CHAPTER 5

STUDIES ON Pt – Sn/Al_2O_3 CATALYSTS PREPARED BY SOL-GEL TECHNIQUE

5. Studies on Pt-Sn/Al_2O_3 Catalysts Prepared By Sol-Gel Method

This chapter primarily deals with dehydrogenation catalyst prepared by the sol gel route. The catalyst preparation methodology is dealt with in detail. The final catalyst characteristics are elaborately discussed here. Various characterization techniques employed include XRD, active metal dispersion, textural properties, acidity, temperature programmed reduction etc.

5.1. Preparation of catalysts and sample codes:

Details of preparation involving two series of Pt-Sn/Al_2O_3 catalysts, **ASG** and **BSG,** have been described in Chapter 3. **ASG** corresponds to catalysts prepared at pH- 3.0 and **BSG** at pH-9. In both the cases, mono metallic as well as bimetallic catalysts with Sn/Pt atomic ratios (maintaining a constant Pt loading of 0.4% w/w of alumina) of 0, 2, 4 and 8 have been prepared. Further variations in preparation methods have been introduced in the separation of the alumina gel from the solvent after aging. Separation of the solvent from the gel has been achieved in two ways: by distillation (D) and filtration (F) since it is known that the nature of the solvents that reside in the pores during the drying step would govern the evolution of the pore structure of the final catalysts. In order to study the influence of metal and acidic functions on the model reaction, n-decane dehydrogenation, catalysts with mono as well as bifunctional character have been prepared by controlling the level of residual chloride in the final catalysts. Fig 3.2 describes in detail, the intricacies involved in preparation of catalysts by sol gelroute.

Sample codes that represent these variations in the preparation methods and chemical composition have been adopted. Samples via ASG route, i.e., sol gel (SG) preparation under acidic pH (= 3.0), consist of four different sets of catalysts with four catalysts in each set, as described below:

Sample codes	Description
ASGPSXMF	Set of four monofunctional (M) catalysts with Sn/Pt atomic ratio (X) of 0,2,4 and 8 adopting filtration (F) route
ASGPSXMD	Set of four monofunctional (M) catalysts with Sn/Pt atomic ratio (X) of 0,2,4 and 8 adopting distillation (D) route
ASGPSXBF	Set of four bifunctional (B) catalysts with Sn/Pt atomic ratio (X) of 0,2,4 and 8 adopting filtration (F) route
ASGPSXBD	Set of four bifunctional (M) catalysts with Sn/Pt atomic ratio (X) of 0,2,4 and 8 adopting filtration (D) route

Similarly four more sets of catalysts (with four in a set) via BSG route, i.e., SG preparation under basic pH (= 9.0), have been prepared and coded in a similar manner. In order to investigate the inter-relationship between preparation-characterization- catalytic performances, a total of 32 catalyst samples via sol-gel route have been prepared for investigation.

5.2. Method of preparation:

It is pertinent to mention here that two common methods of preparation of Pt-Sn/Al_2O_3 catalysts via sol-gel route have been reported. Gomez et al **(1)** have adopted a route wherein Sn as tetra butyl Sn is added to a solution of ASB in n-butanol prior to hydrolysis and Sn/Al_2O_3 is obtained by sol-gel process. Sn/Al_2O_3 on drying at 70^{0}C and calcination at 300^{0}C is then impregnated with Pt as H_2PtCl_6, dried and calcined. The authors have adopted this method of preparation with the specific aim of:

- Promoting Sn-alumina interaction, leading perhaps to the formation of Sn aluminate
- Avoiding Pt-Sn alloy formation.

Such a configuration of the active phase is expected to be suitable for its application in naphtha reforming process.

Balakrishnan and Gonzalez **(2)**, on the other hand, have prepared the catalysts by the simultaneous addition of $SnCl_4$ and H_2PtCl_6 to ASB solution prior to hydrolysis. The resultant alumina gel containing Pt and Sn precursors is then dried and calcined to get the final catalyst. Such a procedure is expected to yield more homogeneous catalyst with a better interaction between Pt and Sn, besides the interactions with the support. This method is based on the work of Armor et al **(3)**.

In the present case, the activity for dehydrogenation of n-decane, a structure insensitive reaction, is governed by the dispersion of platinum, while the selectivity and stability by the interactions between Pt and Sn and the extent of modification of the support by Sn. For such an application, the second method, wherein Pt and Sn precursors are co-gelled with the support precursor, ASB, during hydrolysis is expected to be more suitable. This procedure has been adopted in the current study for the preparation of all SG catalysts.

A number of reports **(1,2,4)** on application of Pt-Sn/Al_2O_3 catalysts prepared by SG route for catalytic reforming process are available. However, there have been just two reports on application of such catalysts for dehydrogenation of paraffins, one on dehydrogenation of iso-butane **(5)** and the other on dehydrogenation of propane **(6)**. To the best of our knowledge there has not been any report so far on the use of Pt-Sn/Al_2O_3 catalysts prepared by SG route for dehydrogenation of long chain C_{10}-C_{14} n-paraffins.

5.3. Characterization of catalysts

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

Based on the study of the SG preparation methods described in Chapter 4, it is observed that all Pt-Sn/Al_2O_3 catalyst precursors, irrespective of preparation methods or chemical composition consist of pseudo boehmite phase, which on calcination at 600^0C yield gamma alumina. X-ray diffractograms of some typical calcined catalysts, presented in Figs 5.1 to 5.4 indicate highly amorphous character and exhibit d-lines corresponding to gamma alumina. All catalysts, irrespective of the method of preparation, chemical composition, mono or bifunctional, show similar XRD patterns. XRD pattern for a typical conventional catalyst (No.3 in Fig 5.3) on the contrary shows much better crystallinity. Even at the highest Sn loading corresponding to Sn/Pt atomic ratio of 8, no d-lines due to oxides of Sn are noticed, indicating extremely fine dispersion of Sn and possibly strong

