Catalysis Letters 14 (1992) 51–56

Accelerated sintering of PtRh/Al_2O_3 catalysts in an oxygen periodic pulse flow

R. Taha and D. Duprez *

Laboratoire de Catalyse en Chimie Organique, 40, Av. Recteur Pineau, 86022 Poitiers Cedex, France

Received 27 February 1992; accepted 1 April 1992

PtRh catalysts were prepared by coimpregnation, with chlorine-free precursors of a γ-alumina. They were sintered at 973 K under a continuous flow of O_2 (1% in Ar or air) or of a flow of Ar into which pulses of O_2 were injected periodically. Under the latter conditions the sintering was significantly accelerated, particularly for a certain value of the period of O_2 pulses.

Keywords: Platinum-rhodium catalysts; accelerated sintering of PtRh bimetallics; sintered metal catalysts, characterization of

1. Introduction

Recently, Murakami et al. proposed a method, a periodic pulse reaction technique, to accelerate sintering of Pt/Al_2O_3 catalysts under reaction conditions for the rapid estimation of catalyst life in C_2H_4 oxidation [1]. With this technique, C_2H_4 and O_2 were fed alternately and repeatedly (period: 20–60 s) over the catalyst at 588 K: under these conditions, platinum sintering was shown to be significantly more rapid than the sintering observed during the continuous flow reaction $C_2H_4 + O_2$. Similar results were obtained with Cu and Ag catalysts [2,3]. Studying the conversion of exhaust gas under laboratory conditions, Onal showed that PtRh/CeO_2-Al_2O_3 catalysts sintered more rapidly in a net oxidizing gas mixture than in a net reducing one [4]. However, under conditions of oscillating concentration (net oxidizing/net reducing, 0.25 Hz), there was apparently no accelerated sintering. It seems thus that this phenomenon is not systematically observed: sintering rates depend probably on the nature of the catalyst, on the chemical composition of the gaseous atmosphere, on the amplitude and period of pulses ... We report here the results obtained under conditions of oscillating concentration (pulses of O_2 in Ar at 973 K) for

---

* To whom correspondence should be addressed.

Table 1
Composition of the catalysts

Catalyst	PtRh 0 (Pt/Al_2O_3)	PtRh 9	PtRh 22	PtRh 35	PtRh 60	PtRh 100 (Rh/Al_2O_3)
wt% Pt	1.17	1.01	0.75	0.70	0.45	0
wt% Rh	0	0.05	0.11	0.20	0.36	0.51
Pt + Rh (μmol atg^{-1})	60.0	56.6	49.1	55.3	58.1	49.5

the sintering of catalysts readily characterized by chemisorption and titration techniques ($PtRh/Al_2O_3$ catalysts).

2. Experimental

2.1. CATALYSTS

A series of $PtRh/Al_2O_3$ was prepared by successive impregnation with aqueous solutions of dinitrodiammine platinum(II) and of rhodium(III) nitrate. The carrier was a γ-alumina (120 m^2 g^{-1}, main impurities $Na_2O + CaO$, 2000 ppm, SiO_2, 400 ppm and Fe_2O_3, 300 ppm) provided by IFP (French Institute of Petroleum). The support was crushed, sieved to 0.1–0.2 mm and calcined in air at 850°C before impregnation by the metallic salts. After impregnation the catalysts were dried at 393 K and calcined in air at 723 K for 4 h (fresh catalysts). They are referred to as PtRh X, where X is the atomic percentage of rhodium: %(Rh/Pt + Rh) (table 1).

2.2. SINTERING CONDITIONS

Different samples of each catalyst (0.5 g) were sintered for 2 h at 973 K under various conditions (table 2). In each case, except for mode F (sintering in air), argon was the carrier gas (Air Liquide 99.9999%, 30 cm^3 mn^{-1}).

Table 2
Sintering conditions (2 h, 973 K)

Conditions	Gas composition (0.28 cm^3 per pulse)
A	continuous flow: pure Ar
B	pulses of O_2 in Ar; period: 120 s; equivalent conc.: 0.5% vol% O_2
C	pulses of O_2 in Ar; period: 60 s; equivalent conc.: 1% vol% O_2
D	pulses of O_2 in Ar; period: 30 s; equivalent conc.: 2% vol% O_2
E	continuous flow: 1% O_2/Ar
F	continuous flow: air

