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Influence of the Metallic Precursor and of the Catalytic Reaction on the Activity and Evolution of Pt(Cl)/δ-Al_2O_3 Catalysts in the Total Oxidation of Methane

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In the light-off temperature range of methane total oxidation (250–600°C), two types of Pt/δ-Al_2O_3 catalysts prepared from H_2PtCl_6 or $Pt(NH_3)_4(OH)_2$ show different catalytic behaviors. Initially very active, fresh chlorine-free catalysts deactivate in isothermal conditions of reaction, while fresh chlorine-containing catalysts, initially poorly active, undergo an activation with time on stream. Consequences of dechlorination of chlorine-containing catalysts and of impregnation by various amounts of NH_4Cl on both types of catalysts are examined. Chlorine is responsible for the inhibition observed on ex-H_2PtCl_6 catalysts, which could be attributed, more specifically, to the chloride ions remaining at the platinum–support interface after reduction of platinum. After aging of the catalysts under reaction, sintering of the platinum particles is observed on all samples, regardless of their preparation mode. This phenomenon is linked to the presence of oxygen in excess in the gas phase and can account for the deactivation of chlorine-free catalysts. The water produced during the reaction removes the inhibiting chlorine on all chlorine-containing catalysts. The activity of the largest sintered particles is shown to vary with the nature of the fresh catalyst, the aged ex-H_2PtCl_6 catalysts giving the best results: the molecular nature of the fresh catalyst would also affect the activity of the stable aged catalyst. Both the initial presence of chloride ions at the metal–support interface and the composition of the reacting mixture are key factors to this positive reconstruction.

Key Words: **methane; total oxidation; aging; platinum; catalysts; chlorine; alumina; sintering.**

INTRODUCTION

Catalysts with low light-off temperatures are desirable for catalytic combustion to produce heat and for total oxidation to destroy traces of pollutants (1–9). However, the progress has been slow when methane is the hydrocarbon to burn catalytically or the pollutant to oxidize because this molecule is very difficult to activate.

Palladium and iridium catalysts are considered to be the best methane oxidation light-off catalysts but platinum is often used because it is less prone to deactivation than palladium and to volatilization than iridium. Iridium, which volatilizes at low temperatures (around 420°C) (10), is used only in a few specific applications—where it is used only once such as in rocket fuel ignition. Palladium is considered to be the most active for methane total oxidation at low temperature (2, 6), but when supported, it undergoes deactivation in the presence of water (11–13), in the presence of sulfur-containing compounds (7, 9, 14, 15), or upon sintering or unexpected wetting of the support by palladium oxide (16–18).

Though active at slightly higher temperatures, alumina-supported platinum appears to be more stable toward these chemical constraints since platinum oxidizes only superficially and does not form thermally stable hydroxides or sulfates. However, platinum catalysts are sensitive to other factors such as chlorine (19). Additionally, they reconstruct under reaction conditions at 600°C, leading to large faceted metal particles associated with a high turnover rate (TOR) (20)—the dependence of the reaction TOR to the size of the platinum particles still being debated (21, 22).

On one hand, we investigate here the influence of chlorine—introduced either with the metallic precursor (H_2PtCl_6) or by an exogenic chlorination—on the activity of Pt/δ-Al_2O_3 catalysts, not only fresh but also aged under reaction conditions: the latter is representative of the catalysts at steady state in actual operation. On the other hand, the role played by each component of the reacting mixture on the catalyst evolution during reaction is also studied. From the dependence of the activity of the catalyst on chlorine exposure and time on stream, supplemented by catalyst characterization, we will endeavor to correlate the light-off properties and evolution under reaction of platinum catalysts with chemical phenomena occurring at the molecular level, in relation to the presence of chlorine in the precursor.

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EXPERIMENTAL

Catalyst Preparation

Catalysts were prepared by wet impregnation of aluminas (Rhône–Poulenc) with an aqueous solution of $Pt(NH_3)_4(OH)_2$ (Alfa Products; samples hereafter referred to as N-type samples) or H_2PtCl_6 (Aldrich, solution stabilized by HCl; samples hereafter referred to as C-type samples). The main characteristics of the samples obtained are given in Table 1. Two types of aluminas were used: E6135 (δ-alumina, specific area of 69 $m^2\ g^{-1}$) and SCM129 ($\gamma + \delta$-alumina, 100 $m^2\ g^{-1}$). Both supports had a granulometry in the range 80–180 μm and a pore volume of 0.7 g cm^{-3}.

The volume of the 2×10^{-2} mol L^{-1} platinum complex solution needed to reach the aimed final platinum content was added dropwise to a suspension of 5 g of alumina in 30 cm^3 of water under stirring. The mixture was stirred for 1 h after completion of the platinum introduction, at room temperature (samples N0, C1, and C3) or at 70°C (sample C2). Water was removed under vacuum (10^4 Pa = 0.1 bar) at 70°C.

The solid was then ground and dried at 90°C overnight. It was calcined in helium (flow rate: He = 10 mL min^{-1}; heating ramp = 2°C min^{-1} up to the reduction temperature and 1 h at that temperature) and reduced in dilute hydrogen (flow rates: H_2 = 5 mL min^{-1}, He = 10 mL min^{-1}; duration = 16 h). Ex-$Pt(NH_3)_4(OH)_2$ sample N0 was reduced at 350°C and ex-H_2PtCl_6 samples C1, C2, and C3 were reduced at 500°C. BET surfaces of the supports were checked to not have varied after reduction of the catalyst.

Fractions of reduced samples N0 and C1 underwent incipient wetness impregnation treatments with solutions of NH_4Cl followed by drying at 90°C overnight to increase their chlorine content (samples N1 to N7 and C4). BET surfaces of the samples were not modified by this treatment and no peak of crystallized NH_4Cl was observed by X-ray diffraction. Sample C5 was prepared from a fraction of reduced sample C3: after reduction, it underwent a 2-h treatment in boiling water followed by a filtration, leading to the elimination of some chlorine from the sample.

Characterization Methods

Chemical analyses of platinum, nitrogen, and chlorine were performed by the CNRS Service of Analysis in Vernaison.

Transmission electron microscopy (TEM) experiments were performed on a JEOL 100 CXII UHR microscope. All freshly reduced catalysts exhibited a similar narrow particles size distribution centered on Ø = 15 Å, except sample C2, impregnated at 70°C, for which the particles were smaller (Ø = 10 Å).

Powder X-ray diffraction (XRD) measurements were performed on a Siemens D500 diffractometer, using the $K\alpha$ radiation of copper (1.5418 Å). XRD was used as a second method to assess the average platinum particle size of the samples; when higher than 30 Å, the Laue–Scherrer equation was applied to the (111) diffraction peak of platinum particles ($2\theta = 39.7°$). Good agreement was reached by the two methods.

