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Propane and propene oxidation over platinum and palladium on alumina: Effects of chloride and water

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Abstract

The oxidation of propane and propene was investigated on palladium and platinum supported catalysts. Catalyst intrinsic activities, evaluated by light-off temperatures in slightly oxidizing reactant mixture (5% excess oxygen), show an optimum particle size which maximizes the catalytic activity for a given metal loading. On catalysts prepared from chloride containing precursor salts, chloride poisons the metallic activity whatever the particle size. Moreover, reaction isotherms under varying oxygen levels point out that the effect of chloride is more detrimental under oxidizing conditions. After successive oxidation cycles, this poisoning effect disappears as a consequence of the removal of chloride from the catalyst surface by water produced during propane and propene combustion. On the other hand, addition of relatively large quantities of water (equivalent to the content of the exhaust gas) inhibits the oxidation of hydrocarbon. Poisoning effects of chloride and water are explained by a decreasing active surface for the reactions under consideration.

Key words: chloride poisoning, exhaust catalysts, palladium, platinum, poisoning, propane oxidation, propene oxidation, water

1. Introduction

Catalytic combustion is the process used for removal of hydrocarbons from automobile gas exhaust. Catalytic converters contain the noble metals platinum, palladium or rhodium as active components which are deposited on alumina modified by additives like ceria. Because of the high cost and limited availability of these metals, it is important to use as

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low a noble metal concentration in these catalysts as feasible. This can be accomplished by keeping the active metals at a high degree of dispersion. However, kinetic studies have shown that larger crystallites catalyze the oxidation of hydrocarbons more effectively [1–8]. Moreover, some papers on methane oxidation reported that chloride containing metallic salts produce catalysts inferior in performance to others made without chloride [5,9–11].

The objectives of this work are (i) to determine the effect of metallic dispersion on the intrinsic catalytic activity of platinum and palladium for propene and propane oxidations, (ii) to examine the effects of chloride from the precursor salts on the activity of catalysts with different particle sizes, and (iii) to study the effects of water on the oxidation properties of supported palladium and platinum.

2. Experimental

2.1 Catalyst preparation

Catalysts were prepared by impregnation using chloroplatinic acid (H_2PtCl_6), dinitrodiammine platinum ($\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$), bis-(acetylacetonato) palladium ($\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$) and palladium chloride (PdCl_2) precursors. The support used was $\gamma\text{-Al}_2\text{O}_3$ with a BET area of $100\text{ m}^2/\text{g}$.

The different catalysts were dried at 120°C overnight, calcined in air for 4 h at either 300°C (Pd) or 450°C (Pt) and reduced in pure hydrogen for 4 h at 500°C . Then, the different samples were calcined under dry or wet oxidizing atmosphere (1% O_2 in nitrogen) at increasing temperatures in order to decrease metallic accessibility. After sintering, catalysts were reduced again at 500°C under hydrogen.

2.2 Surface area measurements

The metal dispersion was determined by volumetric chemisorption in a conventional glass system equipped with a turbomolecular pump. The system is capable of a dynamic vacuum typically below 10^{-4} Pa . Prerduced samples were reduced again at 500°C , then outgassed at this temperature and cooled to room temperature. Metal accessibilities were obtained by the hydrogen–oxygen titration method at 25°C for platinum [12] and hydrogen chemisorption at 70°C for palladium [13].

2.3 Hydrocarbon oxidation activity measurements

Hydrocarbon oxidation was studied with a flow reactor system equipped with a flame ionization detector (FID). The reactant mixture was composed of 0.2% propene and 0.2% propane in nitrogen with 2% oxygen (5% excess oxygen). In the course of oxidation under wet atmosphere, injection of water (10%) was done using a calibrated motor-driven syringe. The gas flow-rate was set at ca. $15\,000\text{ ml/h}$. The catalyst weight was typically 50 mg diluted in 250 mg $\alpha\text{-Al}_2\text{O}_3$. Catalysts were evaluated by studying their light-off behaviour with a constant flow-rate of the gas mixture from 100°C to 500°C at a heating rate of 3° min^{-1} .

