reaction is the highest one, as could be forecasted from the stability curve (Fig. 12).

In order to eliminate the hypothesis of a possible dispersion change effect on the activity of Pt_{Cl_4}/Al_2O_3 catalyst during the reaction of toluene oxidation, platinum

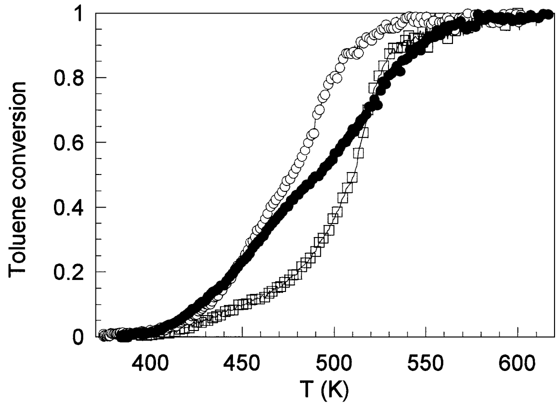

FIG. 11. Ignition curves of toluene complete oxidation over Pt_{NH_3}/Al_2O_3 doped with 1.6% of chlorine pretreated in H_2 at 573 K for 1 h (●), after 2.5 h of stability test (□), and after 14 h of stability test (○).

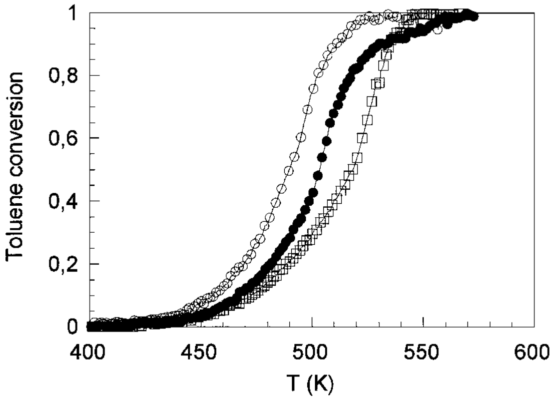

FIG. 13. Ignition curves of toluene complete oxidation over Pt_{Cl_4}/Al_2O_3 pretreated in H_2 at 300°C for 1 h (●), after 10 h under reaction conditions (□), and after 30 h of stability test (○).

TABLE 2

Rate of Reaction and TON under Differential Conditions at 463 K of Fresh Pt_{Cl_4}/Al_2O_3 Catalyst, and the Catalyst after 10 h and 30 h of Toluene Oxidation Reaction

	Catalyst		
	Pt_{Cl_4}/Al_2O_3	Pt_{Cl_4}/Al_2O_3 after 10 h of reaction	Pt_{Cl_4}/Al_2O_3 after 30 h of reaction
Rate of reaction ($mol \cdot s^{-1} \cdot g_{cat}^{-1}$)	1.05×10^{-7}	0.91×10^{-7}	1.61×10^{-7}
TON (s^{-1})	5.68×10^{-3}	5.37×10^{-3}	12.5×10^{-3}

dispersion measurements were carried out by HREM. The catalyst dispersion was measured before the reaction, after 10 h of reaction, and 30 h of reaction. The HREM technique gave us an initial average dispersion of 36%, which decayed only slightly to 33% after 10 h, ending at 25% after 30 h of reaction. As can be seen, the small but constant decrease of the dispersion during the reaction cannot explain the important activity changes observed.

Furthermore, reaction rates under different conditions were measured for Pt_{Cl_4}/Al_2O_3 before the stability test and after 10 and 30 h of toluene oxidation, and the turnover number (TON) values were calculated. The reaction rate measurements were carried out with the same procedure as that used for stability tests, under isothermal conditions, but at lower temperature (463 K) and with a lower amount of catalyst, in order to obtain conversions lower than 10%. The results are reported in Table 2. It can be said that the rate of reaction decreases after having the catalyst for 10 h under reaction conditions, and increases above the value of the fresh catalyst after 30 h of reaction. The turnover numbers follow the same trend. This again confirms the trend of activity seen in the stability test, even if in the case of the stability test the conversion change is more pronounced due to the exothermic character of the toluene oxidation, which modifies the bed temperature. This is why the temperature has been also plotted in the stability test graphic.