The platinum metallic fraction exposed (or dispersion) was measured using H_2–O_2 volumetric titrations according to Benson and Boudart; H : Pts and O : Pt_S stoichiometries were chosen to be 1 : 1 (23). Measurements on sample N0 led to a dispersion value of 95%; measurements on samples

TABLE 1

Characteristics of Reduced Catalysts

	Alumina	Platinum salt	Pt (wt%)	Additional treatment	Final Cl (wt%)	Atomic Cl/Pt ratio	Particle diameter (Å)[b]	Dispersion (%)[c]
N0	δ	$Pt(NH_3)_4(OH)_2$	1.5	none	0	0	15	95
N1	δ	$Pt(NH_3)_4(OH)_2$	1.5	N0 + NH_4Cl	0.03	0.10	15	—
N2	δ	$Pt(NH_3)_4(OH)_2$	1.5	N0 + NH_4Cl	0.07	0.25	15	—
N3	δ	$Pt(NH_3)_4(OH)_2$	1.5	N0 + NH_4Cl	0.09	0.35	15	—
N4	δ	$Pt(NH_3)_4(OH)_2$	1.5	N0 + NH_4Cl	0.21	0.80	15	—
N5	δ	$Pt(NH_3)_4(OH)_2$	1.5	N0 + NH_4Cl	0.39	1.40	15	—
N6	δ	$Pt(NH_3)_4(OH)_2$	1.5	N0 + NH_4Cl	0.50	1.80	15	—
N7	δ	$Pt(NH_3)_4(OH)_2$	1.5	N0 + NH_4Cl	0.74	2.70	15	—
C1	δ	H_2PtCl_6	1.5	none	0.43	1.60	15	42
C2[a]	δ	H_2PtCl_6	1.5	none	0.22	0.80	10	65
C3	$\gamma + \delta$	H_2PtCl_6	2.0	none	0.60	1.65	15	48
C4	δ	H_2PtCl_6	1.5	Cl + NH_4Cl	0.77	2.80	15	—
C5	$\gamma + \delta$	H_2PtCl_6	2.0	C3 + dechlorination	0.20	0.50	15	53

[a] Sample impregnated at 70°C.
[b] Average particle size determined by TEM.
[c] Measured by H_2–O_2 titrations.

C1, C2, C3, and C5 led to values of 42, 65, 48, and 53%, respectively (Table 1). It must be noted that the dispersion values could not be determined satisfactorily on the dried NH_4Cl-impregnated samples due to low gas adsorption and irreproducibility of the measurements.

Catalytic Reaction

The catalytic reaction was performed at atmospheric pressure and the corresponding apparatus can be divided into three circuits. The first circuit allowed the reduction of the catalyst metallic surface with dilute hydrogen (flow rates: $H_2 = 5$ mL min^{-1}, He $= 10$ mL min^{-1}; heating ramp $= 5°$C min^{-1}). Chemical analyses showed that these conditions also led to the total elimination of nitrogen on NH_4Cl-impregnated samples without their chlorine content being modified. It has been reported recently that NH_4Cl could induce a dramatic sintering of platinum during a stay at moderate temperature in a reducing atmosphere (24); it was checked that in our conditions the platinum particle size was not modified by this temperature ramp in dilute hydrogen. The second circuit containing helium (flow rate: He $= 10$ mL min^{-1}) was used for purge before the reactants were introduced. The third circuit contained the reactants mixture, highly diluted in helium and in excess of oxygen (flow rates: He $= 95$ mL min^{-1}, $O_2 = 4$ mL min^{-1}, $CH_4 = 1$ mL min^{-1}). The gases (methane N55, helium U, oxygen C, and hydrogen U) were provided by L'Air Liquide and used without any further purification.

The catalyst was maintained in a tubular quartz reactor, placed inside an Abiss vertical oven connected to a Eurotherm temperature regulator. The space velocity of the gases through the catalyst bed was calculated to be 7800 h^{-1}. It was checked that the reaction was not diffusion controlled and heat-transfer limitations were negligible. The analysis of the effluents was performed by gas chromatography after sampling in an inox loop (chromatograph Varian 300, column Chrompack Carboplot P7 25 m $\times$ 0.53 mm in fused silica, detection by catharometry) and quantification on-line using a Spectra Physics SP4270 integrator. No carbon monoxide was detected in our experiments. The carbon balance did not reveal any loss or excess of carbon in the effluents after reaction.

The conversion (expressed in molar fraction) was measured as the ratio of the partial pressure of CO_2 produced to the initial partial pressure of CH_4. The measurement of the conversion led to the calculation of the average rate per mole of platinum

$$v = \text{conversion} \times \frac{CH_4 \text{ molar flow rate}}{\text{catalyst mass}} \times \frac{\text{Pt molar mass}}{\text{Pt wt\%}}$$

(mol of CH_4 mol of Pt^{-1} s^{-1})

and to the TOR of the reaction on the catalyst, considering that all the platinum surface atoms Pt_S measured by chemisorption behaved as catalytic sites:

$$\text{TOR} = \frac{v}{\text{dispersion evaluated by chemisorption}}$$

(mol of CH_4 mol of Pt_S^{-1} s^{-1}).

Partial orders of the reaction toward methane and oxygen were calculated to be 1 and 0, respectively, at conversions lower than 10%.

Testing Procedure

The samples were tested in the 250–600°C temperature range: none of them could perform the catalytic oxidation of methane below 250°C and all gave a 100% conversion at 600°C. Bare alumina could only convert 3% of methane to carbon dioxide at 600°C.

The quantity of platinum was taken as constant (20 μmol) and the mass of catalyst tested was chosen consequently (200 to 270 mg). The reduced N- or C-type catalyst (called hereafter "fresh catalyst") was first characterized by its conversion curve at increasing temperature. Every heating to the temperature of reaction was performed in dilute hydrogen, followed by a 2-min purge in helium before admission of the reactants mixture. At a temperature T, the catalyst was left to age under reaction. The conversion was monitored during the whole aging period. The catalyst aged at temperature T (called hereafter "RT catalyst," for *reconstructed at temperature T* (°C)) was then characterized first by its conversion curve, usually at decreasing temperature, and then by the physicochemical techniques described above. No variation of the platinum content was observed after reaction and aging.

RESULTS

(1) Activity of the Fresh Catalysts

Catalyst N0, which was the only chlorine-free catalyst, appeared to be the most active toward the total oxidation of methane (Fig. 1a). Conversion started as low as 275°C; 50% of the methane introduced was converted into CO_2 at about 410°C and 90% at about 480°C. There was a 80°C shift compared with the curves given by the ex-H_2PtCl_6 catalysts (50% methane converted at 490°C). C1 to C5 catalysts exhibited close activity, whatever their chlorine content or origin. TORs calculated for catalysts N0 and C1 were found to be higher on the chlorine-free sample (Fig. 1b).