The influence of oxygen concentration on propane oxidation was determined in reaction isotherms and oxygen levels varying from rich to lean mixtures

3. Results

The characteristics of the different catalysts are summarized in Table 1. The values of metallic dispersion show that platinum/alumina and palladium/alumina sinter with increasing calcination temperature.

3.1 Catalytic activity — effect of chloride

Catalysts were evaluated by their light-off temperature in temperature-programmed experiments.

The effect of chloride on platinum/alumina catalysts is shown in Figs. 1 and 2 where light-off temperatures for propane and propene oxidations are plotted versus the metallic dispersion. The results point out that catalysts prepared using a chloroplatinic precursor are less active than catalysts from a dinitrodiammine precursor whatever the metallic particle

Table 1
Characteristics of the different catalysts (*W = 1% O₂/N₂, 10% H₂O)

Catalyst	Precursor salt	Pt (wt -%)	Pd (wt -%)	Cl (wt -%)	Sintering 1% O ₂ /N ₂	D (%)
A ₁	H ₂ PtCl ₆	1.0	—	0.47	—	56
A ₂	H ₂ PtCl ₆	1.0	—	0.47	5 h, 525°C	30
A ₃	H ₂ PtCl ₆	1.0	—	0.46	10 h, 525°C	20
A ₄	H ₂ PtCl ₆	1.0	—	0.47	10 h, 600°C	10
A ₅	H ₂ PtCl ₆	1.0	—	0.39	10 h, 800°C	4
A ₆	Pt(NH ₃) ₂ (NO ₂) ₂	1.0	—	—	—	40
A ₇	Pt(NH ₃) ₂ (NO ₂) ₂	1.0	—	—	1 h, 550°C	28
A ₈	Pt(NH ₃) ₂ (NO ₂) ₂	1.0	—	—	1 h, 600°C	17
A ₉	Pt(NH ₃) ₂ (NO ₂) ₂	1.0	—	—	1 h, 800°C	4
B ₁	Pd(C ₅ H ₇ O ₂) ₂	—	1.0	—	—	88
B ₂	Pd(C ₅ H ₇ O ₂) ₂	—	1.0	—	—	75
B ₃	Pd(C ₅ H ₇ O ₂) ₂	—	1.0	—	—	64
B ₄	Pd(C ₅ H ₇ O ₂) ₂	—	1.0	—	10 h, 640°C	36
B ₅	Pd(C ₅ H ₇ O ₂) ₂	—	1.0	—	10 h, 730°C	28
B ₆	Pd(C ₅ H ₇ O ₂) ₂	—	1.0	—	*w-10 h, 600°C	16
B ₇	Pd(C ₅ H ₇ O ₂) ₂	—	1.0	—	*w-10 h, 700°C	12
B ₈	Pd(C ₅ H ₇ O ₂) ₂	—	1.0	—	10 h, 800°C	9
B ₉	Pd(C ₅ H ₇ O ₂) ₂	—	1.0	—	*w-10 h, 800°C	7
B ₁₀	Pd(C ₅ H ₇ O ₂) ₂	—	1.0	—	10 h, 900°C	2
B ₁₁	Pd(C ₅ H ₇ O ₂) ₂	—	1.0	—	*w-10 h, 900°C	<2
B ₁₂	PdCl ₂	—	1.0	0.50	—	92
B ₁₃	PdCl ₂	—	1.0	0.45	10 h, 500°C	68
B ₁₄	PdCl ₂	—	1.0	0.44	10 h, 600°C	52