Several authors have remarked on the activation suffered by the supported noble metal catalysts during complete oxidation reactions, when the catalysts had been prepared with chlorinated salts. Marceau *et al.* (6) observed an increase in the activity during the oxidation of CH_4 over Pt/Al_2O_3 prepared with H_2PtCl_6. Marècot *et al.* (5) also saw this activation, which they assumed is caused by the chlorine elimination by the H_2O produced during combustion. Cant *et al.* (8) reported that the reduction of a supported noble metal catalyst prepared from a chlorinated precursor enhances its activity, but even after reduction some chlorine remains on the Al_2O_3, as has also been pointed out by Lieske *et al.* (28). To eliminate the chlorine from the support, Cant *et al.* (8) and Straguzzi *et al.* (7) proposed the addition of H_2O to the reduction stream. Furthermore, Stencel *et al.* (13) suggested another means of chlorine mobility in Pt/Al_2O_3 catalysts prepared from chlorinated precursors. They proposed that in the reduction step, the chlorine concentration on the surface of platinum particles decreases, while it increases again when the catalyst is subjected to an oxidant flow.

Taking into account this background information and our experimental results, we will try to explain the observed stability trends with a model of chlorine mobility.

First, as has been seen in Fig. 8, the Pt/Al_2O_3 catalyst prepared with the nonchlorinated salt, Pt_{NH_3}/Al_2O_3, presents a constant activity for toluene complete oxidation over time. Marècot *et al.* (5) have also seen the high stability of the Pt/Al_2O_3 catalysts prepared from nonchlorinated platinum salts. However, when chlorine is added to this catalyst from NH_4Cl, its stability changes.

The chlorine impregnation over Pt_{NH_3}/Al_2O_3 will produce a homogeneous spreading of the chlorine on the catalyst. So, the largest part of the chlorine will be located on the Al_2O_3, which presents a higher surface than Pt. The toluene oxidation reaction will produce H_2O, which can react with the deposited chlorine to form HCl or mobile species as suggested by the groups of Marècot, Straguzzi, and Cant (5, 7, 8). From the activity decrease observed during the initial steps of the stability test, those mobile species will move to the active centres first. The accumulation of chlorine species near the platinum particles will produce the activity minimum, observed after 2.5 h in our reaction conditions. However, a further production of H_2O during the reaction will cause the elimination of chlorine from the active phase, and the increment of the catalytic activity. The conversion obtained at the end is very similar to the initial one, because not much chlorine is near the platinum particles at the beginning of the reaction.

In contrast, in Pt_{Cl_4}/Al_2O_3, the chlorine will be mainly next to the platinum particles, or even forming oxychloride platinum species, as can be proposed from our TPR experiments, and as has been reported in the literature (5, 16, 28). The chlorine mobility scheme proposed is presented in Fig. 14. The Pt_{Cl_4}/Al_2O_3 reduction at 573 K will produce both a transition of the chlorine from the surface of the platinum to its interior (13) and to the Al_2O_3 surface (8, 28). The start of the toluene oxidation reaction will bring about two effects: on one hand the chlorine that had entered the platinum particles will come back to the surface under the oxidant atmosphere (13) and on the other hand the H_2O formed by the oxidation of toluene will mobilise the chlorine on the support. In the first steps of the reaction this mobilisation can move the chlorine from the Al_2O_3 back to the platinum particles (28). This effect, together with the chlorination of Pt surface, will produce the initial decrease of the oxidative activity of the catalyst, until a minimum is reached at 10 h under our reaction conditions. The