In contrast, the catalysts prepared from $Pt(NH_3)_4(OH)_2$ and impregnated with NH_4Cl appeared to fall in activity with increasing chlorine content (Fig. 2). It was checked that a catalyst prepared by impregnation of $Pt(NH_3)_4(OH)_2$ on a chlorided alumina (0.03 wt% of chlorine) gave the same results as sample N1. Only 0.07 wt% of chlorine deposited from NH_4Cl could reduce by half the catalyst conversion

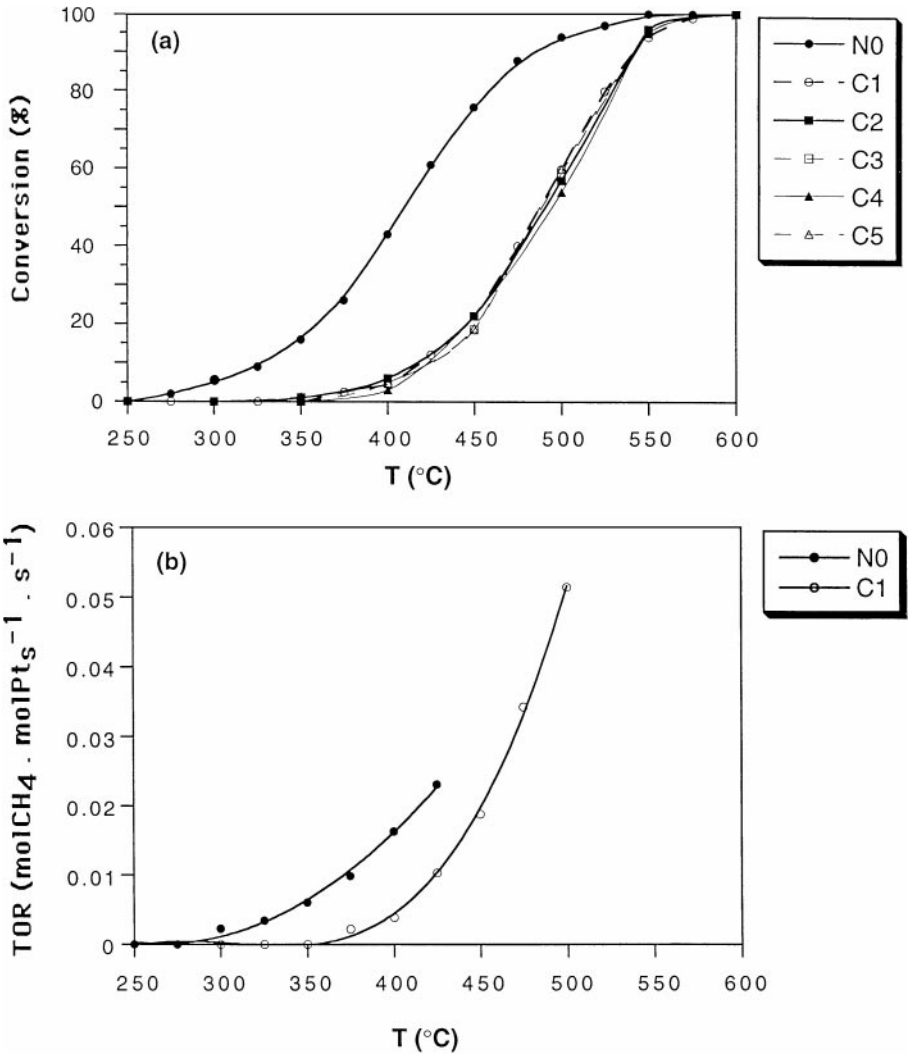

FIG. 1. (a) Evolution of conversion with temperature for samples N0 and C 1-5. (b) Evolution of TOR with temperature for samples N0 and C1.

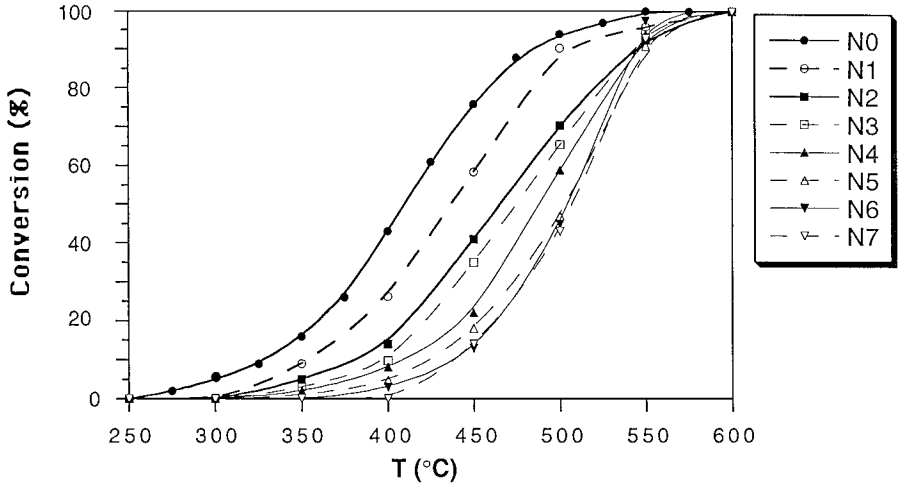

FIG. 2. Evolution of conversion with temperature for samples N0-7.

TABLE 2

Activation Energies Calculated from the Activity Curves of Fresh Catalysts at Increasing Temperature

Catalyst	Activation energy (kJ mol^{-1})
N0	64
N1	72
N2	74
N3	82
N4	90
N5	108
N6	112
N7	104
C1	112
C2	116
C3	111
C4	113
C5	108

at 450°C, compared with the chlorine-free catalyst. At chlorine contents higher than 0.4 wt% (from N5 to N7), the catalyst activity seemed to reach a limit and did not decrease any more. In that domain and for a similar Cl/Pt atomic ratio, NH_4Cl-impregnated catalysts appeared to be less active than ex-H_2PtCl_6 catalysts ($T_{10} = 440$°C and $T_{50} = 510$°C for catalyst N7, compared with 420 and 490°C on catalyst C4).

Activation energies could be calculated from the slopes of the linear Arrhenius plots giving ln(TOR) vs $1/T$, at conversions lower than 10% (Table 2). Sample N0 exhibited the lowest activation energy and samples C1 to C5 the highest. Activation energies measured for samples N1 to N7 increased from 70 to about 110 kJ mol^{-1} and then from the value given by sample N0 up to the values given by the ex-H_2PtCl_6 catalysts.

(2) Evolution of the Catalysts under Reaction

Catalysts were left in isothermal conditions at various temperatures until their conversion appeared to be constant. The higher the aging temperature, the shorter the stay in temperature until stable activity was reached. Samples C1 and N0 were aged at 450, 490, 550, and 600°C (and C1 at 400°C) and the other samples at 450 and 600°C.