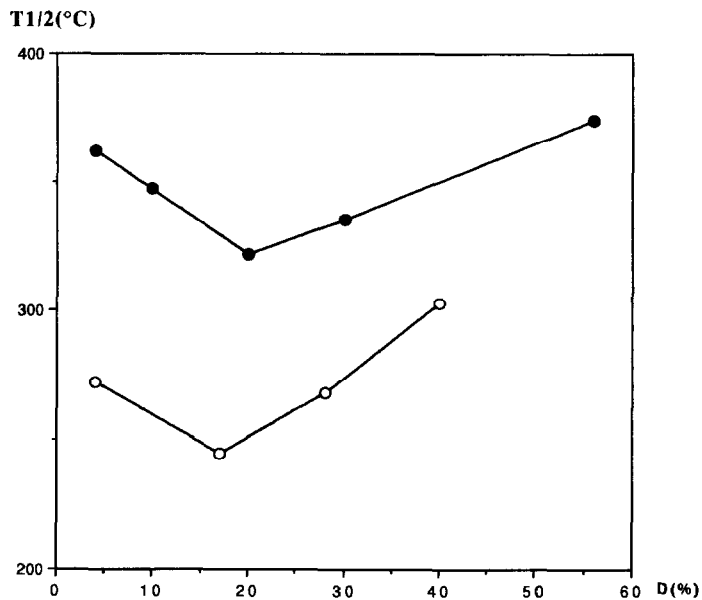


Fig. 1. Light-off temperatures for propane oxidation versus the metallic dispersion of Pt/Al₂O₃ catalysts prepared using H₂PtCl₆ (●) or Pt(NO₂)₂(NH₃)₂ (○).

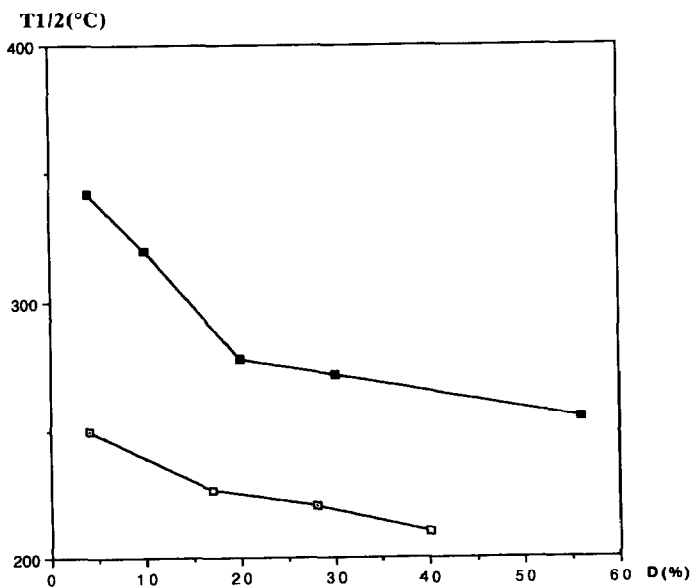


Fig. 2. Light-off temperatures for propene oxidation versus the metallic dispersion of Pt/Al₂O₃ catalysts prepared using H₂PtCl₆ (■) or Pt(NO₂)₂(NH₃)₂ (□).

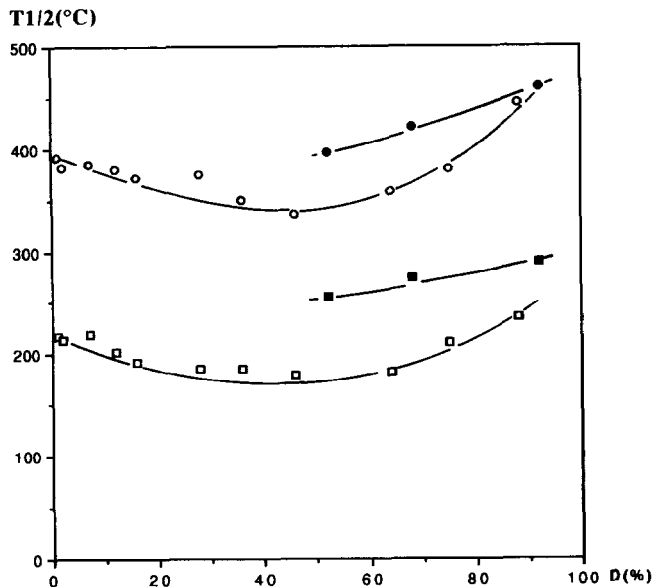


Fig 3 Light-off temperatures for propene (■, □) and propane (●, ○) oxidations versus the metallic dispersion of Pd/Al₂O₃ catalysts prepared using PdCl₂ (●, ■) or Pd(C₄H₇O₂)₂ (○ □)