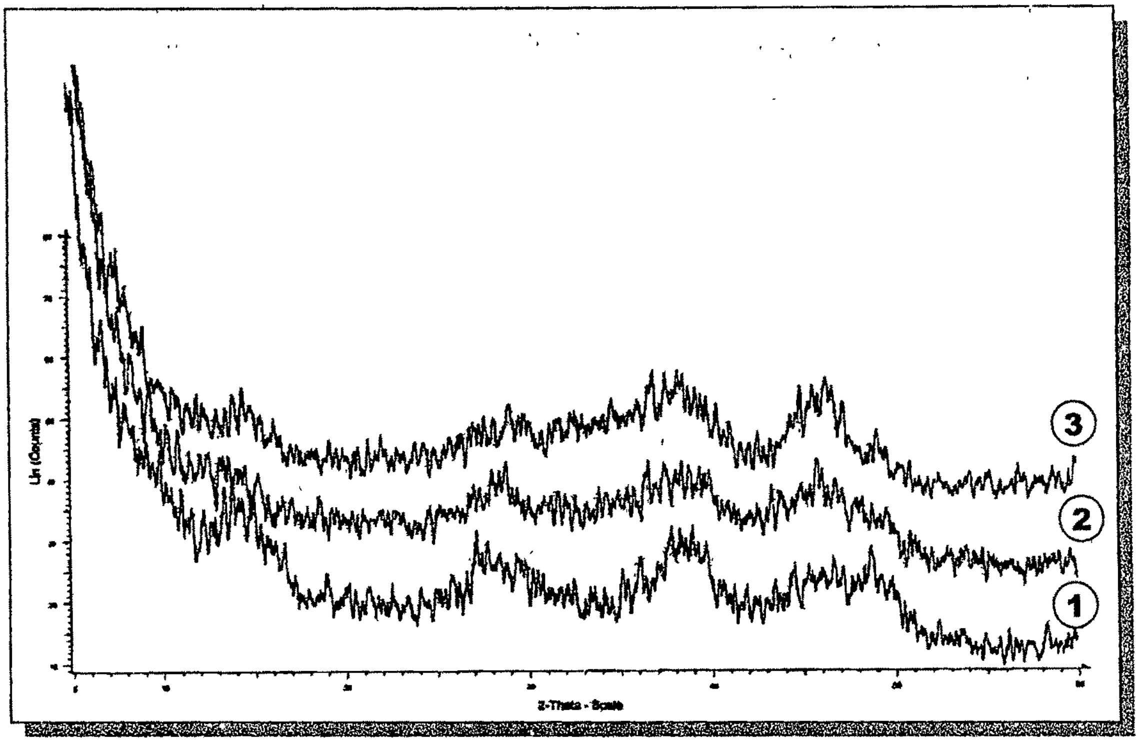


Figure 5.1 : X – Ray Diffractograms of A SG PS D samples
1. A SG PS 2D 2. A SG PS 4D 3. A SG PS 4D

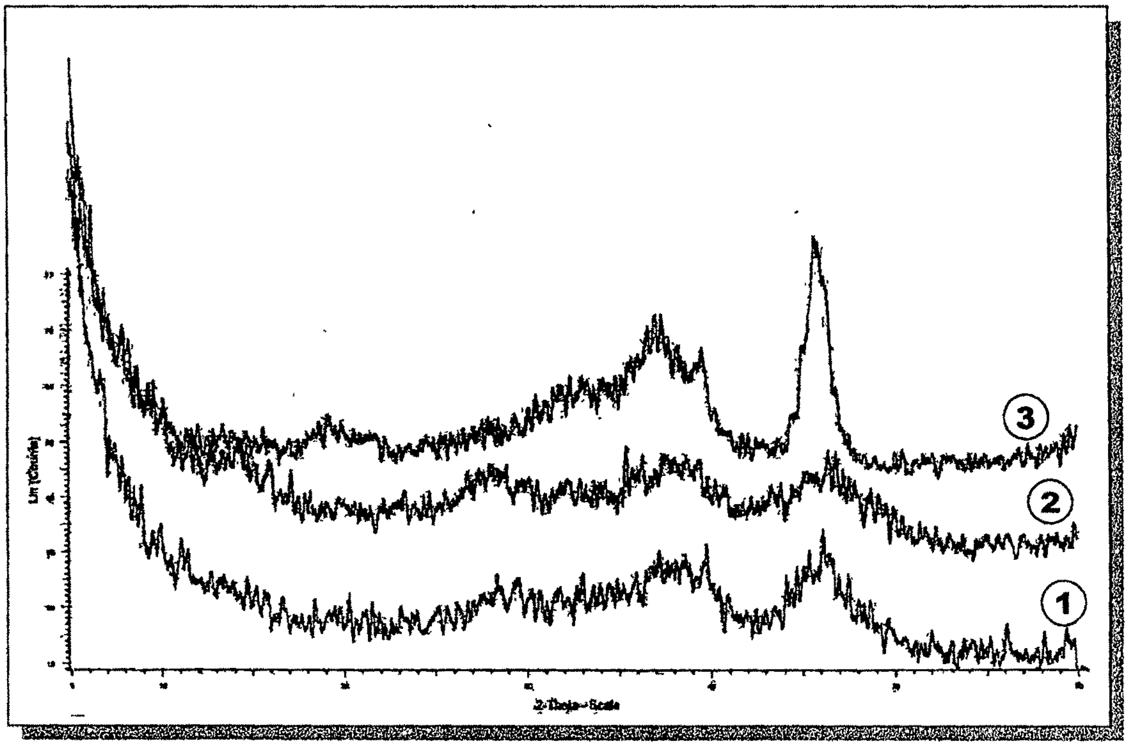


Figure 5.2 : X – Ray Diffractograms of B SG PS D samples
1. B SG PS 2D 2. B SG PS 4D 3. IMP PS 4

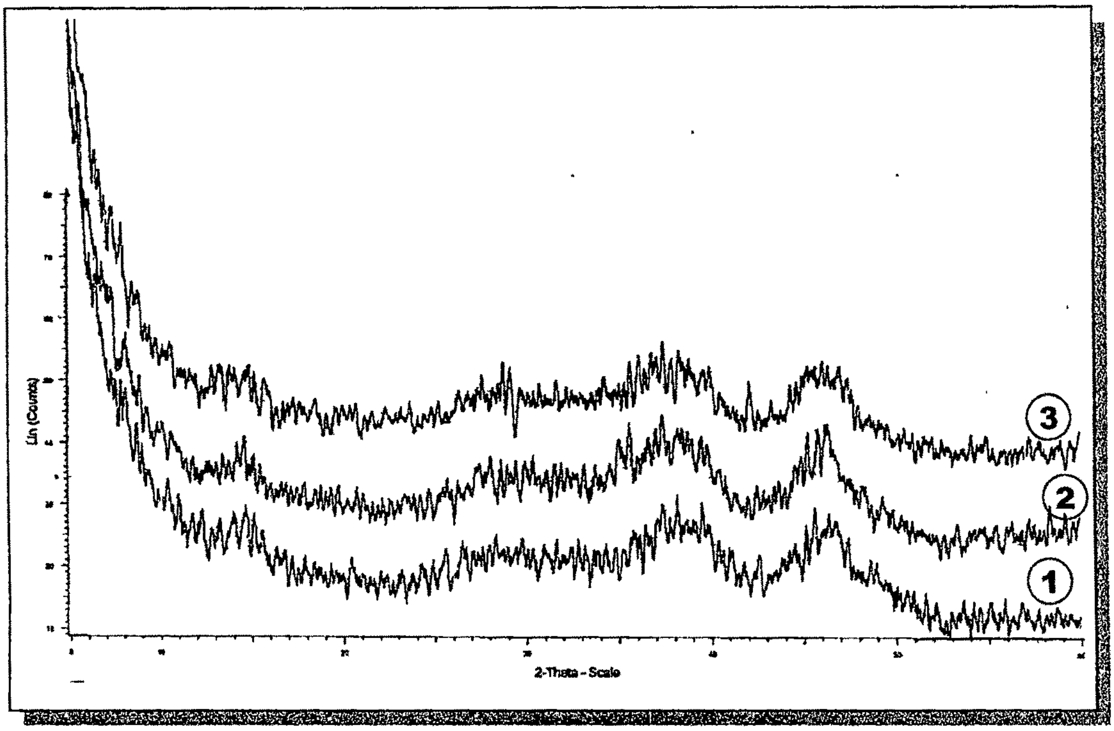


Figure 5.3 : X – Ray Diffractograms of B SG PS F samples
1. B SG PS 2F 2. B SG PS 4F 3. B SG PS 4F