The C1 catalyst underwent activation at any aging temperature, even as low as 400°C (Table 3). This activation was characterized by a global increase in conversion. The activation at 450°C of C2 to C5 samples was similar to the one observed on C1. At the highest aging temperatures, a maximum conversion was measured at the time noted t_{max}, followed by a decrease in conversion until a stable conversion was attained at the time noted t_{st}.

The same experiments conducted on the chlorine-free sample N0 led in all cases to a deactivation in the same lapse

TABLE 3

Evolution of Conversion with Time during Aging of the C1 Catalyst

T (°C)	Initial conversion (%)	t_{max} (h)	Maximum conversion (%)	t_{st} (h)	Final conversion (%)
400	4	—	—	170	12
450	23	—	—	60	44
490	62	8	77	40	70
550	80	4	93	25	90

of time. The most spectacular effect was already reported to occur at 450°C, where the conversion was divided by 2 in 60 h and reached the value finally given by the aged ex-H_2PtCl_6 samples at the same temperature (19).

The catalytic behavior of samples N1 to N7 during aging depended on their chlorine content. Below 0.07 Cl wt% (N1), the catalyst underwent deactivation at 450°C (Fig. 3). Above this value (N4 to N7), activation was observed. It can be noted that samples N2 and N3 (0.07 and 0.09 Cl wt%) exhibited nearly similar activity before and after aging.

For all the catalysts, the conversion at 600°C was 100% from the beginning and the aging duration was chosen to be 16 h.

(3) Characterization of the Aged Catalysts

It was checked that the supports of the catalysts kept their crystallographic structure and BET surface after aging. Chemical analyses showed that chlorine became undetectable (<0.03 wt%) on all chlorine-containing samples after aging, except R400 sample C1 (0.3 Cl wt% remaining).

On all the samples, TEM and XRD showed that aging under reaction led to a sintering of the platinum particles, identical on all the catalysts and more pronounced as the aging temperature increased (Table 4 gives the results obtained on C1). Simultaneously, the dispersion measured by H_2–O_2 titrations was observed to decrease in agreement

TABLE 4

Average Particle Size and Platinum Dispersion of Aged C1 Catalysts

Aging temperature (°C)	Average Ø (Å) (XRD/TEM)	Dispersion (%) (H_2–O_2 titrations)
400	30	41
450	40	40
490	50	24
550	90	18
600	100	12

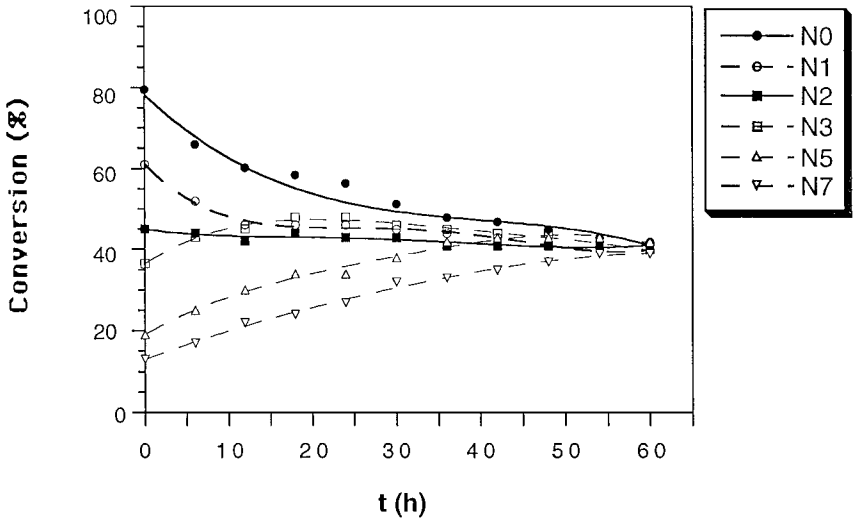

FIG. 3. Evolution of conversion with time at 450°C for sample N0 and five initially NH_4Cl-impregnated samples.

with the increasing sintering, except for the R400 sample C1, which presented a low value of dispersion compared with its average particle size.

Increase of the particle size, decrease of the dispersion, and loss of chlorine were checked to occur progressively on sample C3 with time on stream at 600°C (Fig. 4). These results are consistent with those obtained at 450°C on a similar ex-H_2PtCl_6 catalyst (19). In contrast, chlorine was no longer detected on sample N5 after only 1 h under reaction at 600°C. The evolution of the average particle size with time followed the same trend on sample N0 at 600°C.

(4) Influence of the Composition of the Gaseous Atmosphere on Platinum Sintering at 600°C

Samples N0 and C1 were treated in several gas mixtures at 600°C for 16 h. The average particle size was then measured by XRD and found to be identical for a given treatment on both catalysts. Chlorine was dosed on sample C1 after every heat treatment. Results relative to this sample appear in Table 5.

On both samples, platinum sintering in helium was moderate (40 Å) and 0.12 Cl wt% was dosed on sample C1 after heat treatment. The introduction of 2% H_2O in helium through a saturator at ambient temperature did not modify the sintering but dropped the chlorine content to 600 ppm. The same treatment applied to a chlorided alumina led to a nonmeasurable chlorine content after 2 h. In contrast, the introduction of 2% O_2 in helium increased the particle size to 70 Å without the content of chlorine being depleted below 0.1 Cl wt% for catalyst C1. The presence of 2% O_2 and 2% H_2O in helium combined both effects, sintering as well as chlorine removal. Introduction of 1% CO_2 led to identical results. This gas mixture reproduced the atmosphere obtained at 600°C at total conversion. The reaction