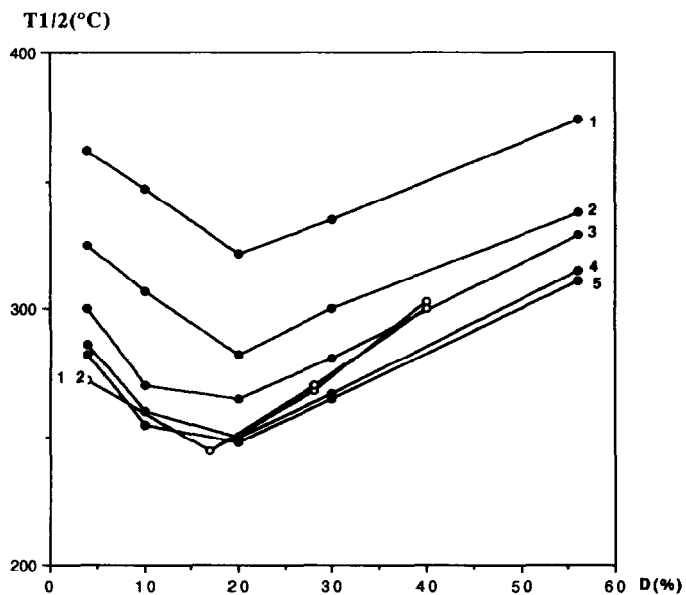


Fig 4 Effect of successive oxidation cycles on the light-off temperatures of Pt/Al₂O₃ catalysts for propane oxidation 1–5 number of oxidation cycles, (●) H₂PtCl₆ as precursor salt, (○) Pt(NO₂)₂(NH₃)₂ as precursor salt

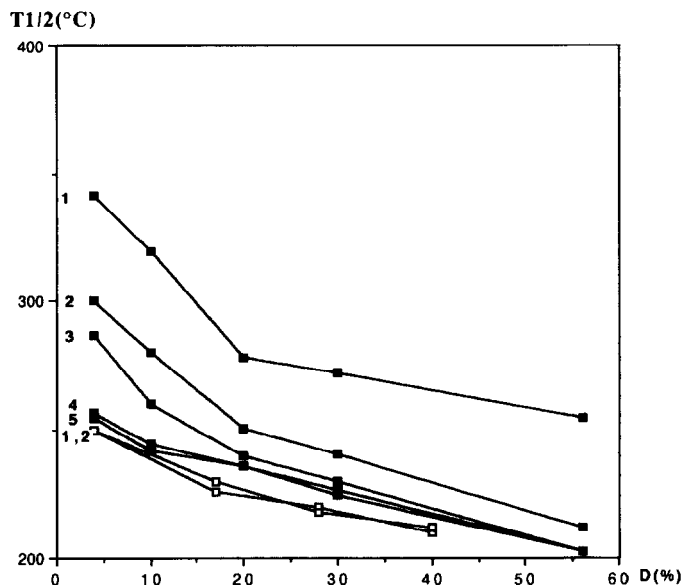


Fig. 5. Effect of successive oxidation cycles on the light-off temperatures of Pt/Al₂O₃ catalysts for propene oxidation: 1–5, number of oxidation cycles; (■) H₂PtCl₆ as precursor salt, (□) Pt(NO₂)₂(NH₃)₂ as precursor salt.

size. In addition, a maximum in catalytic activity for propane oxidation appears for a metallic dispersion near 20%, whereas well dispersed catalysts are the most active for propene oxidation (Fig. 2).

