CHAPTER 6

STUDIES ON Pt – Sn/Al_2O_3 CATALYSTS PREPARED BY CONVENTIONAL METHOD

6. Studies on Pt-Sn/Al_2O_3 Catalysts Prepared By Conventional Method

This chapter exclusively deals with Pt – Sn catalysts prepared by conventional method with oil – drop alumina. In particular, these catalysts were characterized by the same techniques as for the catalysts prepared by the sol – gel techniques, which is described in the previous chapter.

6.1. Preparation of catalysts and sample codes

Details on the preparation of two IMP series of catalysts by conventional co-impregnation of Pt and Sn on pre-formed alumina support are given in Chapter-3 (Figure 3.2) The first series consists of one mono and three bimetallic catalysts, with the sample code IMP PSX B, where X (Sn/Pt atomic ratio)= 0, 2 4 and 8. Since the residual chloride content in these catalysts is ~1 wt%, this series is termed as bifunctional (B)

The second series of four catalysts is obtained by dehalogenation of the corresponding members in the first series. The general sample code is IMP PSX M, where X= 0, 2, 4 and 8. Residual chloride content in these catalysts is <0.1wt% and hence termed as monofunctional catalysts (M).

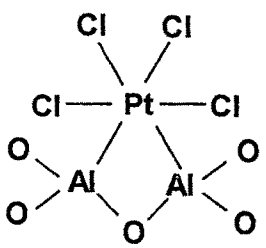
In all, 8 catalyst samples have been prepared by conventional method and characterized for all the physico-chemical properties so as to compare with those observed for the catalysts obtained through sol-gel technique.

6.2. Characterization of catalysts

6.2.1. Powder X-ray Diffraction (XRD) studies:

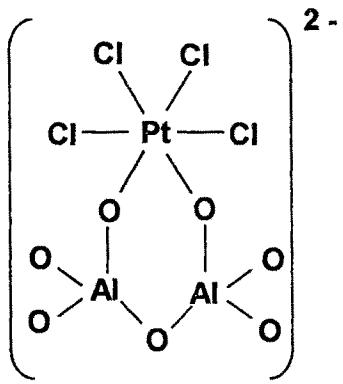
The diffraction pattern for a typical conventional catalyst, IMP PS2 B, has been included along with those observed for SG catalysts in Figure 5.2, No.3. It displays d-lines attributed to gamma alumina and is partly

amorphous. However the sample displays better crystallinity compared to sol-gel catalysts. Diffraction patterns for all mono as well as bifunctional catalysts obtained by conventional routes are observed to be similar. d-lines observed in all cases correspond to gamma alumina only indicating that Pt and Sn are finely dispersed over the support. Measured crystallite size for conventional catalysts is in the range 50-60 Å. In comparison, crystallite size for sol-gel catalysts is in the range 40- 50 Å and they are highly amorphous.



When Chloroplatinate ions bond with the strong Lewis acid sites of alumina

Figure 6.1



when Chloroplatinate ions bond with the weak Bronsted acid sites of alumina

6.2.2. Active metals composition

Data for IMP series of catalysts, as presented in Table 5.2 reveal that there is no significant loss of Pt or Sn during preparation steps. According to conventional method, Pt and Sn are impregnated as anionic Pt-Sn chloro complex, $[Pt\ Cl_4\ (SnCl_3)_2]^-$, in aqueous solution under highly acidic conditions. Since alumina is an anion absorber under pH below its zeta potential (pH-7), the complex is firmly held on the surface through chemical interaction. Even after calcination at 500°C to " fix" the Pt, it is known to exist as surface oxy-chloro species, PtO_xCl_y, **(1)** bound to alumina. However, when the catalyst is treated with hot NH_4OH solution in order to minimize the residual chloride level (so as to obtain

monofunctional catalysts), some loss of Pt into ammoniacal solution is possible. Due to this reason Pt contents in monofunctional catalysts are slightly less compared to those observed in bifunctional catalysts (Table 5.2).