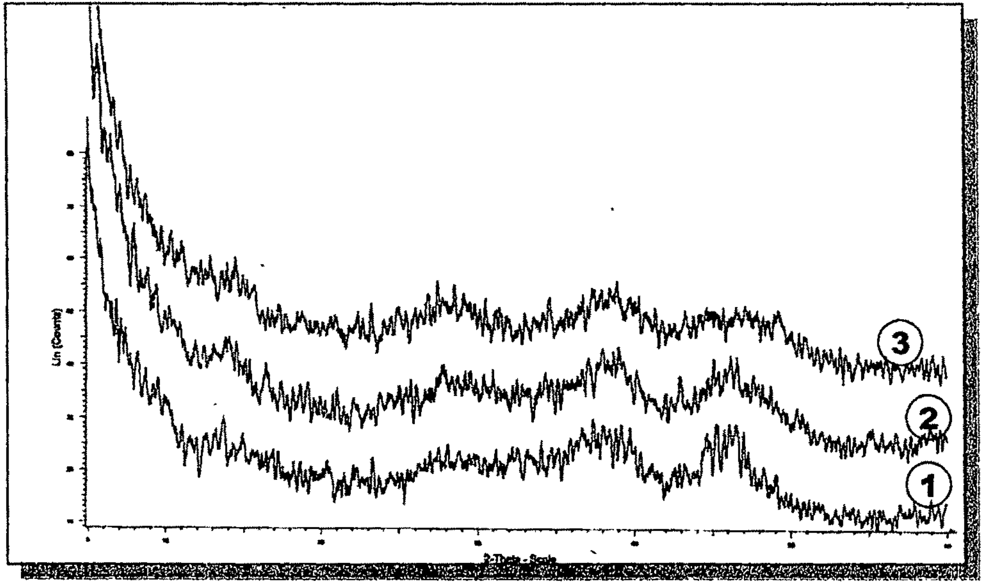


Figure 5.4 : X – Ray Diffractograms of A SG PS F samples
1. A SG PS 2F 2. A SG PS 4F 3. A SG PS 4F

interaction with alumina. This is in line with the observations of Gomez et al **(7)** for Pt-Sn/Al_2O_3 catalysts prepared by SG route, wherein Sn could not be detected by EDAX technique. XRD studies thus clearly establish strong interaction between Sn and alumina support.

5.3.2. Yield and active metals composition

Table 5.1 presents the data for calculation of the yield in the case of 12 different catalyst preparation batches. More than 90 % catalyst yield is obtained in all the cases, indicating that the overall efficiency of the process is excellent.

Composition of active phase for mono and bifunctional SG catalysts along with those observed for catalysts obtained by conventional impregnation method, are given in Table 5.2. Significant difference is noticed in Pt and Sn contents, as designed and actual.

Table 5.1 Yield calculations of Sol gel catalysts

	n – Butanol ml	ASB g	H_2PtCl_6 ml	$SnCl_2$ g	Aimed for g	Yield g	Yield %
ASGPtSn2 D	320	49.5	1.004	0.0953	10	9.45	94.5
ASGPtSn4 D	320	49.5	1.004	0.1907	10	9.65	96.5
ASGPtSn8 D	320	49.5	1.004	0.3815	10	9.24	92.4
ASGPtSn2 F	320	49.5	1.004	0.0953	10	9.14	91.4
ASGPtSn2 F	320	49.5	1.004	0.1907	10	9.26	92.6
ASGPtSn2 F	320	49.5	1.004	0.3815	10	9.45	94.5
BSGPtSn2 D	320	49.5	1.004	0.0953	10	9.15	91.5
BSGPtSn4 D	320	49.5	1.004	0.1907	10	9.11	91.1
BSGPtSn8 D	320	49.5	1.004	0.3815	10	9.23	92.3
BSGPtSn2 F	320	49.5	1.004	0.0953	10	9.15	91.5
BSGPtSn2 F	320	49.5	1.004	0.1907	10	9.06	90.6
BSGPtSn2 F	320	49.5	1.004	0.3815	10	9.56	95.6

Such discrepancies between design and actual metal loading in the case of SG catalysts have been recorded in earlier work **(2,4,8)**. Lambert and Gonzalez **(9)** have studied this aspect in detail, which is observed especially in the case of SG catalysts and have concluded that active metal(s) could be lost during catalyst preparation, drying or pretreatment. A number of factors, like, volatility of the metal precursor, loss during weighing, variations in the degree of hydration, incomplete sol to gel transformation and the drying method adopted (leading to xerogel or aerogel formation) could affect the final metal loading. Lambert and Gonzalez **(9)** have also observed that even in the case of catalysts prepared by conventional ion-exchange impregnation method, losses could occur due to removal of weakly adsorbed metal precursors during washing.

Current investigations have brought in focus three important points in this aspect, that have not been considered in earlier investigations, i.e.,

- Nature of the alumina precursor formed (pseudo boehmite)
- Mode of separation of the gel from the mother liquor
- Adsorption behaviour of alumina based on its zeta potential

All SG catalysts at the dried stage contain pseudo boehmite phase. It is well known that the platinum/Sn precursors have little or no interaction with pseudo boehmite in general. So, when the dried catalysts were calcined in a downward flow of air, part of metal precursors could be lost, thus lowering the overall platinum and Sn content in the final, calcined catalyst. Loss of metals was not observed in catalysts prepared by conventional impregnation of Pt precursors on pre-formed gamma alumina (IMP series in Table 5.2). It can be reasoned out that the dried catalyst, by nature of its method of preparation is predominantly in the γ - phase. Therefore, the Pt precursors are so firmly anchored that calcination does not result in any leaching.

As described in Chapter 3, separation of gel from the mother liquor is achieved in two modes, distillation (D) and filtration (F). Some loss of metal precursors is likely in the filtration mode, which involves washing with solvent. Besides, interaction / retention of precursors by pseudo boehmite phase may also be related to the pH (acidic (ASG) or basic (BSG)) during SG process. The trends in Pt loss observed for different catalysts support such hypotheses:

ASG (D) < ASG (F) < BSF (D) < BSG (F)

Table 5.2 Active metal compositions of Sol gel catalysts

				Bifunctional*		Monofunctional	
Catalyst	Sn/Pt mole ratio	Pt and Sn taken during preparation.		Pt and Sn composition after calcination		Composition after dehalogenation with NH_3	
		Pt (Wt%)	Sn (wt%)	Pt (Wt%)	Sn (wt%)	Pt (Wt%)	Sn (wt%)
ASG PS 0 D	0	0.400	0.00		0.00	0.351	0.00
ASG PS 2 D	2	0.400	0.48	0.34	0.41	0.320	0.39
ASG PS 4 D	4	0.400	0.97	0.37	0.89	0.350	0.85
ASG PS 8 D	8	0.400	1.94	0.37	1.77	0.349	1.69
ASG PS 0 F	0	0.400	0.00	0.37	0.00	0.350	0.00
ASG PS 2 F	2	0.400	0.48	0.32	0.39	0.303	0.37
ASG PS 4 F	4	0.400	0.97	0.34	0.83	0.327	0.79
ASG PS 8 F	8	0.400	1.94	0.34	1.63	0.320	1.55
BSG PS 0 D	0	0.400	0.00	0.36	0.00	0.342	0.00
BSG PS 2 D	2	0.400	0.48	0.30	0.37	0.290	0.35
BSG PS 4 D	4	0.400	0.97	0.32	0.77	0.211	0.51
BSG PS 8 D	8	0.400	1.94	0.40	1.92	0.377	1.82
BSG PS 0 F	0	0.400	0.00	0.35	0.00	0.330	0.00
BSG PS 2 F	2	0.400	0.48	0.23	0.28	0.220	0.27
BSG PS 4 F	4	0.400	0.97	0.21	0.50	0.198	0.48
BSG PS 8 F	8	0.400	1.94	0.27	1.29	0.253	1.23
IMP PS0	0	0.400	0.00	0.389	0.000	0.388	0.000
IMP PS2	2	0.400	0.48	0.392	0.468	0.380	0.460
IMP PS4	4	0.400	0.97	0.398	0.952	0.385	0.932
IMP PS8	8	0.400	1.94	0.390	1.873	0.389	1.883

** (contains 1.2 to 1.6 wt% Chloride)*

Another interesting observation is that, in spite of such leaching discussed above, the Sn to Pt ratio remains as conceived, within experimental error limits. In all sol-gel catalysts, monofunctional catalysts have relatively less Pt in final catalyst, compared to bifunctional ones. The reason for this could be the loss of some Pt during ammonia treatment for chloride removal.

