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Influence of chlorine ions in Pt/Al_2O_3 catalysts for methane total oxidation

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Abstract

Residual chlorine ions on a Pt/Al_2O_3 catalyst surface prepared from chlorine-containing precursors appear to inhibit the total oxidation of methane. At 450°C, as chlorine is eliminated with time on stream, the reaction rate increases despite the sintering of the platinum particles. The steady state reaction rate which is reached after 60 h is identical to that obtained with a catalyst prepared from a precursor containing no chlorine. Whether chlorine is present or not in the initial state of the catalyst does not appear to have an influence on the evolution of the platinum particle size.

Keywords: Pt/Al_2O_3 catalysts; Oxidation inhibition

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1. Introduction

One of the main problems raised by the use of natural gas for heat production by flame combustion in air is the release of a large quantity of nitrogen oxides (NO_x) due to the high temperature reached in the flame (ca. 1800°C). The use of a catalyst allows the temperature to be controlled and maintained below 1400°C, and thus to decrease the amount of NO_x formed during the reaction. A segmented catalytic bed is often used, for example in a gas turbine application: the first stage is designed to initiate the reaction at a temperature as low as possible and the second stage has to ensure the total oxidation at the high temperature reached in the end part of the reactor, without the formation of hot spots or flame.

In the 50s, studies of methane total oxidation performed on polycrystalline platinum ribbons showed by microscopy an increase in the size of the crystalline domains after reaction [1]. On supported platinum and palladium catalysts prepared from a chlorine-containing precursor, an irreversible increase of the catalytic activity with time on stream was observed [2–6]; metallic particles grew simultaneously with catalytic activity [7–9]. The higher catalytic activity of large particles was assigned to their inability to be completely oxidized during the reaction as expected for small particles, the oxide phases being poorly active for methane oxidation [5,10]. Moreover, a facetting of some large platinum particles was observed after reaction at 600°C,

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suggesting that the catalytic methane total oxidation could be structure sensitive [8,9]. The purpose of the present study is to investigate the role of chlorine in the evolution of platinum particles and in the behaviour of the catalyst in methane total oxidation.

2. Experimental

2.1. Catalysts preparation

In order to investigate the influence of the platinum precursor on the reactivity of the catalyst, samples were prepared from H_2PtCl_6 (Aldrich) and $Pt(NH_3)_4(OH)_2$ (Alfa Products) on four different alumina supports (Table 1).

Chlorided alumina was prepared from γ-Al_2O_3 (ref. E6135) by contact of 5 g of alumina with 300 ml of an aqueous solution of HCl (10^{-3} mol l^{-1}) for 24 h at room temperature. The excess of solution was then evaporated at 70°C under reduced pressure (0.1 bar). The resulting solid was finally ground and dried overnight at 100°C. Its chlorine content was measured to be 0.17 wt.-%.

Samples A, B, C, E and F were prepared by contacting for 1 h 10 g of the alumina support maintained in 60 ml of water with an aqueous solution of the platinum precursor (2.10^{-2} mol l^{-1} Pt), added dropwise. Water was then removed at 70°C under reduced pressure (0.1 bar). The catalyst precursor was ground and dried overnight at 100°C.

Sample D was prepared by incipient wetness impregnation of γ-alumina (pore vol. = 0.73 cm^3/g) with an aqueous solution of $Pt(NH_3)_4(OH)_2$. After drying at 80°C for 24 h, the sample was calcined overnight at 300°C and 2 h at 400°C.

The catalyst precursors were reduced overnight under a H_2/He (1/2) mixture at 500°C for samples A, C and F or 350°C for samples B, D and E.

2.2. Particle size measurements

The mean particle size was determined by transmission electron microscopy (TEM) on a JEOL JEM 100CX1 apparatus. The metal dispersion was estimated from the particles size histogram [11] and from H_2/O_2 titrations, following the method described by Benson and Boudart [12].

2.3. Chemical analyses

Platinum and chlorine amounts were measured respectively by ICP and potentiometric titration by $AgNO_3$, by the Service of Microanalysis of CNRS (Vernaison).

2.4. Catalytic measurements

Before each experiment, the reduced catalyst was thermally treated in situ by flowing the H_2/He mixture up to the working temperature. The reactants were introduced after a He purge at the same temperature for 10 min.