6.2.3. Textural properties

Nitrogen adsorption-desorption isotherms and pore size distribution curves obtained for IMP PS2 BF are shown in Figure 6.2. Adsorption isotherm belongs to Type IV as per Braunauer's classification and represents meso porous character. Shape of the hysteresis loop corresponds to Type A as per the classification by de Boer **(2, 3)** and indicative of the presence of meso pores. The shape of the hysteresis loop also indicates the presence of cylindrical as well as slit shaped pores. Predominantly meso porous character is also revealed by the pore size distribution curve, which also shows the presence of some micro pores. However the size distribution is broad compared to that observed for sol-gel catalysts

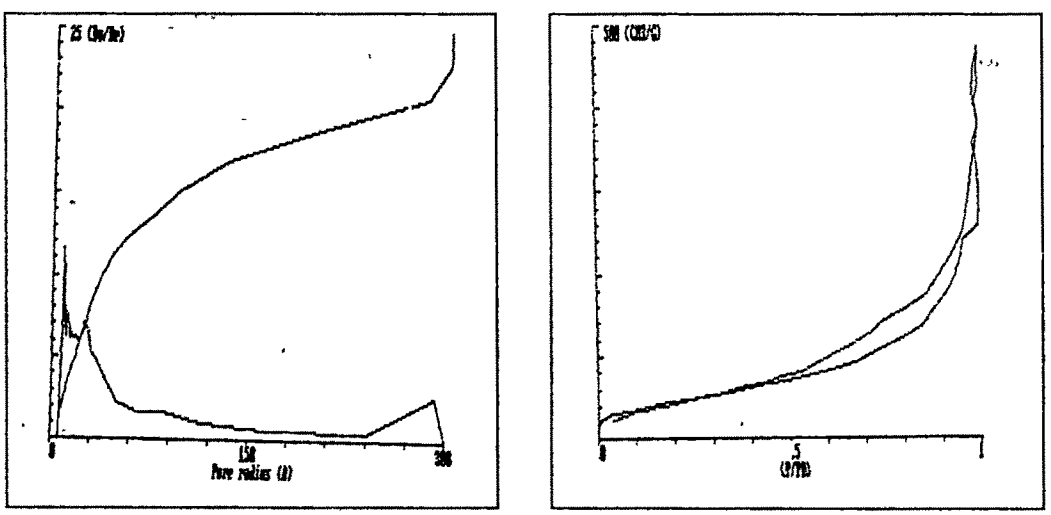


Figure 6.2: (a) Pore Size Distribution Curve and (b) Hysteresis curve of IMP PS2 BF catalysts

BET surface area for IMP PS2 B is 169 m^2/g, which is less compared to 200-300 m^2/g observed for sol-gel catalysts, while the pore volume of 0.69 mlNTP/g is comparable. However mean pore radius for IMP PS2 B is 82Å, which is higher than the range of values (40-70Å) observed for sol-gel catalysts. This is due to the alumina support used for the preparation of the conventional catalyst, which is highly porous in nature, with wide pores.

Other members of the IMP series, mono or bifunctional catalysts, irrespective of Sn/Pt atomic ratio display similar textural characteristics, having low surface area (160-170m^2/g), nominal pore volume (0.6-0.7ml NTP/g), mesoporous in nature, with wide pores (80-90Å mean value) and broad size distribution.

6.2.4. Acidity

Total acidity of conventional monofunctional catalysts expressed as milli moles/g of ammonia adsorbed at 100°C (Table.6.1), are close to those observed for the corresponding sol-gel catalysts (Table .5.4).

Table.6.1 Total acidity data for monofunctional catalysts

Sample	Ammonia uptake at 100°C (milli moles/g)
IMP PS0 M	0.704
IMP PS2 M	0.653
IMP PS4 M	0.445
IMP PS8 M	0.531

This observation is in line with that of Gomez et al **(4)** who reported 0.34 and 0.30 meq of ammonia/g for Pt-Sn-alumina catalysts via sol-gel and conventional routes respectively. A parabolic relationship between acidity and Sn/Pt ratio as observed for SG catalysts is observed for conventional catalysts too. Influence of Sn/Pt ratio on acidity is more pronounced than

changes in preparation methods. As expected conventional bifunctional catalysts display higher total acidity compared to monofunctional ones

6.2.5. Temperature Programmed Reduction

TPR patterns for bifunctional IMP series catalysts are presented in Figure 6.3.

In the case of bifunctional mono metallic catalyst, Pt/Al_2O_3 (IMP PS0 B) TPR pattern shows single reduction maximum at 264^{0}C, due to Pt oxy chloro species bound to alumina. Introduction of Sn shifts this maximum to higher temperatures, 289^{0}C for IMP PS2 B, 309^{0}C for IMP PS4 B and 339^{0}C for IMP PS8 B, due to simultaneous reduction of Pt and Sn. At higher Sn loading, shoulders appear on the main peak, one on low temperature side and the other on high temperature side, possibly indicative of different levels of interaction between Pt and Sn as Sn loading increases. The one at low temperature side however is located above 200^{0}C indicating that the species under consideration is not free Pt oxide. One significant observation is that free Pt oxides are not observed, a pointer towards highly effective interaction between Pt and Sn

In the case of monofunctional monometallic catalyst (IMP PS0 M) two reduction maxima are observed, one at 165^{0}C due to free Pt oxide and the other at 246^{0}C due to Pt oxy chloro species bound to alumina. It is likely that loss of chloride in mono metallic system lowers the binding of Pt to alumina resulting in some free Pt oxide and a relatively weakly bound Pt that gets reduced at lower temperature compared to bifunctional mono metallic catalyst. With the introduction of Sn in monofunctional catalysts, reduction maximum at 246^{0}C shifts gradually upwards with the increase in Sn loading, with the peak due to free Pt oxide reduction being intact.