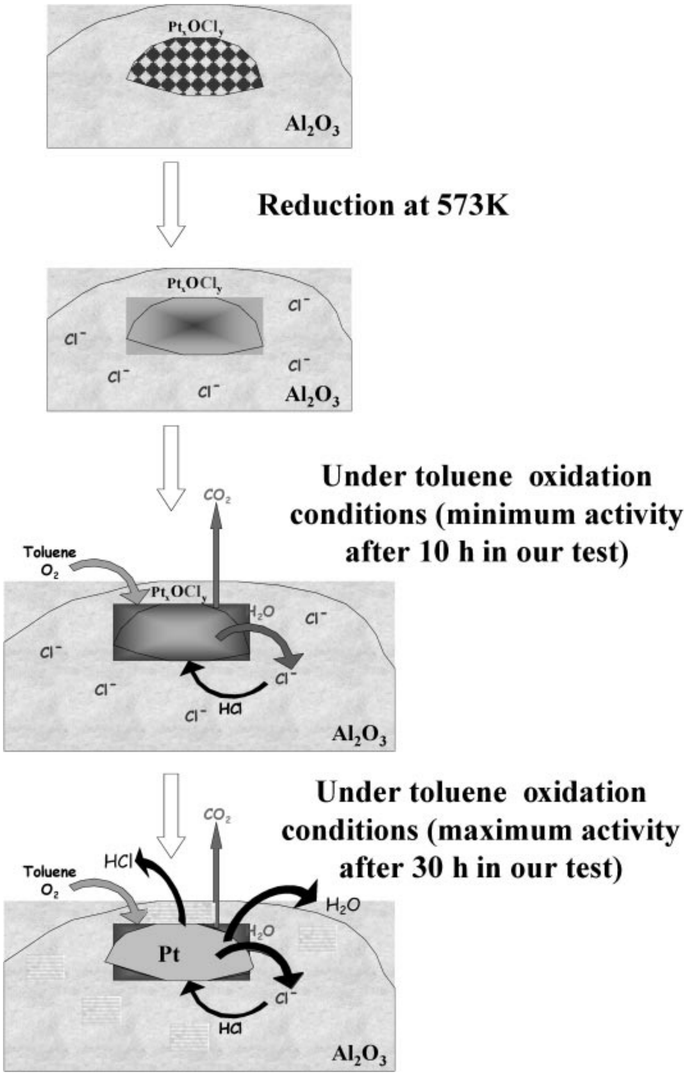

FIG. 14. Proposed model of chlorine mobility during the pretreatment and toluene oxidation reaction on Pt_{Cl_4}/Al_2O_3.

further evolution of the toluene oxidation will bring about the elimination of the chlorine present in the platinum particles with the H_2O formed (7, 8, 29, 30), and the improvement of the oxidation activity of the catalyst. Once all the chlorine is eliminated, the catalyst activity reaches a maximum conversion, which in this case is higher than the initial one, because at this stage chlorine that was initially in contact with platinum has been completely eliminated.

In the same way, the anomalous behaviour of the ignition curve of $Pt_{NH_3}/Al_2O_3 + 1.6\%$ Cl in Figs. 7 and 11 can be understood with this chlorine mobility model. In fact, the ignition curve moves from that of the sample without chlorine to that partially deactivated by the chlorine. This chlorine, present mainly on the support initially, would have been moved toward the platinum particles, due to the mobilisation induced by the water produced in the oxidation reaction itself.

To corroborate our chlorine mobility model and the role of water in the model, we have carried out two kinds of experiments. On one hand we have followed the HCl evolution during the stability test of Pt_{Cl_4}/Al_2O_3, with an online MS detector. The results of the evolution in time of toluene ($m/z = 91$), CO_2 ($m/z = 44$), and HCl ($m/z = 36$) are shown in Fig. 15. As can be seen, the activity trend is the one described in Fig. 12, with an initial decrease and a final increase. If we consider the $m/z = 36$ signal, we can see that HCl evolves from the catalyst as the stability test runs, indicating that chlorine is being eliminated after reactioning with water. The end of the HCl peak, when no more HCl flows out the reactor, coincides with the recuperation of the activity in a plateau.

On the other hand, we have pretreated Pt_{Cl_4}/Al_2O_3 catalyst under wet streams, in order to see if these pretreatments eliminate chlorine from the catalyst and the negative effect of chlorine's presence on the activity. The

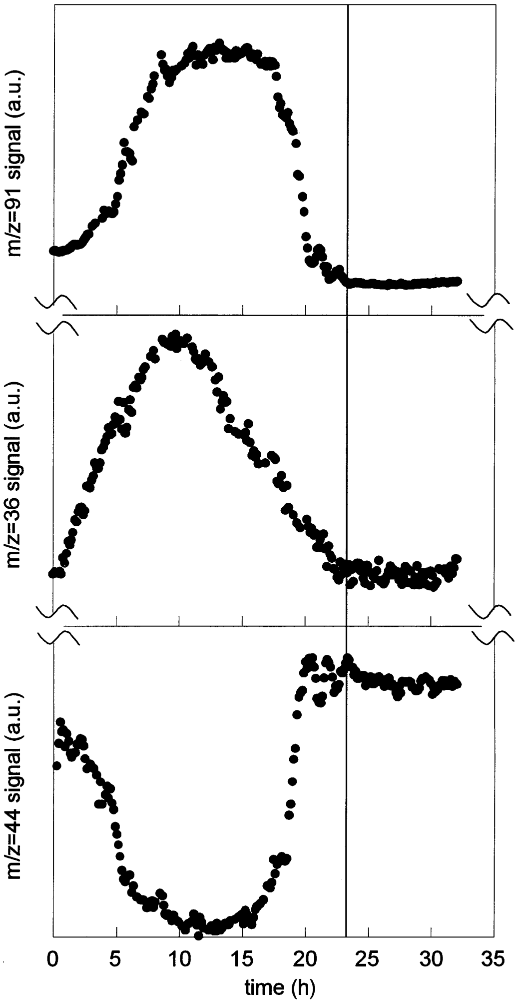

FIG. 15. Stability test of Pt_{Cl_4}/Al_2O_3 in the toluene complete oxidation reaction followed by online mass spectrometry. Toluene ($m/z = 91$), CO_2 ($m/z = 44$), and HCl ($m/z = 36$) signals are represented.

