ELSEVIER

Thermochimica Acta, 242 (1994) 265–269

thermochimica
acta

Note

A study of silica-supported platinum catalysts by temperature programmed reduction

M. Afzal *, F. Mahmood

Department of Chemistry, Quaid-I-Azam University, Islamabad, Pakistan

(Received 26 October 1993; accepted 27 February 1994)

Abstract

Temperature programmed reduction (TPR) has been used to study the reduction pattern of silica-supported platinum catalysts. It is observed that Aerosil impregnated with H_2PtCl_6 gives one reduction peak with T_{max} equal to 436°C, whereas Aerosil impregnated with $[Pt(NH_3)_4](OH)_2$ gives two distinct peaks in the regions of 207 and 399°C; the integrated peak area is not affected by variation in the heating rate. TPR profiles show that in each case, the reduction peak was immediately followed by a small but clear hydrogen desorption trough with a minimum always around 580°C. This indicates that there is evidently an overlap between the process of reduction (including hydrogen chemisorption) and hydrogen desorption. After correction for the overlap between hydrogen uptake and desorption, the hydrogen consumed in the reduction was calculated and interpreted.

Keywords: Catalyst; Chemisorption; Desorption; Hydrogen; Platinum; Reduction; TPR

1. Introduction

The reduction processes of supported metals are currently receiving considerable attention due to their widespread industrial importance as catalysts [1–3]. The TPR technique has been extensively applied to study the reducibility of supported metals

---

* Corresponding author.

SSDI 0040-6031(94)01781-B

under different conditions [4–6]. In TPR, the reduction of the supported and unsupported metal oxides is carried out by flowing hydrogen mixed with some other inert gas such as argon, nitrogen or helium. The technique makes use of the high thermal conductivity of hydrogen. The choice of the inert gas is usually made by considering its reactivity and thermal conductivity. The thermal conductivity of this gas should be quite different from that of hydrogen. The thermal conductivity of helium is not very different from hydrogen and nitrogen can be reactive during the reduction process, especially in iron catalysts. Therefore, argon is the best choice and a reducing gas mixture of 6% hydrogen in argon is usually used. The reducing gas mixture is allowed to pass through the reactor containing the solid catalyst to reduce the metal ions into metallic atoms. The sample is heated at a predetermined rate. After reducing the catalyst, the effluent gas is passed through a cold trap (195 K acetone + dry ice), to purify the gas by condensing the reduction products, and is finally directed towards the outlet of a conductivity detector. The difference in the conductivity of the reducing gas mixture before and after the reduction is measured by a Wheatstone bridge arrangement of the thermal conductivity detector. During the whole process a constant gas flow is used; therefore, the change in thermal conductivity gives the amount of hydrogen consumed for reduction. Each reduction process appears as a distinct peak in the TPR profile.

2. Experimental

The silica-supported platinum catalysts used in this study were prepared by the impregnation technique. Sample 1 (S_1) containing 0.6%Pt/SiO_2 was prepared by impregnation of Aerosil 200 with aqueous H_2PtCl_6 and dried at 110°C. Sample 2 (S_2) containing 0.6%Pt/SiO_2 was prepared by impregnation of Aerosil with aqueous $[Pt(NH_3)_4](OH)_2$.

The apparatus employed for temperature programmed reduction is shown schematically in Fig. 1. An accurately weighed amount of the sample was placed in a gradientless U-shaped quartz reactor. The reactor was connected to the rest of the system and placed inside the furnace at a temperature low enough to prevent reaction (usually room temperature) and the reducing gas mixture was allowed to flow through the system. In all the experiments reported in this paper, unless otherwise specified, a heating rate of 10 K min^{-1} was used, with 6% hydrogen in argon at a total pressure of 1 atm, and 300 mg of sample.

The experimental details were entered into a computer program. The system was left to stabilize for about half an hour to obtain a straight baseline. Once this was obtained the reduction of the solid was started by switching on the temperature programmed furnace and the hydrogen consumed was monitored by a thermoconductivity detector (TCD). After reduction, the whole system was calibrated by injecting a known volume of hydrogen into the detector (hydrogen sampling loop of 0.125 ml) and the number of moles of hydrogen consumed were calculated.