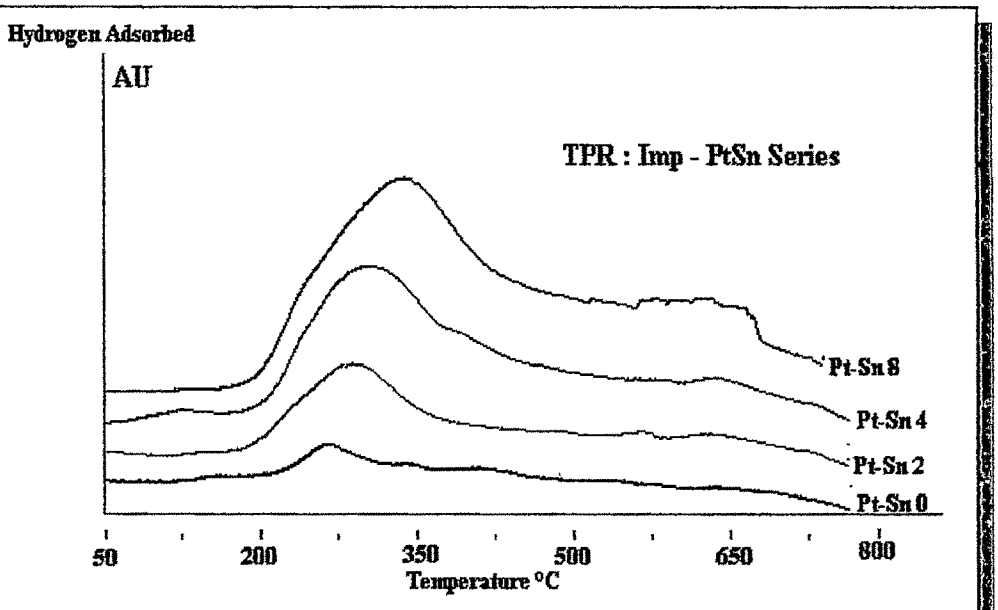


Figure 6.3: TEMPERATURE PROGRAMMED REDUCTION PROFILES OF BIFUNCTIONAL IMP SERIES

TPR patterns in the case of conventional catalysts thus clearly bring out the pivotal role played by residual chloride **(5)**, which, by retarding the reduction of Pt, brings out effective interaction between Pt and Sn.

6.2.6. Metal Dispersion

Metal dispersion data on both series of conventional catalysts are presented along with those for SG catalysts in Table.5.7. Conventional catalysts, both mono and bifunctional, show better Pt dispersion compared to those observed for any SG catalyst. Both type of catalysts also show regular increase in Pt dispersion with Sn content, though the ensemble effect by Sn levels off in the case of monofunctional catalysts at higher Sn loading. As expected, bifunctional (conventional) catalysts display better Pt dispersion compared to monofunctional ones, bringing into focus again the role of chloride in bifunctional catalysts. Another interesting feature is the higher degree of alloying by Sn in the case of monofunctional catalysts. Reduced chloride levels in monofunctional catalysts perhaps make the alumina support less reactive (closer to silica), thereby promoting Pt-Sn alloying.

6.3. Summary

XRD studies reveal the presence of only gamma alumina phase, with Pt and Sn well dispersed. Catalysts display better crystallinity compared to SG catalysts

Pt-Sn/Al_2O_3 catalysts prepared by conventional methods are typically meso porous, with a surface area of 160-170 m^2/g and pore volume of 0.6-0.7 ml NTP/g, mean pore radius 80-90 Å and typically broad pore size distribution

Total acidity, expressed as milli moles of ammonia/g, of the conventional catalysts are closer to those observed for sol-gel catalysts and shows parabolic trend with respect to Sn/Pt atomic ratio

TPR studies have shown that Pt-Sn interactions are strong for conventional bifunctional catalysts, while it is a shade less with monofunctional ones.

Conventional catalysts display better platinum dispersion that increases with Sn loading while SG catalysts effect of Sn loading on dispersion is less pronounced.

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