2.3. DISPERSION MEASUREMENTS

The catalysts were characterized in situ: after sintering, they were reduced in H_2 at 773 K for 16 h, degassed in Ar at the same temperature for 3 h and cooled down to room temperature. Hydrogen chemisorption H_C, oxygen titration O_T and hydrogen titration H_T were successively carried out by injecting pulses of H_2 or pulses of O_2 till saturation. Details concerning the procedure and the method for calculating the amount of each gas chemisorbed or titrated are given elsewhere [5]. For Pt, the stoichiometries $H_C:O_T:H_T$ are taken equal to 1:1.5:3 per accessible atom. Pt catalysts, however, can give abnormally high values for H_C [6–8]. Therefore, dispersions (D (%)) were calculated preferably from O_T and H_T and the metal areas (m^2 Pt per gram of catalyst) were deduced from the atomic surface concentration in polycrystalline Pt: 1.25×10^{19} atoms per m^2. For Rh, the stoichiometries 1:2:4 for $H_C:O_T:H_T$ have been observed generally [5,9]. The metal areas were calculated on the basis of 1.33×10^{19} atoms per m^2 Rh. In bimetallics the metal areas (Pt area + Rh area) were estimated as if there was no surface enrichment in the catalyst. Even though this is probably not the case in sintered samples [10–12], this assumption produces only insignificant errors owing to the close resemblance of the two metals.

3. Results and discussion

Dispersion measurements carried out on fresh and sintered catalysts are listed in table 3 for three samples: the two monometallics and the bimetallic PtRh 35. Under transient conditions, a maximum of the sintering rate R_S is systematically observed for mode C (1 pulse per minute). Moreover, for an average concentration of 1% O_2, R_S is always greater under transient conditions (mode C) than under continuous flow conditions (mode E). The decrease of the metal area is particularly marked for rhodium-containing catalysts for which sintering via mode C (pulse, 1% O_2) is still more severe than via mode F (continuous flow, 20% O_2). Increasing or decreasing the pulse period entails a better resistance to sintering. The maximum of R_S observed for a period of 60 s is certainly related to the shape characteristics of the oxygen pulse (fig. 1). Mode C corresponds to oscillations for which the partial pressure of O_2 returns to zero for a minimum of time. In mode D, the period is short: there is a partial overlapping of the O_2 pulses so that the catalyst remains always in an oxidizing atmosphere. In mode B, on the contrary, the period is long and there is alternance of short lapses of time in O_2 with long ones in Ar.

Comparison between sintering via mode C (O_2 pulses equivalent to 1% O_2) with that via mode E (1% O_2 continuous flow) was made over the whole series of catalysts. The results (fig. 2) show that sintering under oscillating conditions is

Table 3
Sintering at 973 K of Pt, Rh and PtRh/Al_2O_3 catalysts. See table 2 for the sintering conditions

Catalyst	Sintering	H_C [a]	O_T [a]	H_T [a]	D (%)	Metal area ($m^2\ g^{-1}$)
PtRh 0	fresh	34	51	98	57	1.64
(Pt/Al_2O_3)	A	15	16	33	18	0.51
	B	11.3	11.6	23	13	0.37
	C	7.5	10.5	20	12	0.34
	D	10.0	15.6	29	17	0.50
	E	12.0	12.0	23	13	0.38
	F	7.0	9.0	16	10	0.30
PtRh 35	fresh	41	74	132	80	1.81
	A	14	28	62	30	0.77
	B	16	24	44	26	0.60
	C	14	20	42	22	0.57
	D	15	32	61	34	0.88
	E	25	48	97	52	1.35
	F	20	24	54	26	0.61
PtRh 100	fresh	43	86	179	87	1.94
(Rh/Al_2O_3)	A	22	45	92	46	1.04
	B	22	52	111	52	1.18
	C	18	40	87	41	0.91
	D	22	48	96	48	1.08
	E	23	53	113	54	1.21
	F	22	48	105	48	1.07

[a] In μmol atg^{-1}.

systematically more severe than under a continuous flow of O_2/Ar. It can be seen from fig. 2 that rhodium-rich catalysts are relatively more sensitive to O_2 oscillations than platinum-rich ones. The transition between the two behaviours is well marked for about $X = 30$ at% Rh. Recently, Kacimi and Duprez [12] showed that sintering of PtRh/Al_2O_3 catalysts in O_2 pulses led to significant changes in the surface composition of the bimetallics: for $X > X^*$, the surface was strongly enriched in rhodium while for $X < X^*$, the opposite was obtained. At 973 K, the inversion of the surface composition occurred for $X^* = 25\%$, a value very close to the one found in fig. 2 for the change in the sensitivity to oxygen oscillations. It seems thus that this sensitivity is essentially governed by the surface composition of bimetallics.

4. Conclusion

An acceleration of the sintering of PtRh/Al_2O_3 in O_2 atmospheres can be observed when the catalysts are treated under oscillating conditions. There