For all further studies, dispersion and Turn Over Frequency (TON) calculations, actual values of Pt and Sn observed in the final catalysts have been used.

5.3.3. Textural properties

It was observed that the textural characteristics of mono and bifunctional catalysts do not exhibit significant variations and hence the data on monofunctional catalysts are presented and discussed here.

Table 5.3: Textural characteristics of monofunctional sol-gel catalysts

Catalyst	Surface area m^2/g	Pore volume (NTP) ml /g	Mean pore radius* (Å)	Type of isotherm**	Type of hysteresis loop***	Pore shape
ASGPS2F	256	0.48	37	Type IV	Type II, non-rigid, percolative	Micro + meso
ASGPS2D	292	0.52	36	Type IV	Type II, Non- rigid, Non-percolative	Micro + meso Predominantly microporous
ASGPS4F	208	0.43	41	Type IV	Type II, rigid, non percolative	Micro + meso
ASGPS4D	316	0.73	46	Type IV	Type III Non-rigid Percolative	Unimodal Predominantly mesoporous
ASGPS8F	282	0.67	47	Type IV	Type III Non-rigid Percolative	Bimodal Predominantly mesoporous
ASGPS8D	253	0.84	67	Type IV	Type IV	Bimodal Predominantly mesoporous
BSGPS2F	211	0.64	61	Type IV	Type III Non-rigid Percolative	Bimodal Predominantly mesoporous
BSGPS2D	243	0.71	68	Type IV	Type III Non-rigid Percolative	Broad
BSGPS4F	253	0.43	34	Type IV	Type III, rigid Non -percolative	Broad
BSGPS4D	280	0.93	67	Type IV	Type III - IV Non-rigid Percolative	Bimodal Predominantly mesoporous
BSGPS8F	255	0.76	60	Type IV	Type IV Non -percolative	Bimodal Predominantly mesoporous
BSGPS8D	215	0.46	43	Type IV	Type I-II Non-rigid Percolative	Bimodal Predominantly mesoporous

* Mean pore radius calculated as 2X pore volume/surface area
** Type of adsorption isotherms, as per Brunauer's concept
*** Hysteresis loop type as per Salmones et al

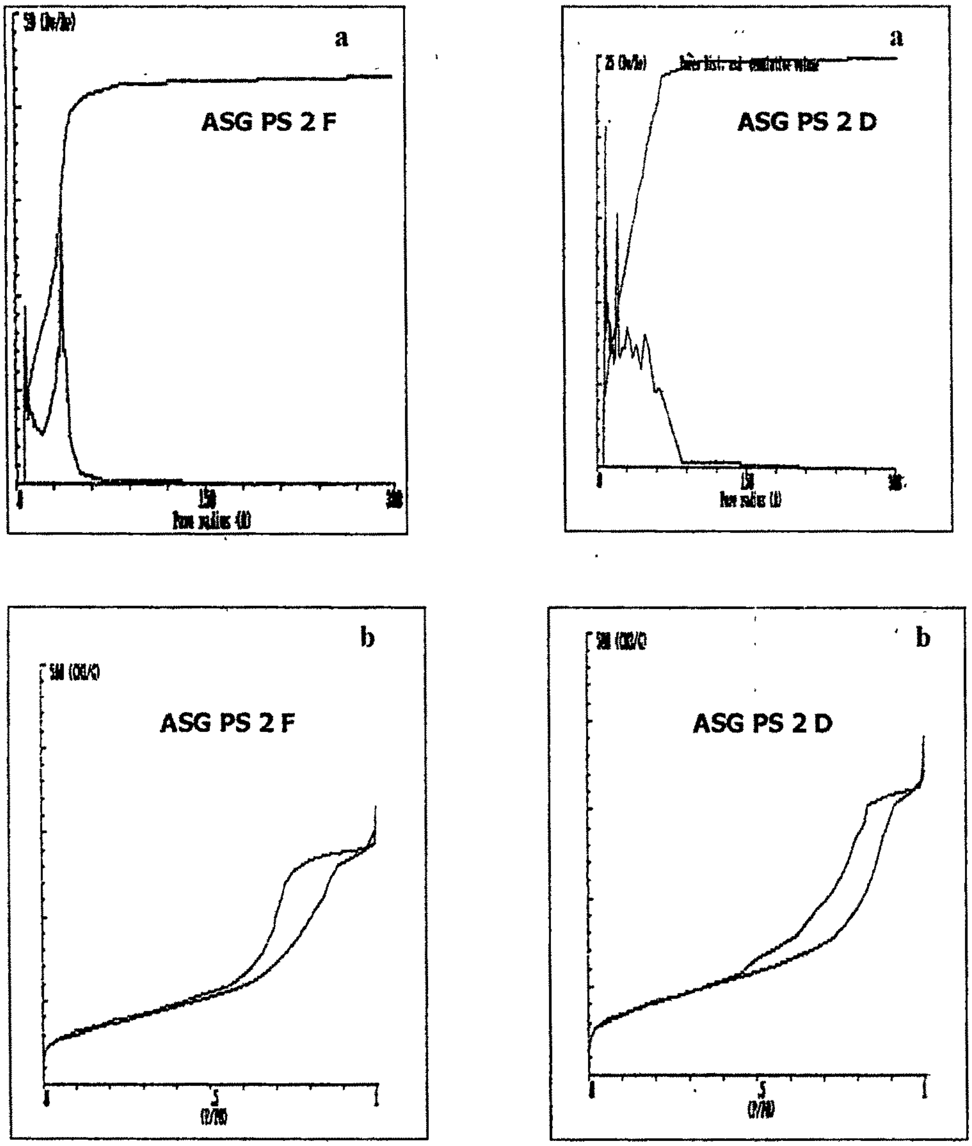


Figure 5.5: A SG PS 2 (a) Pore Size Distribution Curves for filtered and distilled series (b) Hystersis Loop Forms for filtered and distilled series