Kinetic measurements were performed by us-

Table 1
Supports and catalyst precursors

Support			Catalyst		
Alumina (Rhône–Poulenc)	Type	BET surface area (m^2/g)	Ref.	Precursor	Pt (wt.-%)
SCM 129	$\gamma+\delta$	107	A	H_2PtCl_6	2.0
SCM 129 calcined (800°C/24 h)	$\theta+\alpha$	64	B	H_2PtCl_6	1.4
E 6135	γ	69	C	H_2PtCl_6	1.5
			D	$Pt(NH_3)_4(OH)_2$	1.6
			E	$Pt(NH_3)_4(OH)_2$	2.8
E 6135 chlorided	γ	69	F	$Pt(NH_3)_4(OH)_2$	2.9

ing an isothermal fixed bed reactor made of fused silica (internal diameter = 10 mm), heated by an electrical furnace. The reactant feed was made of methane and oxygen highly diluted in helium ($CH_4/O_2/He = 1/4/95$ mol-%, $Q_T =$ 6 l/h) to avoid thermal effects due to the exothermic reaction. The weight of the catalyst (200 to 290 mg) was adjusted in order to keep constant the platinum amount in the reactor: 20 or 30 μmol of Pt for samples A, B, C, D and E, F, respectively. The height of the catalytic bed was about 10 mm. Only water and carbon dioxide were observed as reaction products. The carbon dioxide produced by the reaction and the unconverted methane were separated on-line by gas chromatography and measured by a TCD system. The reaction rate relative to the total amount of platinum in the sample can be calculated from the methane conversion and from the platinum content; the turn-over frequency (TOF) is the ratio of the reaction rate to the number of surface platinum atoms, given by the dispersion measurements (see later).

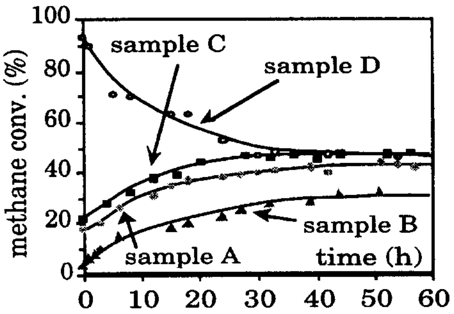

Fig. 1. Variation of the methane conversion with time on stream (samples A to D; reaction temperature = 450°C).

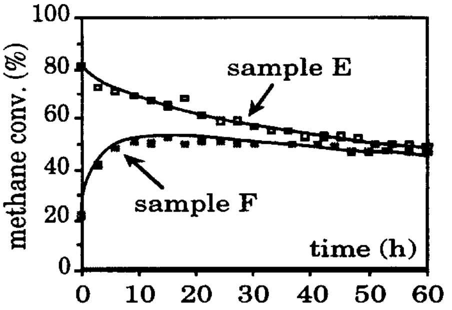

Fig. 2. Variation of the methane conversion with time on stream (samples E and F; reaction temperature = 450°C).

3. Results and discussion

Physicochemical characteristics of the reduced catalysts before the catalytic reaction are summarized in Table 2. The most significant observation concerns the important difference in the dispersions calculated from TEM and from H_2–O_2 titrations on the catalysts prepared from H_2PtCl_6, whereas no significant difference was observed for the catalysts prepared from $Pt(NH_3)_4(OH)_2$. The BET surface areas of the reduced catalysts remained identical to those of the supports. The $\theta + \alpha$-alumina (sample B) seemed to favour the platinum sintering during the reduction.

The catalytic behaviour of the reduced samples was first investigated in isothermal conditions at 450°C. A completely different be-

Table 2

Physicochemical characteristics of the reduced catalysts before the catalytic reaction and catalytic results after 5 min of reaction at 450°C

	Pt (wt.-%)	Cl (wt.-%)	Particle size from TEM (Å)	Pt dispersion (%)		TOF (s^{-1})	rate (mol/h g_{Pt})
				from TEM	from H_2–O_2		
A	2.0	0.8	15	ca. 100	50	0.014	0.12
B	1.4	0.4	47	33	8.5	0.017	0.03
C	1.5	0.3	10	ca. 100	72	0.012	0.15
D	1.6	0	16	ca. 100	95	0.039	0.62
E	2.8	0	15	ca. 100	92	0.025	0.37
F	2.9	0.1	25	61	47	0.012	0.10

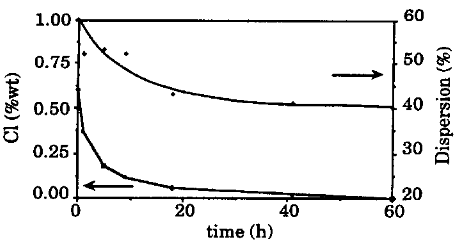

Fig. 3. Evolution of chlorine content and platinum dispersion (measured by chemisorption) with time under reactant feed (Pt (2%)/Al_2O_3, same synthesis as sample A, reaction temperature = 450°C).

haviour was observed between chlorine-containing and chlorine-free catalysts (Figs. 1 and 2). The catalytic reaction rate on chlorine-containing samples increased with time on stream (samples A, B, C and F); a small decrease was noted for sample F after 20 h. A plateau was reached after about 60 h on stream at 450°C. The opposite trend was observed for catalysts without chlorine (D and E), with a continuous decrease in the reaction rate. For both kinds of catalysts, the platinum particles size concomitantly increased with time on stream. Chemical analyses showed that chlorine was progressively eliminated during the catalytic reaction; after the plateau was reached, chlorine was no longer detected (Fig. 3). The dispersion values of the henceforth stable catalysts estimated from TEM and from H_2–O_2 titrations did not show significant differences any more (Table 3).

