

TEMPERATURE PROGRAMME REDUCTION OF ALKALI DOPED EUROPT-I (Pt/SiO₂ CATALYST)

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The technique of temperature programmed reduction (TPR) of alkali doped Europt-I (Pt/SiO₂ catalyst), was used to observe the catalysts at various stages of preparation sequence. The significant changes might be produced in the structure/properties of the catalyst by the alkali dopant. Observed decrease in the reducible area with increasing alkali concentration could be due to loss of total surface area.

Key words: Temperature programmed reducibility, Pt/SiO₂ Catalyst, Alkali doping.

Introduction

Temperature programmed reduction (TPR) is a recently developed technique used to chemically characterise supported metal catalysts [1-9]. This technique has been used to study catalysts at different stages of a preparation sequence. The sample can be bulk [1,3], supported monometallic [3,4], or supported bimetallic materials [5,6].

Bond *et al.* [10] studied a Pt/SiO₂ catalyst (Europt-1) by TPR. Europt-1 has already been well characterised [11,12]. The catalyst in the as-received condition comprised substantially of platinum oxide rather than metallic platinum, notwithstanding the fact that it has been reduced by the manufacturer as part of its preparation.

There is little evidence in the literature of the TPR studies of alkali doped/promoted supported metal catalyst. It would therefore, be impossible to have direct comparison of our results.

Our objective in this paper is to present a detailed study of the influence of potassium doping on the adsorption characteristics of Pt/SiO₂ catalysts.

Material and Methods

Europt-1 is a model catalyst prepared by Johnson Mathey PLC, England. This catalyst has been characterised in detail by many European laboratories [13].

The samples were prepared by soaking 6.3% (wt) Pt/SiO₂ catalyst in known amount of KOH (wt %) solution. The finished material after drying in rotary evaporator and overnight calcination at 110° had alkali concentration of 0.25, 0.5 and 1.0% by weight on Pt/SiO₂ catalyst.

During TPR 5% H₂/Ar was passed through the system at a flow rate of 10 cm³/min. and the reactor was heated at a linear programmed rate of 10° K/min. The signal from the thermal conductivity detector was fed to potentiometric recorder (Kripp and Zonen BD-9). The area under the peak is proportional to

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the amount of hydrogen consumed in the reduction process. The change in hydrogen concentration was monitored by an on-line microcomputer. This allowed the signal from the detectors to be digitized, stored on disk and subsequently to be integrated.

Procedure. Samples of the catalysts (0.05 g) were placed in a quartz reactor, lowered into a tubular furnace, cooled to 190° K by liquid nitrogen. Before starting TPR, pure argon was replaced by a 5% H₂/Ar mixture during an isothermal period (190° K). At this stage the thermal conductivity detector (TCD) was allowed to stabilize for 30 mins. TPR was started by heating in a programmed way.

Results and Discussion

The reduction profile of 0.25% KOH (wt)/6.3% Pt/SiO₂ is shown in Fig. 1. The reduction started at subambient temperature, similar to that observed for undoped 6.3% Pt/SiO₂ as reported [10,14].

The reduction profile consisted of two incompletely resolved peaks. The T_{max} of the main peak (low temperature peak) appeared at 308° K. The hydrogen consumption was 300 μ mole/g catalyst. The small high temperature peak, which appeared at 418° K, seemed to be consistent with the hint of a shoulders previously observed [1] for undoped catalyst at similar temperature.

The desorption peak has a broad minimum at 520° K, which is slightly higher than that reported for undoped catalyst [10]. There is some trace of a further small desorption attributable to the desorption of spillover hydrogen.

The TPR profile of 0.5% KOH doped catalyst as shown in Fig. 1 indicates existence of 3 reducible species shown by shoulders or incompletely resolved peaks. The main peak of the profile is centered at 350° K. A small shoulder at 305° K was followed by a distinct small peak at 430° K.

The desorption trough has a broad minimum at 530° K which appears to increase with increasing alkali concentra-

tion. The peak area corresponding to hydrogen consumption is listed in Table 1. No. further desorption was observed at higher temperature.

In Fig. 1, profile 'C' shows the reduction behaviour of 1% KOH doped catalyst. The reduction again started at subambient temperature, similar to all the catalysts previously observed. The reduction profile consisted of 2 peaks; the first with a maximum centred at 300° K followed by a very sharp peak at 380° K. After reduction, a desorption trough which had a broad minimum at 560° K was observed again. At higher temperature no further desorption was observed indicating absence of spillover hydrogen.

The TPR of the support alone (sorbosil AQU30) and 1% KOH doped support was carried out. No reduction peak was observed at all under the same experimental conditions. Hence there was no reduction of support or alkali.

Bond *et al.* [10] in a recent publication characterized Europt-1 (6.3% wt Pt/SiO₂) catalyst by the TPR technique and reported a symmetric reduction peak centred at 330° K. The authors also carried out a TPR of undoped Europt-1. This was similar to that reported [10]. However this has a shoulder at 418° K. The symmetric reduction profile was indicative of the crystallographic homogeneity of the catalyst. The profile is shown in Fig.1.