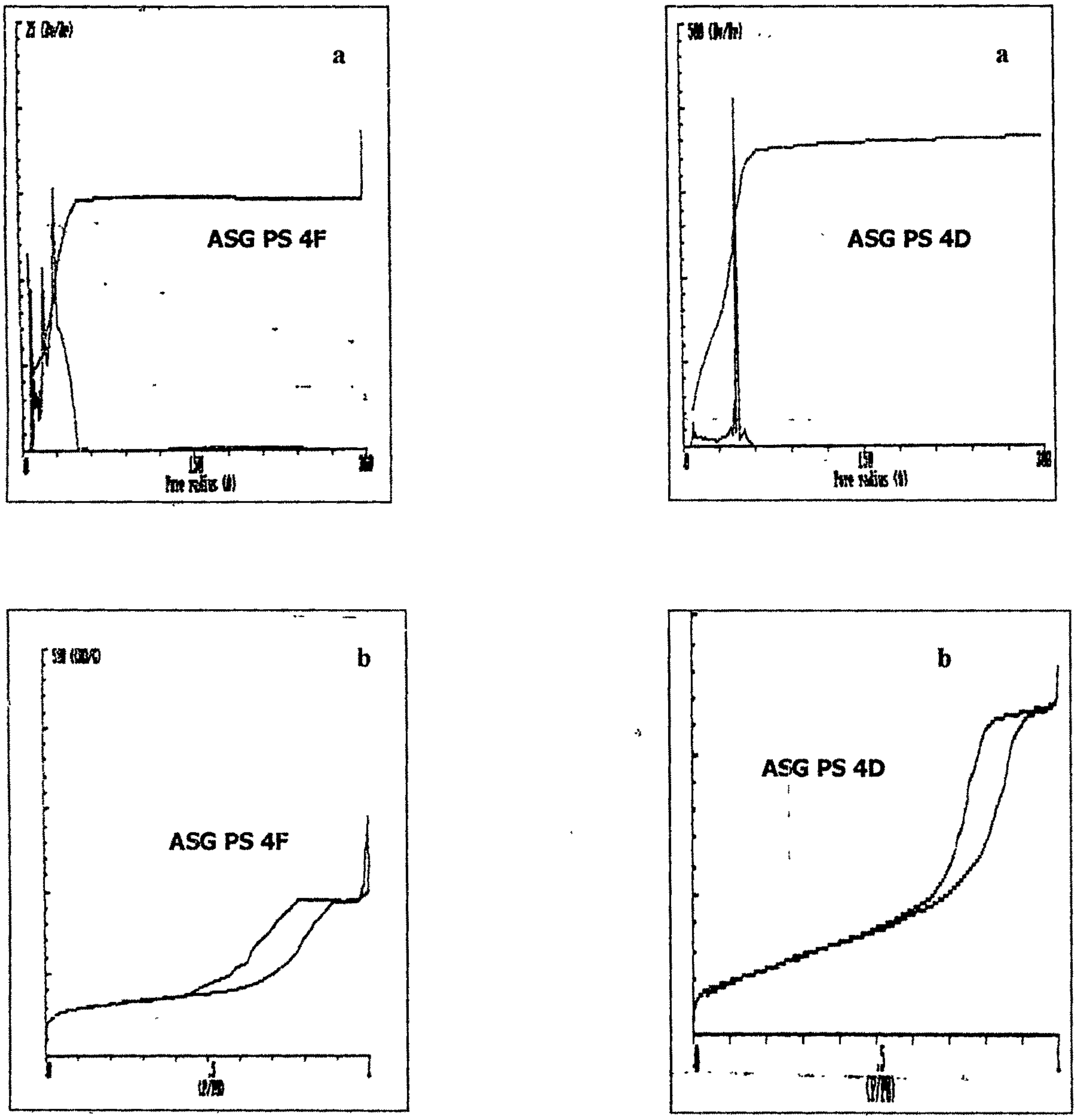


Figure 5.6: A SG PS 4 (a) Pore Size Distribution Curves for filtered and distilled series (b) Hystersis Loop Forms for filtered and distilled series

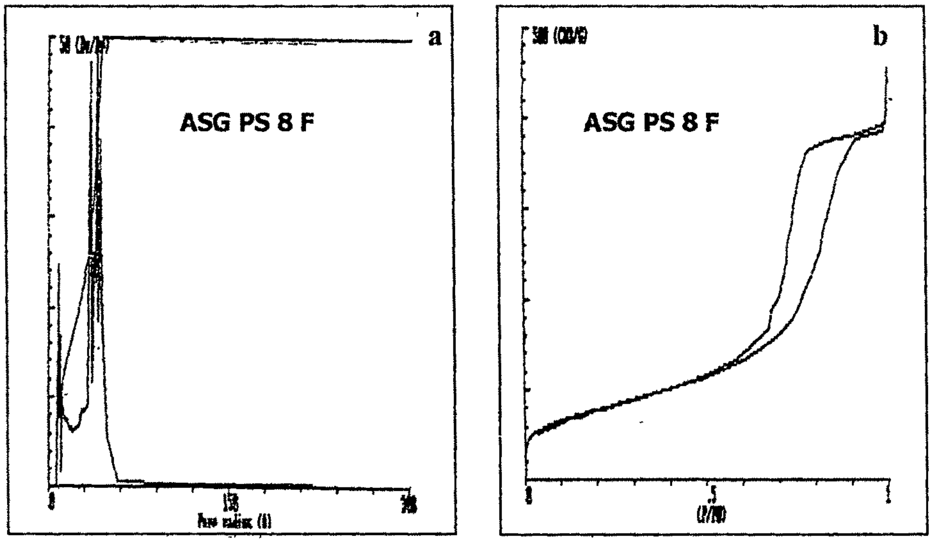


Figure 5.7: A SG PS 8 (a) Pore Size Distribution Curves for filtered series (b) Hystersis Loop Forms for filtered