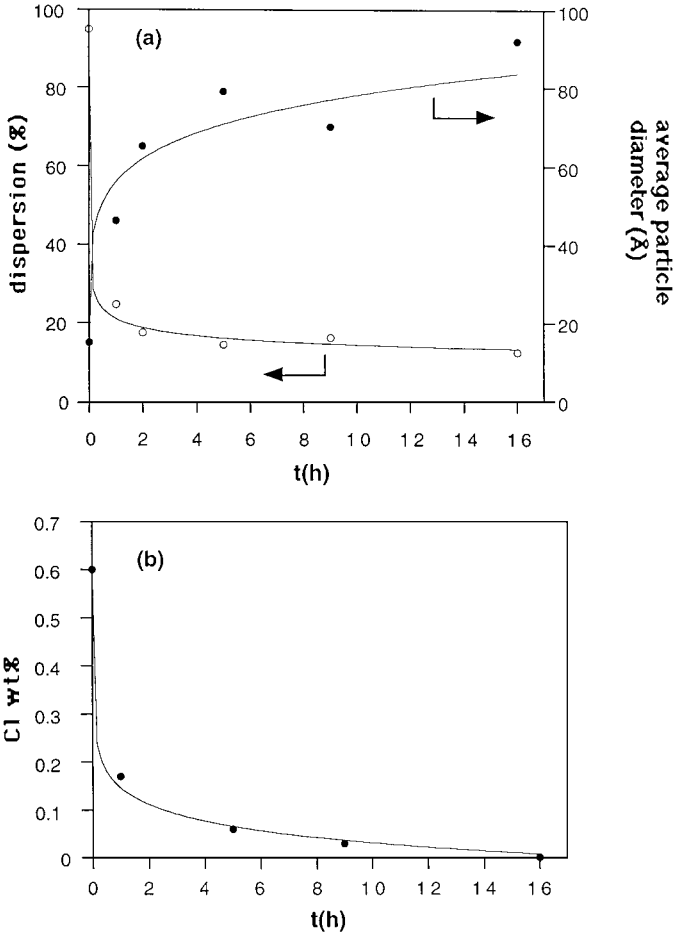

FIG. 4. Evolution of average particle size, dispersion (a), and chlorine content (b) with time at 600°C in reaction conditions for sample C3.

TABLE 5

Average Platinum Particle Size and Final Chlorine Content of C1 Catalysts (C1 wt% = 0.43) Treated in Various Atmospheres at 600°C for 16 h

He flow rate (mL min^{-1})	CH_4 flow rate (mL min^{-1})	O_2 flow rate (mL min^{-1})	H_2O flow rate (mL min^{-1})	CO_2 flow rate (mL min^{-1})	Average Ø (Å)	Cl (wt%)
100	0	0	0	0	40	0.12
98	0	2	0	0	70	0.10
98	0	0	2	0	40	0.06
96	0	2	2	0	70	0.06
95	0	2	2	1	70	0.06
97	1	2	0	0	40	<0.03
94	2	4	0	0	40	<0.03
95[a]	1	4	0	0	100	<0.03

[a] Composition of the gaseous mixture in the catalytic test.

accomplished in stoichiometric conditions led to a moderate sintering (40 Å) and chlorine became undetectable on sample C1 in all cases.

(5) Activity of the Aged Catalysts

Conversions given by R450 samples were identical whatever the aged catalyst. A comparison between the activity of fresh and aged samples showed that, in terms of conversion, the R450-aged catalysts appeared to be more active than fresh ex-H_2PtCl_6 catalysts and NH_4Cl-impregnated samples for which the chlorine content was higher than 0.09 wt% (N4 to N7) (Fig. 5). Fresh and R450-aged samples N3 (Cl wt% = 0.09) exhibited almost the same activity curves. The other catalysts (No, N1, and N2) were deactivated compared with their fresh state.

The same remark could be made for R490 to R600 catalysts N0 and C1 compared with their fresh state. However, increasing discrepancies were observed between aged samples N0 and C1 when the aging temperature increased from 490 to 600°C. TORs were calculated for R450- to R600-aged catalysts coming from sample N0 and C1 (Fig. 6). On both samples and at a given temperature, the TOR was found to increase regularly with the particle size in the range 40–100 Å, but to a greater extent on the R600 sample C1.

After aging at 600°C, R600 catalysts with similar physicochemical characteristics actually presented significantly different activities, the catalysts aged from ex-H_2PtCl_6 samples giving the best results (see for illustration Fig. 5). Activation energies were found to be lower on the ex-H_2PtCl_6 samples (Table 6).

Equally active and chlorine-free R450 catalysts N0 and C1 were submitted to a second aging treatment at 600°C, after or without impregnation by NH_4Cl. In all cases the expected sintering to a 100-Å average particle diameter occurred, leading to "R450/600" catalysts with an equivalent activity to that of the R600 sample prepared from $Pt(NH_3)_4(OH)_2$—that is, the least active R600 catalyst.

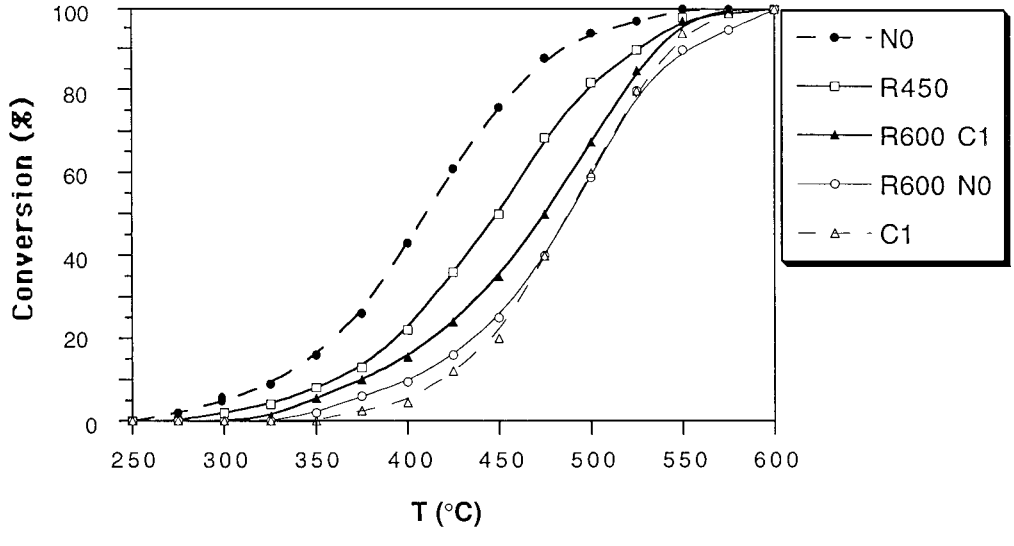

FIG. 5. Comparison of conversions measured on fresh, R450-aged samples, and R600-aged samples N0 and C1.