TOF were calculated at the beginning of the reaction and at the plateau (i.e., TOF of the reconstructed stable catalysts), assuming that the active platinum surface is the surface determined from H_2–O_2 titrations (Tables 2 and 3). All the samples exhibited an increase in the TOF which seemed to be more pronounced for the catalysts which contained chlorine (samples A, B, C and F). The highest values measured at the plateau were obtained for the samples showing the lowest dispersion, suggesting that the larger the particles, the higher the TOF. The reaction rates, relative to the total amount of platinum, did not show significant variations.

The behaviour of the catalysts was also investigated at 600°C. Methane was totally converted into CO_2, even at the beginning of the reaction for chlorine-containing catalysts. The dispersion and, for chlorine-containing catalysts, the amount of chlorine presented a similar but faster decrease with time on stream, the plateau being reached after only 20 h. The dispersions (measured by H_2–O_2 titrations) indicated a higher sintering of the platinum particles after 20 h of reaction at 600°C than after 60 h at 450°C. TOF measured at 450°C on the 600°C stabilized catalysts were twice to three times as high as on the 450°C stabilized catalysts. Reactions rates were higher on catalysts prepared from H_2PtCl_6 (Table 3).

Chlorine could act as a strong inhibitor of the catalytic oxidation of methane [13,14], either by blocking the chemisorption sites if present on the metallic particles [15,16] (which could explain the low metallic surface measured by titra-

Table 3
Physicochemical characteristics of catalysts stabilized at 450 and 600°C and catalytic results at 450°C

	Stabilized at 450°C					Stabilized at 600°C		
	particle size from TEM (Å)	dispersion from TEM (%)	dispersion from H_2–O_2 (%)	TOF (s^{-1})	rate (mol/h g_{Pt})	dispersion from H_2–O_2 (%)	TOF (s^{-1})	rate (mol/h g_{Pt})
A	40	35	36	0.047	0.28	12	0.13	0.26
B	53	29	23	0.054	0.21	10	0.15	0.25
C	36	43	40	0.046	0.31	12	0.13	0.26
D	33	46	42	0.044	0.31	14	0.08	0.19
E	36	42	28	0.048	0.22	6	0.15	0.15
F	40	37	19	0.066	0.21	6	0.18	0.18

tions before reaction) or by attracting the electrons of the metal particles via an inductive effect if present on the platinum or on the support [17]. During the reaction at 450°C, chlorine is slowly eliminated, leading to an increase in the TOF and reaction rates [5,6,18]; simultaneously, the sintering of the platinum particles tends to decrease the reaction rate by decreasing the accessible metallic surface. The two effects are clearly visible for sample F (Fig. 2): during the first 16 h of reaction at 450°C, the increase of the reaction rate due to the chlorine elimination appears to be predominant; the sintering effect (which decreases the reaction rate) begins to be visible for longer reaction time. On chlorine-free samples, only the sintering effect modifies the reaction rate, which decreases to a value close to that reached by chlorine-containing catalysts; the chlorine ions present in the precursor or on the support seem to have no measurable effect on the nature of the catalysts after stabilisation by the methane oxidation reaction at 450°C [19].

For the catalysts stabilized by the reaction at 600°C, the situation is quite similar and confirms the tendency observed with the catalysts stabilized at 450°C: the TOF increases with the particle size [7]. The reaction rates, relative to the weight of platinum, show that the catalysts with the best performances are prepared from the chlorine-containing precursor. The nature of the alumina support seems to play only a minor role.

4. Conclusion

A strong inhibitor effect of chlorine ions on the activity of Pt/Al_2O_3 catalysts toward methane oxidation is observed during the first hours of reaction, whatever the origin of chlorine (from platinum precursor H_2PtCl_6 or from a previously chlorided alumina). The reaction rate increases gradually as chlorine is eliminated. Simultaneously, a sintering of the platinum particles with time on stream occurs, the particle size depending on the reaction temperature. It is observed that the catalysts stabilized by the reaction at 450°C do not present significant differences in their catalytic behaviour, whereas among the catalysts stabilized by the reaction at 600°C, the samples prepared from H_2PtCl_6 exhibit the highest reaction rate.

Acknowledgements

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