Geus *et al.* [15] characterized Pt/SiO₂ catalyst by determining the size distribution by high resolution transmission electron microscopy. Joyner [16] studied X-ray absorption fine structure (EXAFS). These studies thus concluded that 6.3 % Pt/SiO₂ catalyst (Europt-1 contained an even or homogeneous distribution of platinum particles.

The reduction profiles of alkali doped Europt-1 are presented in Fig.1. The changed characteristics (relative to undoped catalyst) are attributed to the presence of potassium. In view of previous literature we could say that potassium doping might affect the uptake of hydrogen during reduction in 3 ways. (i). Each potassium atom may reduced adsorption of many hydrogen atoms by poisoning or by direct site blocking [17]. (ii). Loss of support structure, i.e. sintering of the support during catalyst preparation may cause encapsulation of the metal, making it no longer accessible to reduction, causing a decrease in the consumption of hydrogen. (iii). Changes in the crystallographic morphology of the catalyst, i.e. formation of larger crystallites [18].

Overall, the reduction profiles indicate two or more peaks or shoulders indicating the presence of different reducible species. In other words, potassium doping might have caused inhomogeneity of the catalyst.

Dry *et al.* [18] studied K₂O promoted reduced magnetite catalyst. X-ray line broadening studies showed that,

those samples containing K₂O had larger crystallites. The authors attributed the loss of surface area to the growth of crystallite size and not due to any other reason such as pore blocking.

The sharp peaks/features seen in TPR of each alkali doped Europt-1 catalyst might be related to the originally present shoulder in the reduction profile of undoped Europt-1 as seen in Fig.1. This became distinct in the alkali doped Europt-1 catalysts probably because of the reduction of the overall TPR profile. The experiments on TPR of the support

TABLE 1. TPR MEASUREMENTS ON EUROPT-1.

Catalyst	T _{max} /K		Hydrogen uptake H ₂ μmoles g ⁻¹	H/pt	Hydrogen desorption T _{max} /K
As-received Europt-1	320	-	341	2.10	512
0.25% KOH (wt)/ Europt-1	308	418	300	1.86	520
0.50% KOH (wt)/ Europt-1	305	365	430	280	530
1.0% KOH (wt)/ Europt-1	300	380	243	1.50	560
T _{max} /K±20;	H ₂ μmole g ⁻¹ ± 25s				

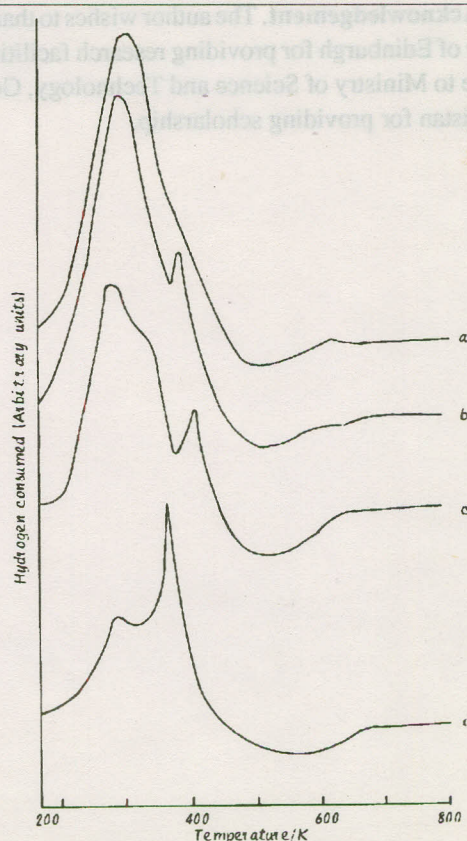


Fig.1. TPR Profiles: (a) as received Europt-1; (b) 0.25% KOH (wt)/Europt-1; (c) 0.50% KOH (wt)/Europt-1; (d) 1.0% KOH (wt)/Europt-1.

alone or alkali doped support may confirm that these sharp features are not associated to the reduction of support or alkali.

It was observed that in each case, there followed immediately after the reduction peak, a small but clear hydrogen desorption trough having a broad minimum. These desorption minima were found to shift to higher temperature as the alkali concentration increases. This indicates that the stability of adsorbed hydrogen increased with alkali concentration.

Among the series of alkali doped catalyst, spillover hydrogen desorption was exhibited by 0.25% KOH doped Europt-1 only. At higher alkali loading there was little evidence of desorption from spillover hydrogen. This could be attributed to the loss of metal surface area corresponding to the decreased metal dispersion, hence it could be concluded that low dispersions may not favour hydrogen spillover.

Conclusion

In the present study based on the results it could be concluded that: (1). Alkali dopant might produce significant changes in the structure/properties of the catalyst. (2). Observed decrease in the reducible area with increasing alkali concentration could be due to loss of total surface area.

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Fig. 1. TPR profiles of Europt-1 catalyst doped with different concentrations of KOH: (a) 0.25% KOH, (b) 0.5% KOH, (c) 1.0% KOH, (d) 2.0% KOH.

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