The detrimental effect of chloride is also evident in Fig. 3 for hydrocarbon oxidation on palladium/alumina catalysts. Moreover, catalysts with a medium accessibility show a higher activity for propane and propene oxidation.

The different platinum catalysts were submitted to successive oxidation cycles between room temperature and 500°C. Figs. 4 and 5 show that light-off temperatures of chloride-containing platinum samples decrease to constant values while no beneficial effect is observed on catalysts prepared from dinitrodiammine precursor. Thus, after successive oxidation cycles, the activity of the catalysts is comparable whatever the metallic precursor salt and it depends only on the crystallite size.

Table 2

Analysis of chloride content after successive oxidation cycles from room temperature to 500°C

Catalyst	Chloride content (initial)	Chloride content (final)
A ₁	0.47	0.13
A ₂	0.47	0.11
A ₃	0.46	0.12
A ₄	0.47	0.11
A ₅	0.39	0.11

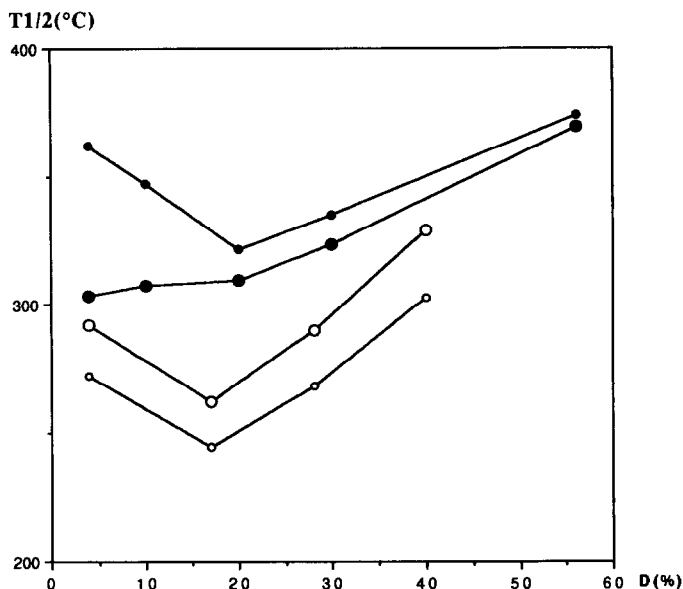


Fig 6 Effect of water (10% in gas mixture) on the light-off temperatures of Pt/Al₂O₃ catalysts for propane oxidation (●, ●) H₂PtCl₆ as precursor salt (○, ○) Pt(NO₂)₂(NH₃)₂ as precursor salt, (●, ○) without water, (●, ○) 10% water

After several cycles of oxidation, analysis of catalysts prepared using chloride containing precursor salts indicated a loss of chloride (Table 2)

3.2 Effect of water on catalytic activity

The effect of water (10% in gas mixture) on platinum activity is demonstrated in Figs 6 and 7. On chloride containing samples water has a beneficial effect both on propane and propene oxidations. On the other hand, on catalysts prepared using non-chlorinated precursor salts, water inhibits the metallic activity for propane oxidation while propene oxidation is little affected. On palladium catalysts prepared using acetylacetonate precursor, water has a detrimental effect for the oxidation of both hydrocarbons (Fig 8).

3.3 Influence of the oxygen/propane ratio

The influence of oxygen concentration on propane oxidation, measured in reaction isotherms, is illustrated by the results shown in Figs 9 and 10. On chloride containing samples, an abrupt decrease in conversion occurs when conditions are changed from reducing or stoichiometric to oxidizing, while propane oxidation over non-chlorinated catalysts is less affected by the gas composition in the given range. Moreover, under oxidizing conditions, platinum activity decreases with increasing oxygen concentration, whereas the opposite effect is observed on palladium catalyst.