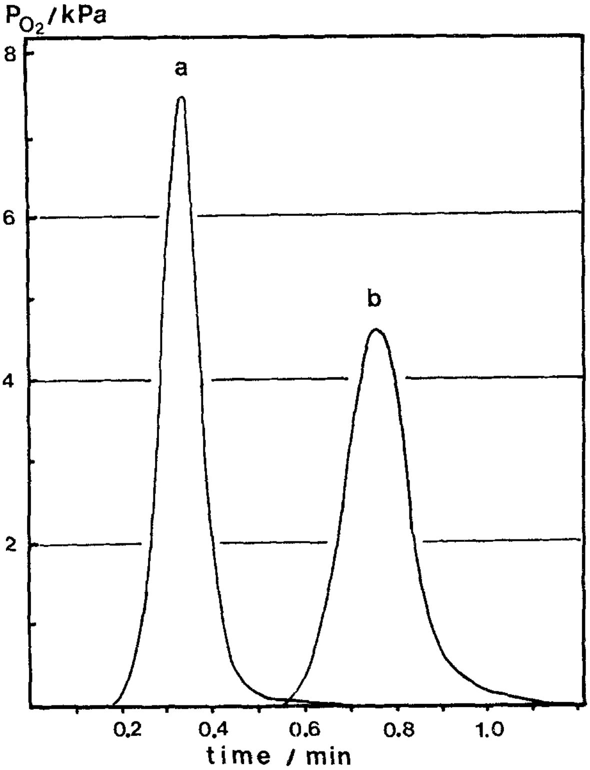

Fig. 1. Shapes of O_2 pulses just before (a) and just behind (b) the catalyst bed.

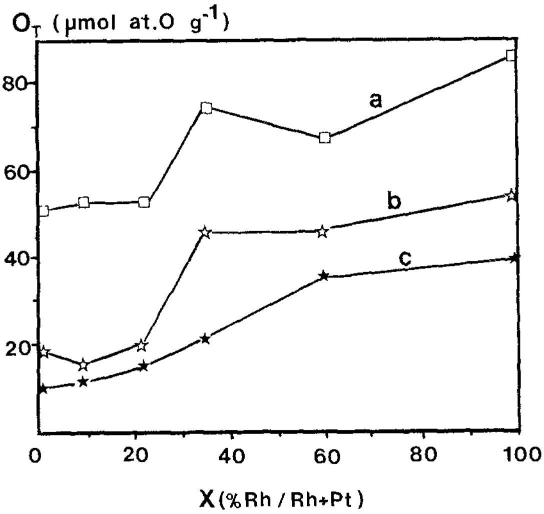

Fig. 2. Oxygen titration of chemisorbed hydrogen on the $PtRh/Al_2O_3$ catalyst. (a) Fresh samples, (b) catalysts sintered at 973 K for 2 h under a continuous flow of 1% O_2 in Ar (mode E), (c) catalysts sintered at 973 K for 2 h under a pulsed flow of O_2 in Ar (mode C, average concentration: 1% O_2).

exists an optimum for the period of the O_2 pulses leading to a maximum for the rate of sintering. Rhodium-rich catalysts are more sensitive than platinum-rich ones to O_2 oscillations.

Acknowledgement

This work was carried out within the Groupement Scientifique Catalyseurs de Postcombustion funded by the Centre National de la Recherche Scientifique, the Institut Français du Pétrole and the AFME (French Agency for Energy Savings).

References

[1] Y. Murakami, S. Komai and T. Hattori, in: *Catalyst Deactivation 1991*, Stud. Surf. Sci. Catal., Vol. 68, eds. C.H. Bartholomew and J.B. Butt (Elsevier, Amsterdam, 1991) p. 645.

[2] S. Komai, T. Hattori, A. Miyamoto and Y. Murakami, Chem. Lett. (1983) 1749.

[3] T. Hattori, S. Komai, T. Hanaichi, A. Miyamoto and Y. Murakami, in: *Catalyst Deactivation 1987*, Stud. Surf. Sci. Catal., Vol. 34, eds. B. Delmon and G.F. Froment (Elsevier, Amsterdam, 1987) p. 415.

[4] I. Onal, in: *Catalyst Deactivation 1991*, Stud. Surf. Sci. Catal., Vol. 68, eds. C.H. Bartholomew and J.B. Butt (Elsevier, Amsterdam, 1991) p. 621.

[5] D. Duprez, J. Chim. Phys. 80 (1983) 487.

[6] J. Prasad, K.R. Murthy and P.G. Menon, J. Catal. 52 (1978) 515.

[7] R. Bacaud, G. Blanchard, H. Charcosset and L. Tournayan, React. Kin. Catal. Lett. 12 (1979) 357.

[8] M. Kobayashi, Y. Inoue, N. Takahashi, R.L. Burwell, J.B. Butt and J.B. Cohen, J. Catal. 64 (1980) 74.

[9] T. Paryjczak, W.K. Jozwiak and J. Goralski, J. Chromatog. 166 (1978) 65, 75.

[10] W.B. Williamson, H.S. Gandhi, P. Wynblatt, T.J. Truex and R.C. Ku, Aiche Symp. Ser. No. 201, 76 (1980) 212.

[11] T. Wang and L.D. Schmidt, J. Catal. 71 (1981) 411.

[12] S. Kacimi and D. Duprez, in: *Proc. 2nd Int. Symp. Catalysis and Automotive Pollution Control, CaPoC 2*, Stud. Surf. Sci. Catal., Vol. 71, ed. A. Crucq (Elsevier, Amsterdam, 1991) p. 581.