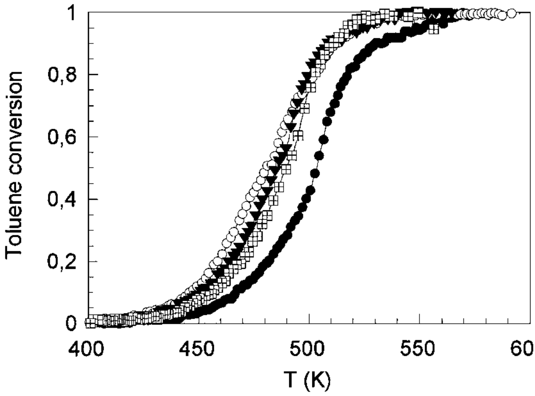

FIG. 16. Ignition curves of toluene complete oxidation over Pt_{Cl_4}/Al_2O_3 pretreated in H_2 at 573 K for 1 h (●), after 18 h under wet air at 773 K (○), after 18 h under wet He at 573 K (▼), and after 30 h of stability test (⊞).

pretreatments have been carried out in wet air and wet He streams, to separate the H_2O action from a possible oxidising action of air. Both streams have been bubbled in a water saturator at 298 K to obtain wet streams. Figure 16 shows the results of Pt_{Cl_4}/Al_2O_3 pretreatment under wet air at 773 K and under wet He at 573 K, compared with the ignition curves for the fresh catalyst and the catalyst fully activated after the stability test (30 h). It can be observed that both wet pretreatments produce a catalyst at least as active as the one fully activated. Therefore, we can assume that activation under reaction conditions corresponds mainly to the elimination of chlorine through the formation of HCl by the water produced by the oxidation reaction.

4. CONCLUSIONS

Three Pt/Al_2O_3 catalysts have been prepared from $Pt(NH_3)_4(OH)_2$, $(NH_4)_2PtCl_4$, and $(NH_4)_2PtCl_6$ precursors. The use of chlorinated precursors has increased slightly the surface acidity, and consequently the adsorption of bicarbonate and carbonate species on the support during CO oxidation has decreased. Furthermore, the use of chlorinated precursors has generated platinum oxychloride species with higher reduction temperature.

The DRIFTS spectra of CO adsorption under oxidising conditions have shown higher activity for CO oxidation of Pt_{NH_3}/Al_2O_3, due probably to the higher electronic density of platinum or to its presence in smoother surfaces suggested by the bridge-bonded CO appearing on this catalyst. On the other hand, Pt_{Cl_4}/Al_2O_3 and especially Pt_{Cl_6}/Al_2O_3 have presented oxidised platinum species at high temperatures, together with lower CO oxidation activity. In the case of Pt_{Cl_6}/Al_2O_3, the higher platinum oxidation state has been attributed to the high dispersion obtained in the catalyst preparation.

The measured catalytic activity sequence is as follows: $Pt_{NH_3}/Al_2O_3 > Pt_{Cl_4}/Al_2O_3 > Pt_{Cl_6}/Al_2O_3$. The addition of 1.6% of chlorine to Pt_{NH_3}/Al_2O_3 resulted in an activity between Pt_{NH_3}/Al_2O_3 and Pt_{Cl_4}/Al_2O_3. Pt_{NH_3}/Al_2O_3 showed an unchanged activity during the stability test, while Pt_{Cl_4}/Al_2O_3 and $Pt_{NH_3}/Al_2O_3 + 1.6\%$ Cl showed an initial decrease in activity followed by an increase until a plateau was reached. The H_2O formed during toluene oxidation has been reported as being responsible for Cl mobilisation. This Cl present mainly on the support in the case of $Pt_{NH_3}/Al_2O_3 + 1.6\%$ Cl, moved to the platinum particles, causing the initial activity decrease. Further reaction would eliminate all the Cl to recover the initial activity. In the case of Pt_{Cl_4}/Al_2O_3, the initial reduction would spread the Cl from the platinum particles to the support and to the inside of the platinum particles. The admission of toluene in the oxidising atmosphere would bring about the movement of Cl to the outside part of platinum particles and from the support back to the platinum particles. All these effects should decrease the catalytic activity. The posterior chlorine elimination by the H_2O formed in the reaction will produce an increase of the activity, reaching a value higher than the initial one.