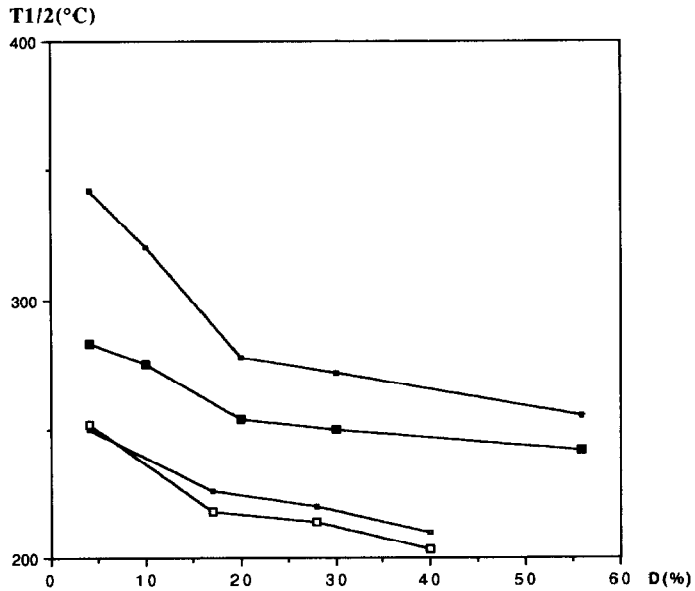


Fig 7 Effect of water (10% in gas mixture) on the light-off temperatures of Pt/Al₂O₃ catalysts for propene oxidation (■, ■) H₂PtCl₆ as precursor salt, (□, □) Pt(NO₂)₂(NH₃)₂ as precursor salt, (■, □) without water, (■, □) 10% water

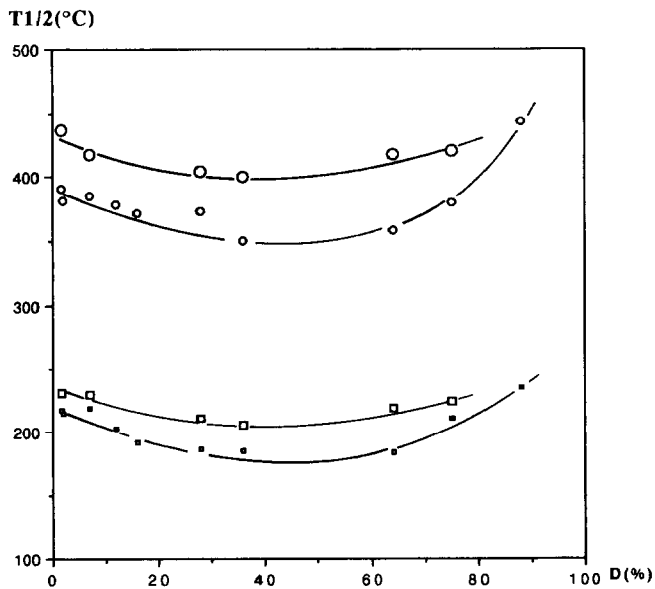


Fig 8 Effect of water (10% in gas mixture) on the light-off temperatures of Pd/Al₂O₃ catalysts (Pd(C₅H₇O₂)₂) for propene (□ □) and propane (○ ○) oxidations (○, □) without water, (○, □) 10% water