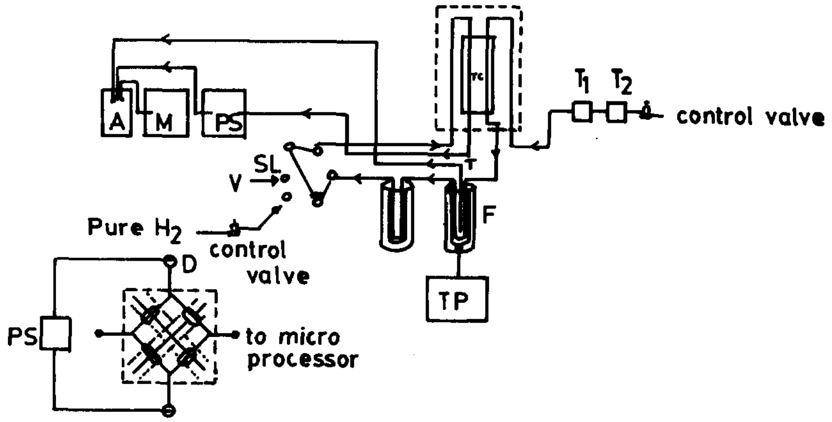
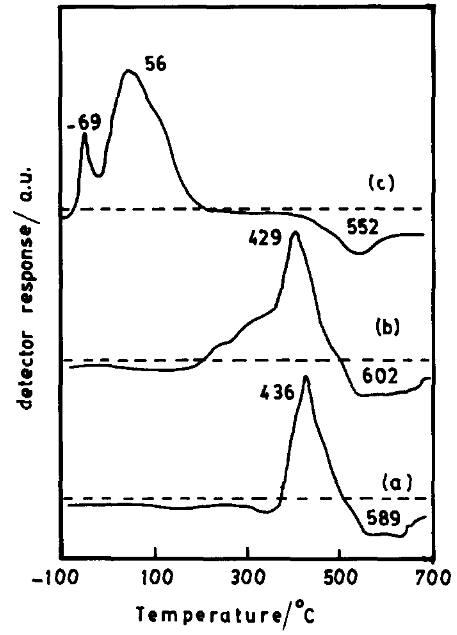


Fig. 1. Schematic diagram of TPR apparatus. A, amplifier; D, detector; F, furnace; M, microprocessor; T, thermocouple; T_1, Pd/Al_2O_3; T_2, 4 Å molecular sieve trap; PS, power supply; SL, sampling loop; SV, sampling valve; TC, thermal conductivity cell; TP, temperature programmer; V, ventilator.

3. Results and discussion

TPR profiles of silica-supported platinum catalysts are given in Figs. 2 and 3. Results are listed in Table 1. Aerosil impregnated with H_2PtCl_6 (S_1) gives one



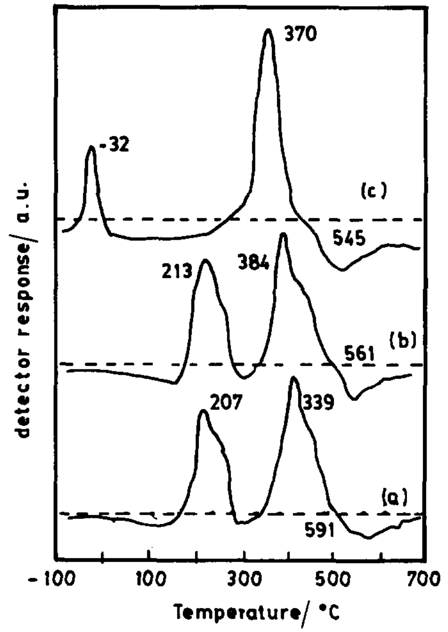


Fig. 2. TPR profiles of S_1. (a) After preparation; (b) after 15 min exposure to air; (c) after oxidation.

Fig. 3. TPR profiles of S_2. (a) After preparation; (b) after 15 min exposure to air; (c) after oxidation.