As a result, it has been concluded that an initial pretreatment under wet streams can lead to a complete activation of the supported Pt catalysts prepared from chlorided precursor salts.

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REFERENCES

1. Spivey, J. J., *in* "Catalysis, a Specialist Periodical Report" (J. R. Anderson and M. Boudart, Eds.), Vol. 8, p. 157. The Royal Chem. Soc., London, 1989.
2. Briot, P., and Primet, M., *Appl. Catal.* **68**, 301 (1991).
3. Simone, D. O., Kenelly, T., Brungard, N. L., and Farrauto, R. F., *Appl. Catal.* **79**, 87 (1991).
4. Peri, S. S., and Lund, C. R. F., *J. Catal.* **152**, 410 (1995).
5. Marècot, P., Fakche, A., Kellali, B., Mabilon, G., Prigent, M., and Barbier, J., *Appl. Catal. B: Environ.* **3**, 283 (1994).
6. Marceau, E., Che, M., Saint-Just, J., and Tatibouët, J. M., *Catal. Today* **29**, 415 (1996).
7. Straguzzi, G. I., Aduriz, H. R., and Gigola, C. E., *J. Catal.* **66**, 171 (1980).
8. Cant, N. W., Angove, D. E., and Patterson, M. J., *Catal. Today* **44**, 93 (1998).
9. Garetto, T. F., and Apesteguía, C. R., "Actas del Simposio Iberoamericano de Catálisis," pp. 1009–1714. Cartagena de Indias, Colombia, 1998.
10. Kondarides, D. I., and Verykios, X. E., *J. Catal.* **174**, 52 (1998).

11. Hicks, R. F., Qi, H., Young, M. L., and Lee, R. G., *J. Catal.* **176**, 295 (1990).
12. Pecchi, G., Reyes, P., Gómez, R., López, T., and Fierro, J. L. G., *Appl. Catal. B: Environ.* **17**, L7 (1998).
13. Stencel, J. M., Goodman, J., and Davis, B. H., *in* “Proceedings, 9th International Congress on Catalysis, Calgary, 1988” (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1291. Chem. Institute of Canada, Ottawa, 1988.
14. Satterfield, C. N., and Sherwood, T. K., “The Role of Diffusion in Catalysis.” Addison-Wesley, London, 1963.
15. Freel, J., *J. Catal.* **25**, 149 (1972).
16. Hwuang, C.-P., and Yeh, C.-T., *J. Mol. Catal. A: Chem.* **112**, 295 (1996).
17. Knözinger, H., *Adv. Catal.* **25**, 184 (1976).
18. Davydov, A. A., *in* “Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides” (C. H. Rochester, Ed.). Wiley, Chichester, 1990.
19. Fisher, I. A., and Bell, A. T., *J. Catal.* **184**, 357 (1999).
20. De La Cruz, C., and Sheppard, N., *Spectrochim. Acta* **50**, 271 (1994).
21. Morterra, C., Zecchina, A., Coluccia, S., and Chiorino, A., *J. Chem. Soc., Faraday Trans. 1.* **73**, 1544 (1977).
22. Tanaka, K., and White, J. M., *J. Phys. Chem.* **86**, 3977 (1982).
23. Horiuchi, T., Hidaka, H., Fukui, T., Kubo, Y., Horio, M., Suzuki, K., and Mori, T., *Appl. Catal. A: Gen.* **167**, 195 (1998).
24. Busca, G., Finnochio, E., Lorenzelli, V., Ramis, G., and Baldi, M., *Catal. Today* **49**, 453 (1999).
25. Hicks, R. F., Qi, H., Young, M. L., and Lee, R. G., *J. Catal.* **122**, 280 (1990).
26. Mojet, B. L., Kappers, M. J., Miller, J. T., and Koningsberger, D. C., *Stud. Surf. Sci. Catal.* **101**, 1165 (1996).
27. Grbic, B., Radic, N., and Terlecki-Baricevic, A., *Sci. Sinter.* **30**, 179 (1998).
28. Lieske, H., Lietz, G., Spindler, H., and Völter, J., *J. Catal.* **81**, 8 (1983).
29. Holmgren, A., Andersson, B., and Duprez, D., *Appl. Catal. B: Environ.* **22**, 215 (1999).
30. Schmal, M., Aranda, D. A. G., Noronha, F. B., Guimaraes, A. L., and Monteiro, R. S., *Catal. Lett.* **64**, 163 (2000).