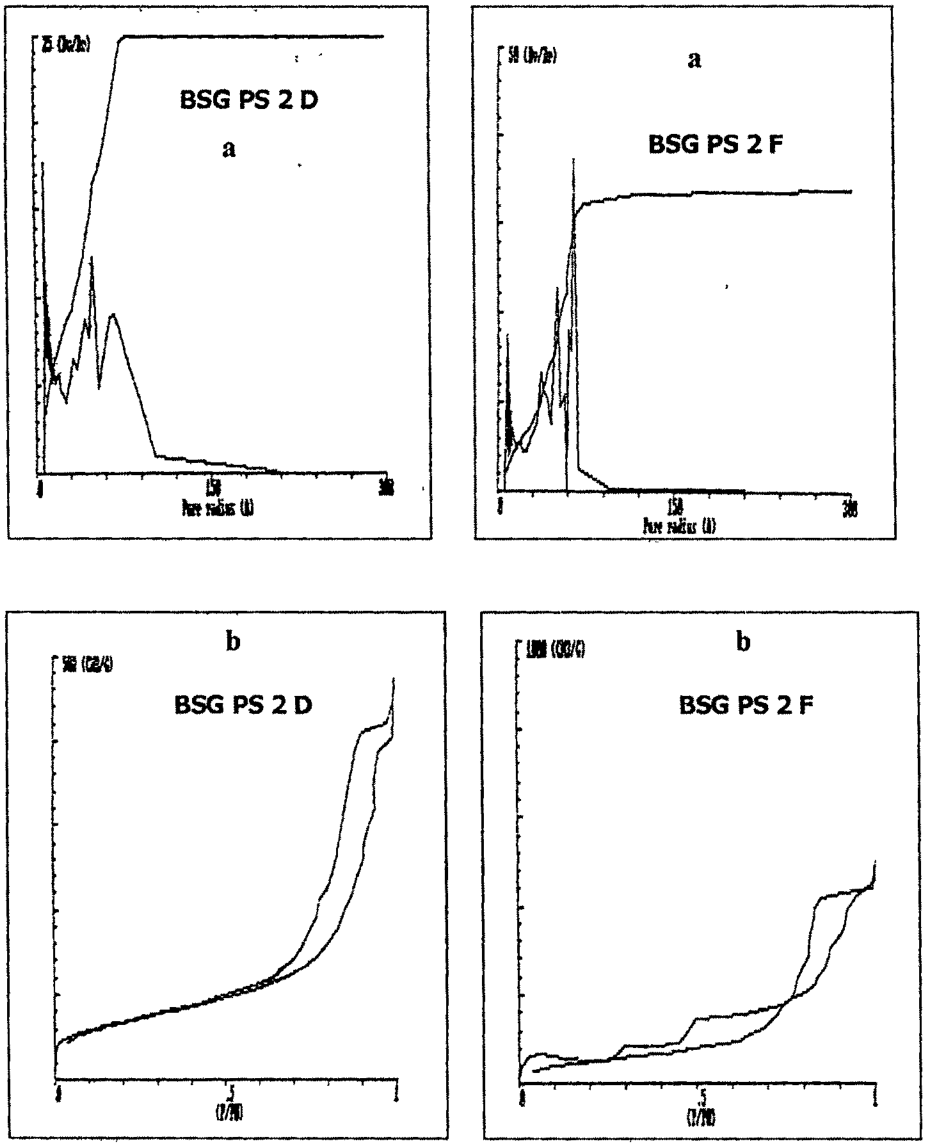


Figure 5.8: BSG PS 2 (a) Pore Size Distribution Curves for filtered and distilled series (b) Hystersis Loop Forms for filtered and distilled series

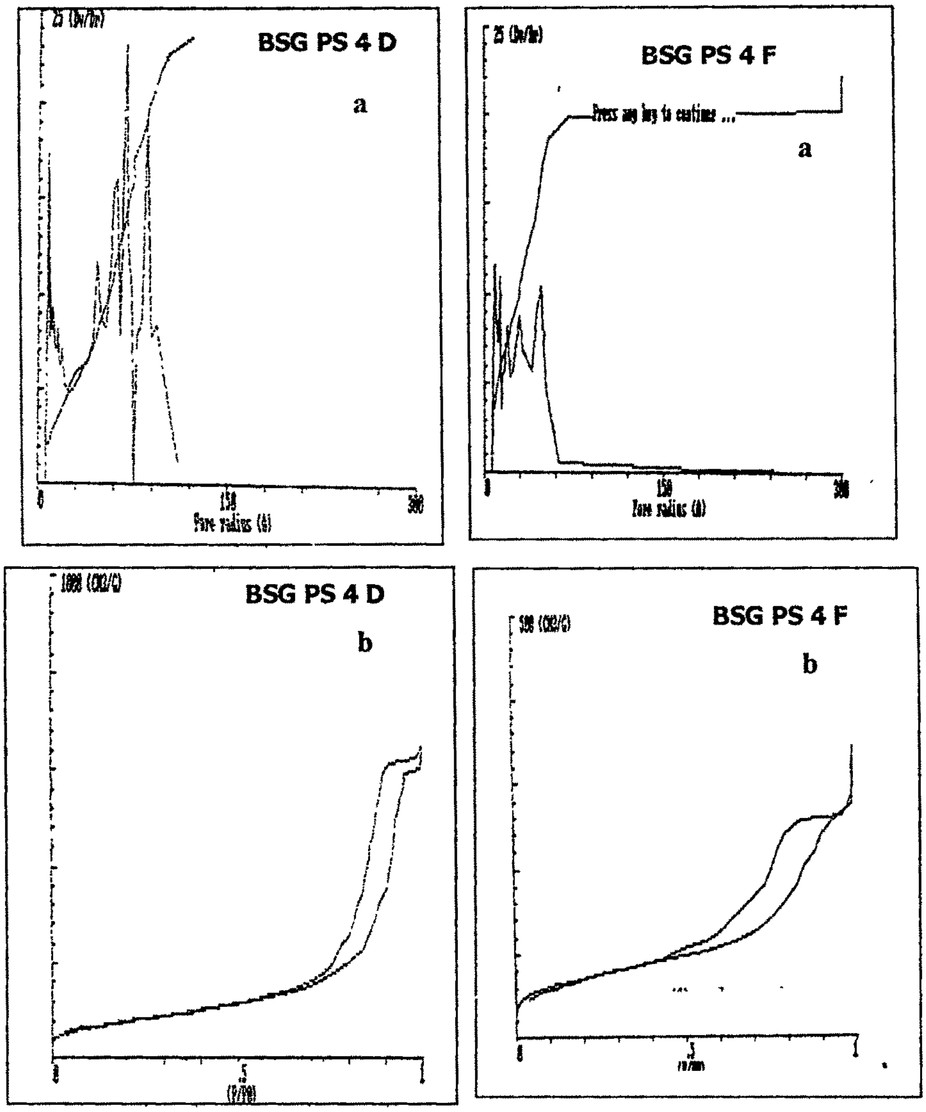


Figure 5.9: BSG PS 4 (a) Pore Size Distribution Curves for filtered and distilled series (b) Hystersis Loop Forms for filtered and distilled series

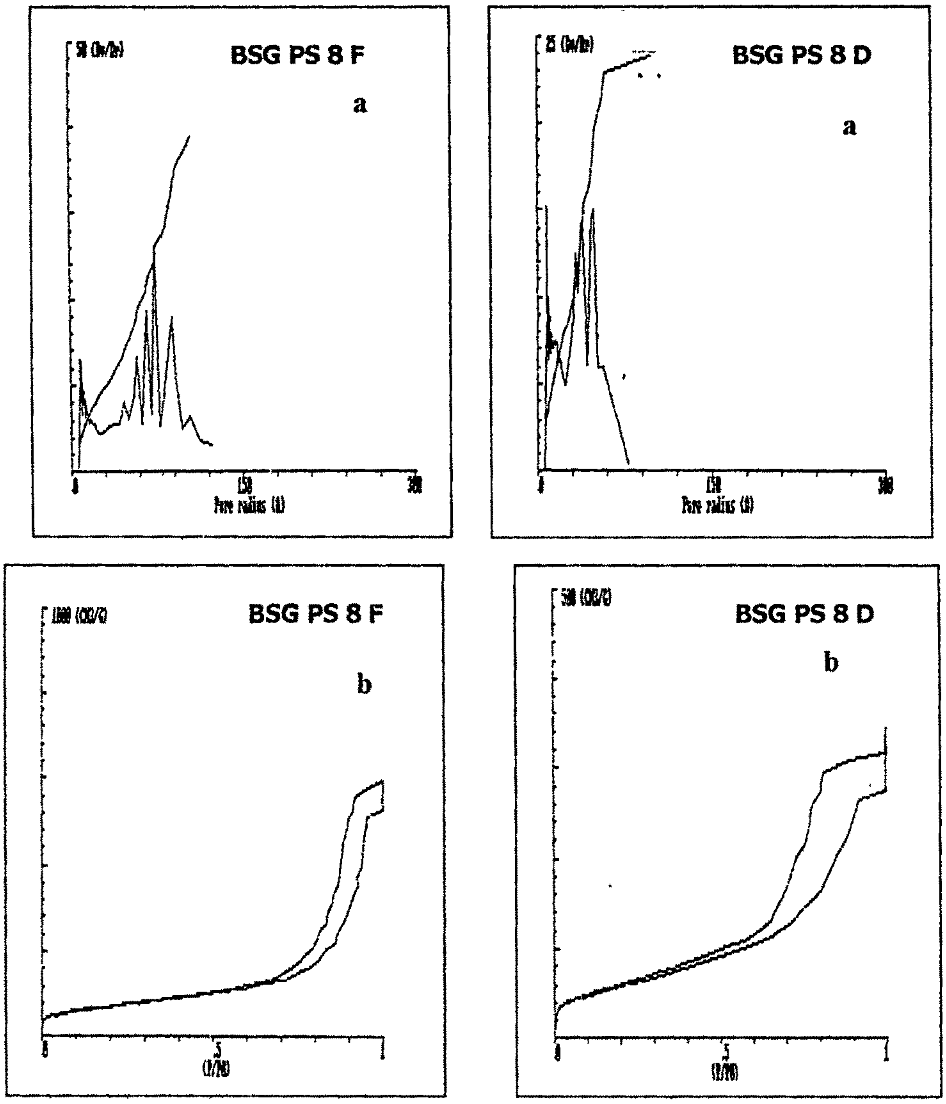


Figure 5.10: BSG PS 8 (a) Pore Size Distribution Curves for filtered and distilled series (b) Hystersis Loop Forms for filtered and distilled series