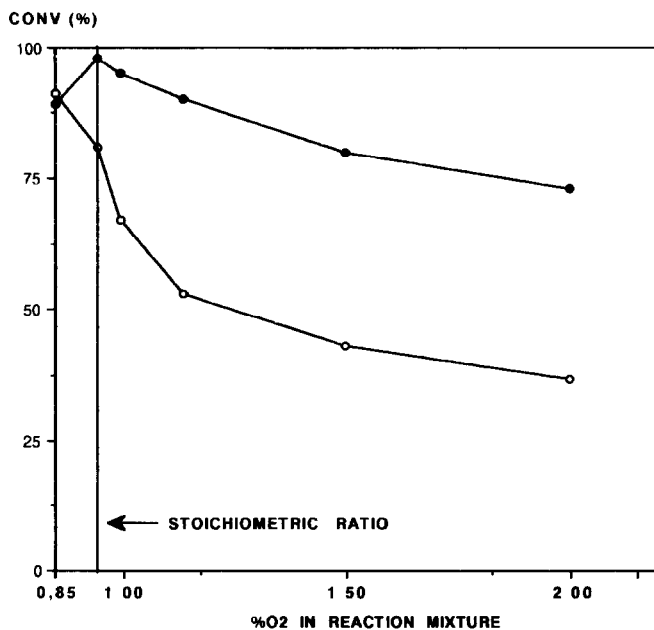


Fig 9 Effect of oxygen pressure in the reaction mixture for propane oxidation on Pt/Al₂O₃ catalysts at 352°C (●) and 367°C (○) Propane concentration in the feed gas = 0.19% (●) Pt(NO₂)₂(NH₃)₂ as precursor salt, (○) H₂PtCl₆ as precursor salt

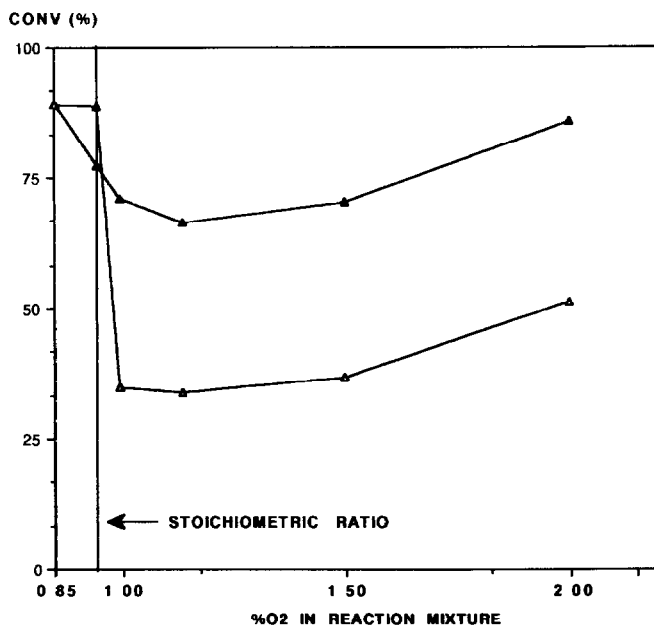


Fig 10 Effect of oxygen pressure in the reaction mixture for propane oxidation on Pd/Al₂O₃ catalysts at 379°C (▲) and 441°C (△) Propane concentration in the feed gas = 0.19% (▲) Pd(C₂H₇O₂)₂ as precursor salt (△) PdCl₂ as precursor salt

4. Discussion

Light-off temperatures of propene and propane oxidation in 5% excess oxygen were determined over a series of platinum and palladium catalysts. The results show an optimum particle size which maximizes the catalytic activity of a given amount of platinum or palladium. For propane oxidation this optimum corresponds to a metallic dispersion near 20% on platinum and 50% on palladium, respectively. With regard to propene oxidation the same optimum appears on palladium, while the well dispersed platinum catalysts show the lowest light-off temperatures. These results are in accordance with previous work on oxidation of hydrocarbons [1–8], and were generally explained by the competitive adsorption of hydrocarbons and oxygen on the same metal sites and by differences in the reactivity of the adsorbed oxygen on the metal surfaces. Moreover, the oxidation of saturated hydrocarbons was described by a rate limiting step which involves a surface reaction of an alkane–oxygen complex, the concentration of which increases rapidly with particle size. On the other hand, in the case of propene oxidation, the double-bond breaking would be rate controlling [2].