Table 1
TPR measurements on silica-supported platinum catalysts

Run No.	Experiment	Hydrogen uptake		Hydrogen desorption		Net Pt/H
		T_{max}/°C	$v(H_2)$/ (μmol/g(cat))	T_{min}/°C	$v(H_2)$/ (μmol/g(cat))	
Sample S_1						
1	TPR of S_1	436	7.59	589	0.65	0.45
2	TPR after 15 min exposure to air	429	7.71	602	0.42	0.47
3	TPR after oxidation	−69.56	15.8	552	1.09	0.95
Sample S_2						
1	TPR of S_2	207.400	9.91	591	0.32	0.62
2	TPR after 15 min exposure to air	213.384	11.70	561	2.54	0.59
3	TPR after oxidation	−32.370	16.32	545	3.13	0.86

reduction peak with T_{max} equal to 436°C, while Aerosil impregnated with $[Pt(NH_3)_4](OH)_2$ (S_2) gives two distinct peaks in the regions of 207 and 400°C. The latter peak is almost in the same region as the reduction peak of the H_2PtCl_6 complex. The integrated peak areas were not significantly affected by changing the heating rate, the hydrogen consumption being 7.5–7.71 μmol g^{-1} (average 7.65 μmol g^{-1}) and 7.51–7.60 μmol g^{-1} (average 7.56 μmol g^{-1}) for S_1 and S_2, respectively. In each case, the reduction peak was followed immediately by a small but clear hydrogen desorption trough with a minimum always around 580°C. The area corresponded to 0.61–0.68 μmol g^{-1} for sample S_1 and 0.28–0.36 μmol g^{-1} for sample S_2, i.e. Pt/H ratios of 0.0980–0.11 and 0.08–0.11 respectively. The trough for sample S_1 lies between 585 and 618°C in run 1, while it lies between 595 and 620°C in run 2. Similar effects appear after oxidation TPR in run 3. The width of the trough for S_2 lies between 598 and 415°C in run 1. A similar effect is observed in TPR of the oxidized sample S_2 but the desorption trough is shifted towards lower temperatures. There is evidently an overlap between the process of reduction (including hydrogen chemisorption) and hydrogen desorption. To obtain the correct ratio of Pt/H for reduction, the amount desorbed was also calculated, according to Bond and Gelsthorpe [7].

The reduction after oxidation for samples S_1 and S_2 (runs 3 and 6) begins at sub-ambient temperatures. Our reactor could be cooled to temperatures as low as −75°C. There are indications in almost all the TPR experiments after oxidation that the reduction perhaps begins at temperatures even lower than −75°C. Above 550°C there is a very broad desorption trough. This seems to be particularly true when the oxidation was performed via a TPO experiment. A further TPR of the oxidized catalyst was then performed (Fig. 3, curve b, run 2); two incompletely resolved peaks were observed (T_{max} = 213,384°C), the total uptake being almost the same as observed before (Fig. 3, curve a, run 1). From this experiment, we concluded that TPO does not give a product identical to the initial catalyst: oxidized platinum is much more easily reduced, although the oxygen contents are apparently the same. The behaviour of the oxidized sample S_2 has some similarities to that of Adams platinum oxide [8–10]. Reduction of the latter begins below room temperature, and is completed by about 100°C. Most of the hydrogen uptake takes place below −70°C, but there is a small subsidiary peak at about 80°C. Oxidation of the catalyst S_2 also gave an oxide phase of greater reducibility.

References

[1] P. Turlier, H. Praliaud, P. Moral, G.A. Martin and J.A. Delmon, Appl. Catal., 19 (1985) 287.
[2] C.H. Bartholomew and R.J. Farrauto, J. Catal., 45 (1976) 41.
[3] J. Zielinski, J. Catal., 76 (1982) 157.
[4] I. Chen and D.W. Shiue, Ind. Eng. Chem. Res., 27 (1988) 429.
[5] B. Mile, D. Sterling, M.A. Zammit, A. Lovell and M. Webb, J. Catal., 114 (1988) 217.
[6] G.C. Bond and S.P. Sarsam, Appl. Catal., 38 (1988) 365.
[7] G.C. Bond and M.R. Gelsthorpe, Appl. Catal., 35 (1987) 169.
[8] R. Adams and V. Voorhees, J. Am. Chem. Soc., 44 (1922) 1683.
[9] B.D. McNicol and R.T. Short, J. Electroanal. Chem., 92 (1978) 115.
[10] S.H. Park, M.S. Tzou and W.M.H. Sachtler, Appl. Catal., 24 (1986) 85.