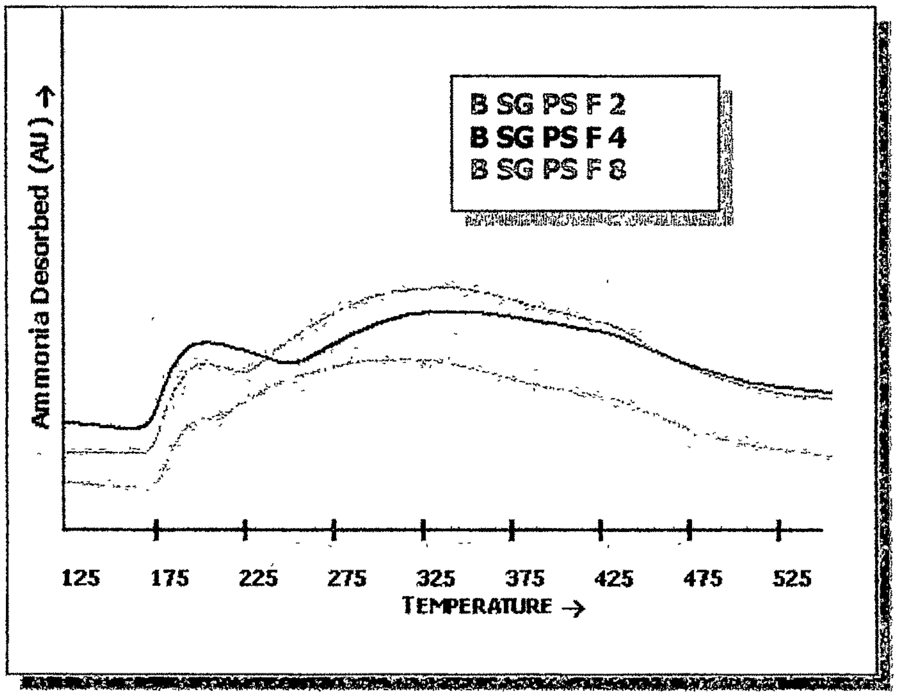


Figure 5.11 a Ammonia TPD Plots of MONOFUNCTIONAL BSG F catalysts

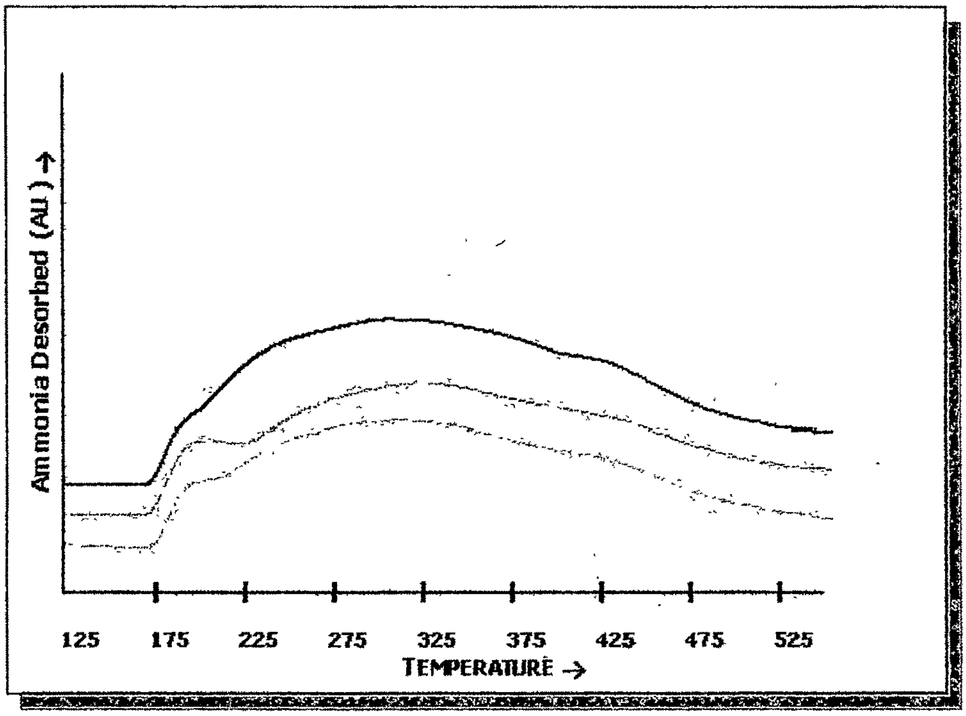


Figure 5.11 b Ammonia TPD Plots of MONOFUNCTIONAL BSG D catalysts

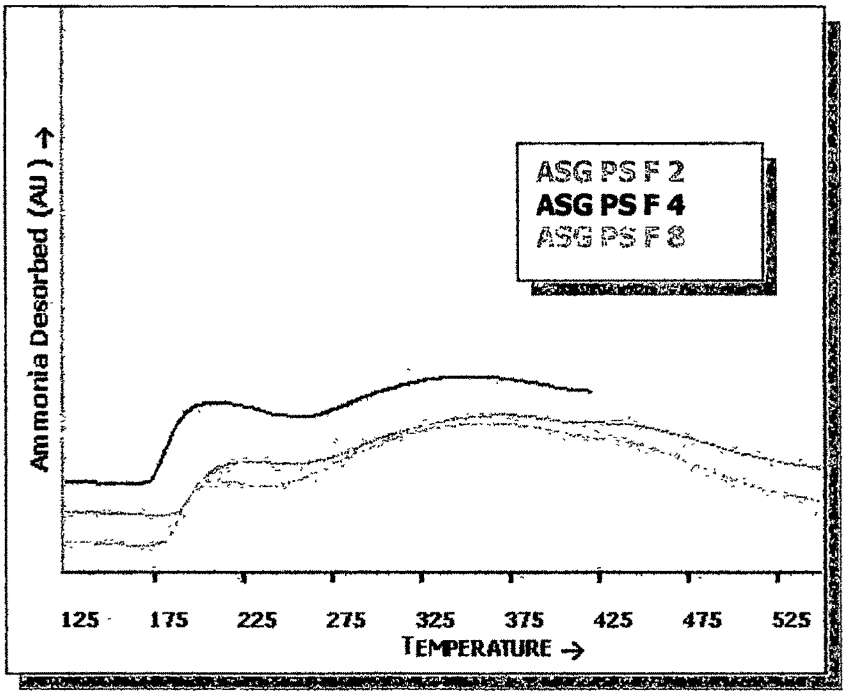


Figure 5.11 c Ammonia TPD Plots of MONOFUNCTIONAL ASG F catalysts

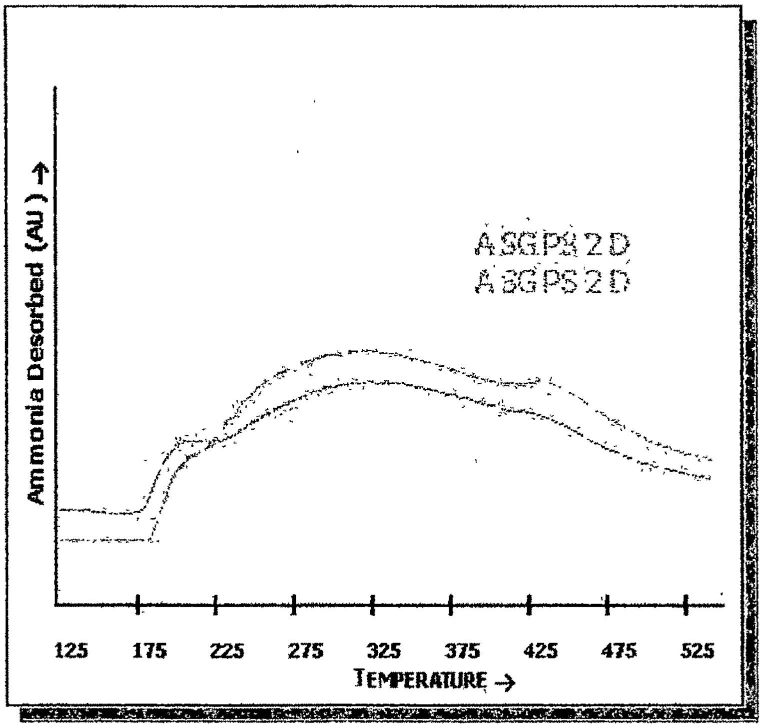


FIGURE 5.11 d Ammonia TPD Plots of MONOFUNCTIONAL ASG D catalysts

Surface area, pore volume, and pore size data and analyses of the shapes of isotherm, hysteresis loops and pore shape for monofunctional catalysts are presented in Table 5.3. Pore size distribution curves, and types of adsorption-desorption isotherms and hysteresis loops are given in fig 5.5 to fig 5.10. It is observed that subtle variations in preparation methods reflect significantly in the textural properties.

One significant observation is that most of the samples prepared through distillation (D) route exhibit higher surface area, pore volume and mean pore radius compared to those obtained though filtration (F) route. This is due to the presence of n-butanol solvent within the pores of D samples during the drying process, which retards pore collapse. In the case of F samples the solvent is removed during filtration by applying vacuum and during subsequent drying process, collapse of the pores is likely. Pores are predominantly meso porous and bimodal in nature, except for (ASGPS2D). Predominantly meso porous nature of the samples is well- supported by the type of adsorption isotherms observed, which is Type IV, as per the classical Brunauer's concept.

Hysteresis loop types have been analyzed on the basis of the two-fold description of the pore structure put forward by Salmones et al **(10)**. In ASG series at low Sn/Pt ratio Type II hysteresis form is observed. With increasing Sn/Pt ratio, it changes to Type III and Type IV. In BSG series, the corresponding change is from Type III to Type IV.

Presence of some amount of micro pores is noted in many cases, more so in the case of ASG series compared to BSG. This is also reflected in the values of mean pore radius, which is relatively low for ASG samples. While an increase in mean pore radius with respect to Sn/Pt ratio could be seen in the case of ASG series, no such trend could be seen with BSG samples. BSG catalysts display relatively higher pore volume compared to ASG series. Such an effect of pH has also been observed in the case of alumina samples in Chapter 4. Another general observation is that pore size distribution is relatively narrow in the case of ASG series compared to BSG.

5.3.4. Acidity