Supported palladium and platinum, prepared using chlorinated precursor salts, endure an increase in their light-off temperature with respect to hydrocarbon oxidation, whatever their particle sizes (Figs 1–3). This loss of activity can be explained by the chemical interaction of the halogen with the catalyst surface. Indeed, a similar interpretation was suggested for the inhibition of methane oxidation by halogenated hydrocarbons which was associated with a deficiency of oxygen at the catalyst surface. In that case, the halogen would be adsorbed on the sites normally needed for the adsorption and activation of oxygen [9]. Another explanation is the formation of platinum or palladium oxide–chloride species which are more stable and consequently less reactive than oxygen species [14–16]. These two effects of chloride poisoning were demonstrated by Hicks et al. [5] with a reduced oxygen adsorption capacity and a reduced reactivity of the adsorbed oxygen with methane. Simone et al. [11] proposed a similar explanation with (i) blocking of metal oxide sites by chloride, thereby decreasing the accessibility of the reactant gas to the catalytic site and/or (ii) chemical interaction of chloride with the catalytically active metal oxide species, resulting in metal oxide–chloride complexes which are less active.

In the present work, propane oxidation under different oxygen/propane ratios has shown that the effect of chloride is more detrimental under oxidizing conditions (Figs 9 and 10). Thus, we can believe that the excess of oxygen interacts with chloride, leading to stable and inactive oxide–chloride species which poison the metallic surface for hydrocarbon oxidation. However, when the oxygen concentration increases under oxidizing atmosphere, the activity of palladium increases while that of platinum decreases (Figs 9 and 10). These results are in accordance with the positive order and the negative order with respect to oxygen determined by Yao for propane oxidation on palladium and platinum, respectively [1].

When chloride containing platinum samples are submitted to successive oxidation cycles between room temperature and 500°C, their light-off temperatures decrease to constant values comparable to that obtained on catalysts prepared using non-chlorinated precursor salts. This increase in catalytic activity cannot be explained by a modification of the metal particle sizes since the same effect is observed whatever the initial catalyst dispersion. On

the other hand, removal of chloride from the catalyst surface by water formed during the total oxidation of hydrocarbon would be responsible for this promoting effect. Indeed, previous work has shown that water vapour accelerates the loss of chloride from the catalyst surface [17–20], the water content of the atmosphere and the temperature being the main factors controlling the rate of loss of chloride.

Moreover, some papers reported that water can dissociate on platinum or palladium [21–24], leading to H and OH species, the recombination of which is very fast when only water is present. On the other hand, on chloride containing samples H species can recombine also with chloride interacting with the metal surface which induces the elimination of hydrochloric acid and therefore the regeneration of the active sites for hydrocarbon oxidation.

The beneficial effect of water on the activity of chloride containing samples for propene and propane oxidations was borne out by adding water to the gas mixture (10%, equivalent to the content of the exhaust gas) while a detrimental effect appears on non-chlorinated catalysts (Figs 6–8). This last result is in accordance with the work of Cullis and Willat [9] which points out that addition of relatively large quantities of water inhibits the oxidation of methane, the degree of inhibition increasing with the water content of the reactant. In the case of palladium catalysts, Cullis et al [25] and Cullis and Nevell [26] concluded that water decreases the catalytic activity as a result of the conversion of palladium(II) oxide to the corresponding hydroxide. Thus, the inhibition of the catalyst activity can be explained by the adsorption of water on metal sites and therefore by a decreasing surface active for the catalytic combustion of hydrocarbons.

5. Conclusion

From the above results, concerning the oxidation of propene and propane on palladium and platinum supported catalysts, the following conclusions can be put forward:

- Light-off temperatures show an optimum particle size which maximizes the catalytic activity of a given amount of platinum or palladium.
- On catalysts prepared using chloride containing precursor salts, chloride poisons the metallic activity whatever the particle size, this effect, which is more detrimental under oxidizing conditions, can be explained by the formation of stable oxide–chloride species.
- Removal of chloride from the catalyst surface by water produced during the total combustion of hydrocarbons would be responsible for the increase in activity after successive oxidation cycles. However, addition of relatively large quantities of water (equivalent to the content of the exhaust gas) inhibits the oxidation of hydrocarbons.

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