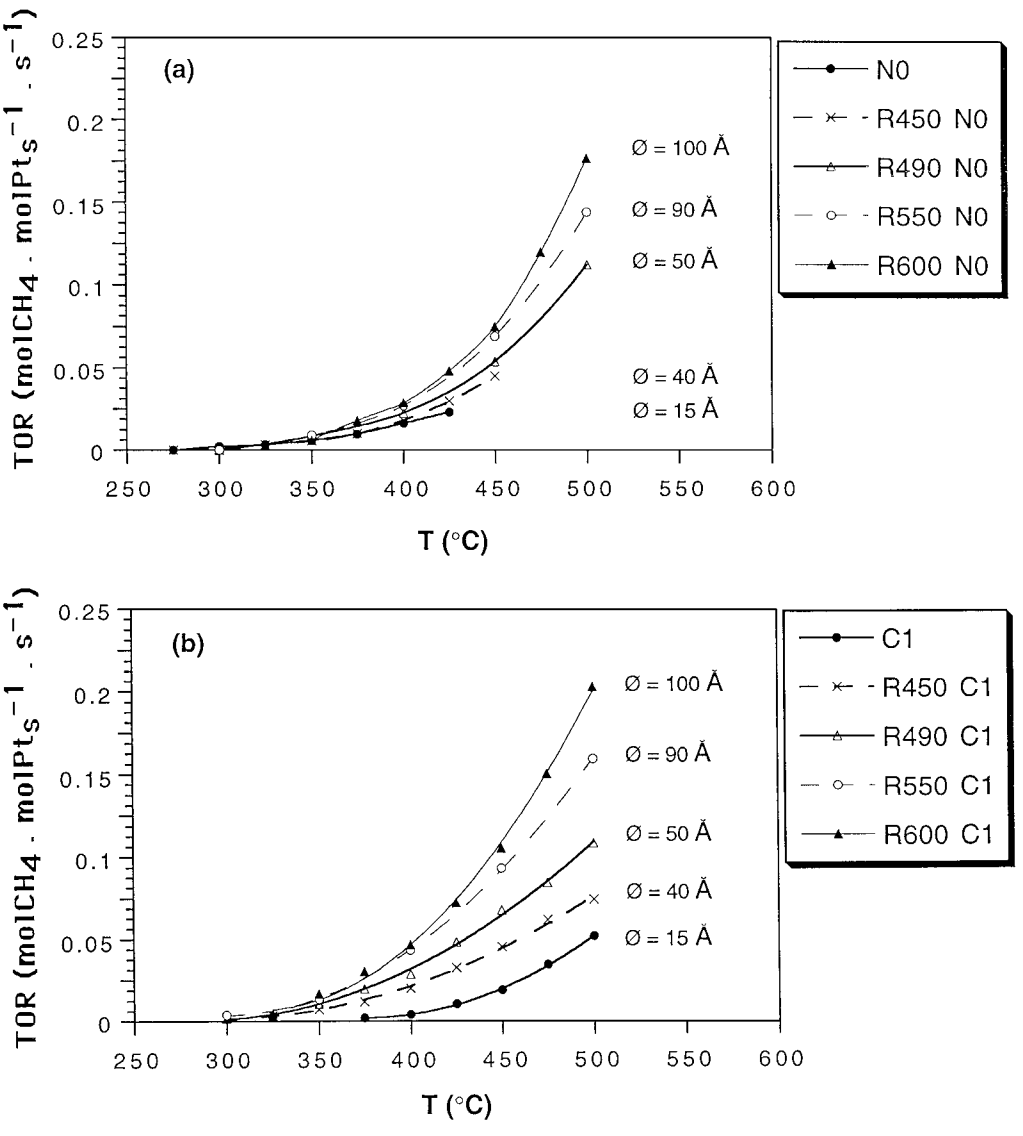

FIG. 6. Evolution of TOR with temperature on fresh and R450- to R600-aged samples N0 (a) and C 1 (b).

DISCUSSION

(1) State of the Art and Generalization

The results given above confirm and allow us to generalize the following features presented in the literature concerning the catalytic combustion of methane on Pt/Al_2O_3:

(i) The different dispersions measured by H_2–O_2 titrations on sample N0 and ex-H_2PtCl_6 samples, despite similar particle sizes (Table 1). Chlorine has been suggested to be responsible for the deficit in chemisorption on chlorine-containing samples (25, 26). The same phenomenon was observed on the R400 sample C1. It can be noted that the partial removal of chlorine carried out on sample C5 did not modify significantly the dispersion measured by gas chemisorption.

(ii) The inhibition toward the reaction observed on fresh chlorided catalysts (lower TORs measured on sample C1 than on N0; activation energies increasing from 65 kJ mol^{-1} on the chlorine-free sample to 105 kJ mol^{-1} in presence of chlorine, Table 2). The inhibiting behavior of residual chlorine toward methane combustion described earlier (19) is confirmed here. It has also been mentioned to be an inhibiting species for propane combustion on platinum (27) and methane on palladium (28, 29).

(iii) The activation phenomena seen on the chlorine-containing catalysts at any temperature, explained by the concomitance of sintering and elimination of chlorine by water (Tables 3 and 4) (19, 21, 27, 30, 31): the global activation is the conjunction of deactivation due to the decrease in the number of active sites and activation induced by the removal of an inhibiting element. Samples N2 and N3 have

TABLE 6

Activation Energies and Pre-exponential Factors Calculated from the TOR Curves of R600 Catalysts as a Function of Temperature (Dispersion = 12%)

Catalyst	E_a (kJ mol^{-1})[a]	ln A[a]
N0	77	10.2
N1	81	10
N2	77	10.3
N3	83	11.2
N4	75	9.9
N5	75	9.9
N6	89	12.2
N7	77	10.2
C1	67	8.8
C2	69	9.2
C3	67	8.7
C4	75	10
C5	70	9.4

[a] $\ln[\mathrm{TOR}(\text{mol of } CH_4 \text{ mol of } Pt_S^{-1}\ s^{-1})] = \ln A - E_a/RT$.

the right chlorine content to display a balance between the initial inhibition caused by chlorine and the final deactivation after aging at 450°C, due to the sintering (Fig. 3). The production of water on the R400 sample C1 is not high enough to remove all chlorine due to a low initial conversion at 400°C. In contrast, at higher temperatures (and higher conversions), the inhibiting effect of chlorine abates rapidly (initial activation until t_{max}) and sintering is the only cause of subsequent and independent deactivation until t_{st}.

(iv) The enhanced activity of sintered particles compared with those of the fresh catalysts (Fig. 6) (20), though this point has been a subject of discussion (21, 22).

Additionally, the experiments described in this article allow us to give a more precise description of the chemical events occurring on the catalyst surface during its stay under reaction.

(2) Localization of Chlorine on Fresh Catalysts

The presence of chlorine on the fresh catalyst surface modifies its activity. This can be clearly seen through the decreasing activities of the NH_4Cl-impregnated samples when their chlorine content increases. In contrast, the activity of the ex-H_2PtCl_6 samples remains globally the same, whatever the history and initial chlorine content. It appears thus that the activity of the catalyst depends on the origin of chlorine. When chlorine comes from the reduction of H_2PtCl_6, only part of it seems to regulate the activity without any effect of exogenic chlorine, while when it comes from NH_4Cl, the activity is regulated by the whole chlorine content.

In line with the recent results from Lebedeva *et al.* (32), it can be assumed that chloride ions coming from NH_4Cl impregnation interact preferably with the alumina support during the initial heating in hydrogen. The comparison with the sample prepared on chlorided alumina supports this interpretation. Chloride ions can actually diminish the electron density of the metal particles through an increase of the acidity of the support by electroattractive effect (33). On the other hand, two types of chlorine species would coexist on δ-Al_2O_3-supported ex-H_2PtCl_6 samples, with distinct influences on their catalytic activity:

—Chloride ions fixed on the alumina support, which would have a minor influence upon the activity of the catalyst. Whether their quantity is increased by NH_4Cl impregnation or they are removed by treatment with boiling water has no consequence on the catalytic activity.

—Chlorine remaining in small constant quantities at a short distance from the platinum particles obtained after reduction (31, 34, 35) and directly influencing the adsorptive and catalytic properties of the metal. These species mask the influence of chloride ions linked to alumina. Two types of species can be considered: chloride ions at the platinum–alumina junction; chlorine atoms linked to platinum atoms on the particle. The second type should probably be dismissed since chlorine atoms adsorbed on platinum surfaces desorb during heating (36). The existence of bridging chloride ions between aluminum and group 8 metal ions in molecular compounds supports the existence of the first type (37).

Platinum atoms at the chlorided metal–support interface would actually behave as poorly reactive oxidized centers, with a lower surface electron density (Fig. 7). Such oxidized sites have already been mentioned on catalysts prepared from H_2PtCl_6 (30, 38, 39) and evidenced by NMR of adsorbed ^{129}Xe (40).

In contrast, on NH_4Cl-impregnated samples N1–N7, chlorine would be localized mainly on alumina as chloride ions. The influence of this type of chlorine would not be masked by the effect of chlorine species linked to platinum as in the former case and the whole chlorine content would play an active role in metal particle deactivation.

(3) Role of the Reactants and Products in the Evolution of the Catalysts

Whether chlorine is present on the catalyst or not, and at any temperature, the metal particles undergo progressive sintering under reaction until they reach a stable size. The extent of sintering increases with and seems only to depend on the aging temperature. The atmosphere component responsible for sintering at 600°C is oxygen, more precisely, the 2% oxygen remaining in excess and characteristic of the catalytic testing conditions: in stoichiometric mixtures, the sintering is moderate and equivalent to sintering in an inert atmosphere (Fig. 7). The role of the heat produced during the combustion of a double quantity of fuel can be discarded. However, the final particle size obtained with oxygen or in an atmosphere mimicking total

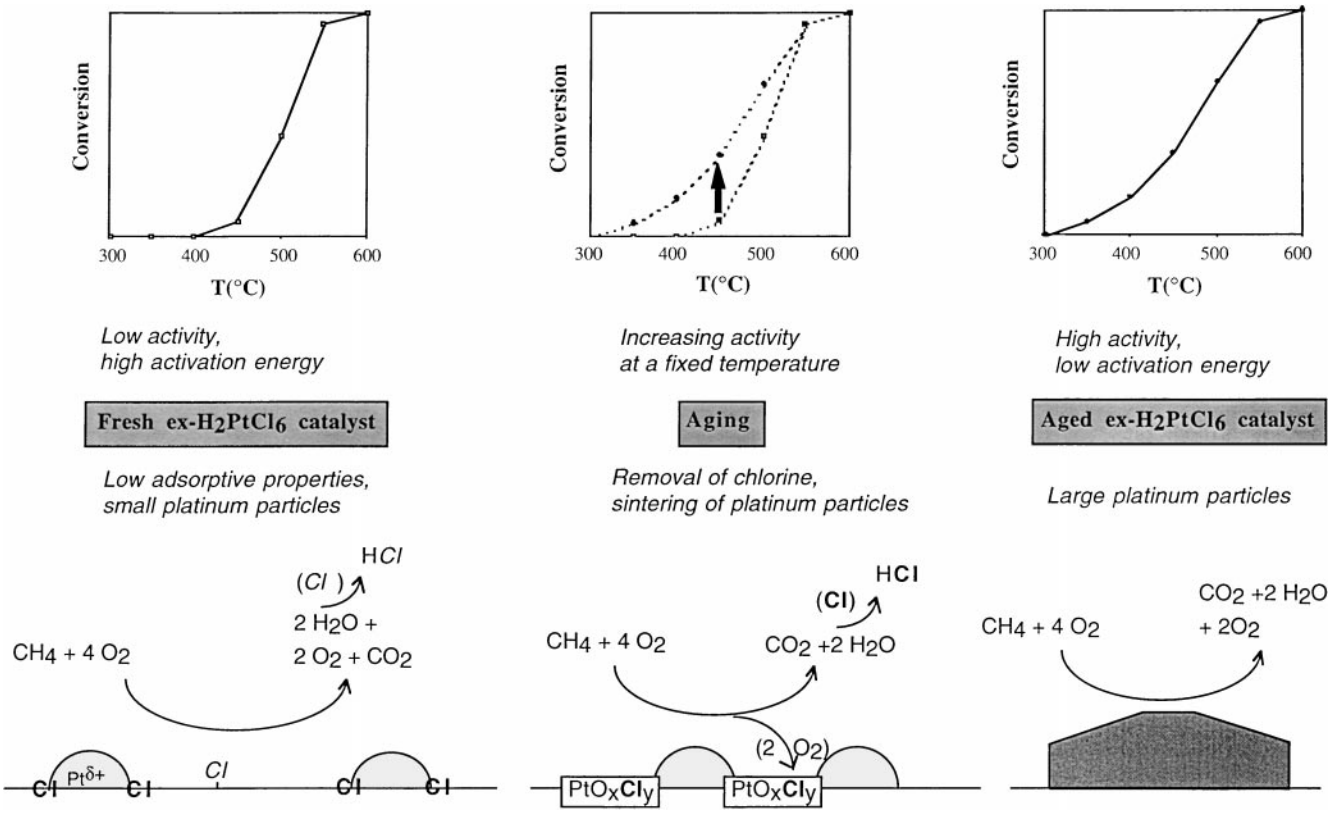

FIG. 7. Molecular model for the structure and aging of an ex-H_2PtCl_6 catalyst.

conversion does not reach the particle size obtained after aging under reaction. This would imply that the mixture constituents are not the only actors of the sintering and the process of the reaction itself plays an important role in it. Sintering appears to be unavoidable in our operating conditions.

It must be noted that it is the water produced by the reaction that leads to the complete elimination of chlorine on ex-H_2PtCl_6 samples and not water present as such in the gas atmosphere. This confirms that on these samples chlorine cannot be assimilated only to chloride ions fixed on alumina: a plain heat treatment with water is enough to remove totally chlorine from chlorided alumina and all chlorine is eliminated from an NH_4Cl-impregnated sample after 1 h under reaction at 600°C. Moreover, dechlorinations of aluminas are usually considered to be first-order reactions relative to chlorine (41), which is not the case of the catalyst dechlorination reported here. Chloride ions that can hardly be eliminated by external water are probably the inhibiting species located at the platinum–alumina interface; only water produced by the reaction on platinum can react with them. The elimination of chlorine observed during aging thus covers two distinct phenomena, leaching of alumina and slower dechlorination of platinum itself.

The quantity of chlorine remaining on the catalyst after treatment with water at 600°C should give an estimation of the amount of inhibiting chlorine species. Cl (600 ppm) on the C1 sample corresponds to the atomic ratio Cl/Pt = 0.2, i.e., 10 chloride ions at the periphery of a particle of 50 Pt atoms. In comparison, Abderrahim and Duprez considered that the oxygen-exchange properties of Rh particles on Rh/Al_2O_3 were altered significantly by chlorine atoms at their perimeter for the atomic ratio Cl/Rh = 0.6 (42).

A molecular model for sintering of platinum in isothermal conditions can be proposed, inspired by the regeneration of reforming catalysts. In the case of a chlorine-free catalyst, nuclei for the sintered particles, emitted around by platinum, are of PtO_x type (43) or platinum atoms (platinum oxides decompose around 600°C (44)). In the case of ex-H_2PtCl_6 catalysts, platinum oxychlorides PtO_xCl_y (44) would come from the fragmentation of the metal particles in an oxidizing atmosphere and from the chloride ions at the metal–support interface. The variation of final dispersion we observe with aging temperature follows the same trend as that presented by Garetto *et al*. for the oxidation of reforming catalysts (45). If a potential dispersion of 60% is supposed for the R400 sample Cl, according to its average particle size and ignoring the inhibiting influence of chlorine on chemisorption, the semilogarithmic plot of

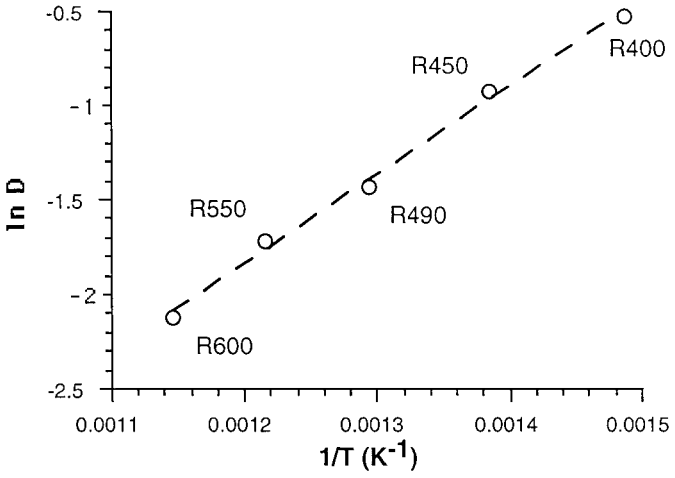

FIG. 8. Semilogarithmic plot of the final dispersion of aged C 1 catalysts as a function of $1/T$.

final dispersion as a function of $1/T$ leads to a "sintering enthalpy" of 40 kJ mol^{-1}, close to the one calculated by Garetto *et al.* for the sintering of a $Pt(Cl)/Al_2O_3$ catalyst (44.7 kJ mol^{-1}) (Fig. 8).

Under the simultaneous action of temperature, water, and reduction by methane, the ionic platinum species decompose by loss of oxygen and HCl. The growth of three-dimension metal particles occurs from these nuclei, and according to Lieske and Völter, it is the rate-determining step of the process (46). This could explain the identical rates of sintering observed on both chlorine-containing and chlorine-free catalysts during aging.

(4) Influence of the Metallic Precursor on the Activity of the Aged Catalysts

Unlike chlorine-free catalysts, ex-H_2PtCl_6 catalysts see their global activity increase after aging in all cases, compared with their initial activity and despite sintering. On the stable aged catalysts, TORs increase with the average size of the sintered particles, provided that the particle diameter is larger than 50 Å. This result conciliates the approach by the Reading group, for which there was no sensitivity of the TOR to the particle size for particles smaller than 40 Å (21), and the approach of other groups that supported the existence of such sensitivity, comparing particle sizes varying over 1 order of magnitude (20, 30, 47, 48).

More surprisingly, it is observed that, on the aged catalysts, and for an average particle size above 70 Å, the conversion varies with the catalyst, despite very similar physico-chemical characteristics. The R600 samples coming from ex-H_2PtCl_6 catalysts give the same conversion as sample R600 N0 at a temperature lower by 20 to 30°C. The increase of the TOR with the particle size is more pronounced on the ex-H_2PtCl_6 sample and the activation energies measured on series C are globally lower than those on series N. The poor activity of the R450/600 samples, treated by NH_4Cl or not, leads to the hypothesis that it is the initial presence of chlorine coming from reduction on the fresh catalyst, at the platinum–alumina interface, that is the key factor for the positive reconstruction of the particles under reaction, to give more active sites after sintering.

Morphology of the particles and possibly faceting have been advanced to account for the high activity of the largest platinum particles on the basis of lower adsorption energies of oxygen (20). It can be suggested that the presence of chloride ions during the sintering of particles could favor a more effective reconstruction than on chlorine-free catalysts. Two explanations can be proposed:

(1) The regularity of the reconstruction could depend on the nature of the nuclei fixed on the surface. Platinum oxychlorides are known to have a stronger interaction with alumina than platinum oxides (25, 43, 44, 49).

(2) The presence of impurities at the basis of the particles could favor the development of preferential crystalline faces, as it has been shown with the action of chlorine on silver (50), or surface substructures where oxygen is less retained (51).

In both cases, the key factor is the presence of small quantities of chlorine at the platinum–support interface, originating from the reduction of H_2PtCl_6. No major role is played by chloride ions fixed on the support.

CONCLUSIONS

Whatever the way chlorine has been introduced on Pt/δ-Al_2O_3 catalysts, it has always an inhibiting effect on the activity of the fresh catalyst toward total methane oxidation. Chloride ions located on the support can act as inhibiting species, as observed on NH_4Cl-impregnated ex-$Pt(NH_3)_4(OH)_2$ catalysts. But on ex-H_2PtCl_6 catalysts, the inhibition seems to be due to chloride ions at the metal–support interface screening the influence on catalytic activity of chlorides adsorbed on alumina.

Chlorine is eliminated by the water produced by the reaction. But this beneficial phenomenon for activity is in all cases conjugated with sintering leading to stable aged catalysts, the final particle size depending only on the aging temperature.

When the reconstruction is conducted at high temperature, aged ex-H_2PtCl_6 catalysts are more active than aged catalysts with initially exogenic chlorine, despite similar physico-chemical characteristics. Oxygen in excess is mainly responsible for sintering during the reaction, which means that the reconstruction is only possible in an oxygen-rich atmosphere. The difference in the nature of the nuclei created in the aging process (platinum oxychlorides or oxides) and their different adsorption properties on alumina are supposed to be responsible for the different modes of

reconstruction of platinum and the subsequent catalytic activity of the sintered particles. The nature of the chemical species present from the preparation step on the fresh catalyst would influence the reconstruction and activity of the stable catalyst obtained after aging under reaction.

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