Uptake of ammonia at 100^{0}C for various monofunctional catalysts are given in Table 5.4 and the corresponding TPD curves are shown in fig 5.11. TPD patterns indicate that acid sites of weak and medium strength are available in both ASG and BSG series but the presence of strong acid sites beyond 425^0 C clearly seen with ASG series of catalysts. Ammonia uptake values show a distinct parabolic trend with respect to Sn/Pt atomic ratio whether the catalysts are obtained by distillation or filtration route. However no specific correlations between preparation methods (ASG/BSG or D/F) and acidity could be observed. It appears that the attenuation of the acidity by Sn takes place up to a certain loading beyond which the nature of interaction between Sn and alumina changes leading to increase in overall acidity.

Table 5.4: Ammonia TPD values for catalysts prepared by sol gel route

Catalyst	Ammonia uptake mmole/g
ASGPS2D	0.52
ASGPS4D	0.35
ASGPS8D	0.46
BSGPS2D	0.48
BSGPS4D	0.38
BSGPS8D	0.51
ASGPS2F	0.44
ASGPS4F	0.46
ASGPS8F	0.65
BSGPS2F	0.77
BSGPS4F	0.41
BSGPS8F	0.49

In the case of bifunctional (distilled) catalysts butene-1 isomerisation reaction was used to study the acidity and the data are presented in Table 5.5.

Table.5.5: Acidity measurements on bifunctional sol-gel (D series) catalysts

Catalyst	1-C_4 Conversion (%)	i-C_4 Conversion (%)	Cis:Trans 2-C_4
BSGPS2BD	43.7	0.67	1.21
BSGPS4BD	19.8	1.03	1.39
BSGPS8BD	31.2	0.72	1.14
ASGPS2BD	24.41	0.76	1.44
ASGPS4BD	22.19	1.10	1.45
ASGPS8BD	31.00	0.72	1.20

In the case of BSG series a clear parabolic relation is evident between conversion of 1-butene and the Pt:Sn mole ratio of the catalyst. Activity for skeletal isomerisation is low but shows a hyperbolic trend with Pt:Sn mole ratio. Double bond isomerisation activity exhibits a pronounced hyperbolic trend with Pt:Sn mole ratio of the catalyst.

Similarly for ASG series too, conversion of 1-butene shows a slight parabolic relation with Pt:Sn mole ratio, similar to that observed in the BSG series. The skeletal isomerisation activity is low but shows a hyperbolic relationship with Pt:Sn mole ratio, also similar to that observed in the BSG series. Double bond isomerisation activity is comparable for Pt:Sn 2 and 4 (as seen by Cis:Trans ratio in 1-C_4 isomerisation) but decreases sharply at Pt:Sn 8. Similar trends are observed for bifunctional catalysts prepared by filtration route.

As observed with monofunctional catalysts, no specific trend could be noticed between preparation methods and acidity.

Between ASG and BSG Series of catalysts, BSG Series (except catalyst BSG-PtSn4) shows distinctly lower activity for double bond isomerisation (as evidenced by the lower Cis:Trans ratio) and skeletal isomerisation than the ASG series.

In the case of bifunctional catalysts residual chloride content could influence the acidity. The residual chloride content of the different bifunctional catalyst samples is given in Table 5.6 below.

Table.5.6: Residual Chloride content of bifunctional catalysts (Distilled)

Sr No	Catalyst Sample	Sn:Pt	Residual chloride (wt%)
1.	ASG-PtSn2	2	0.6
2.	ASG-PtSn4	4	1.1
3.	ASG-PtSn8	8	1.2
4.	BSG-PtSn2	2	0.4
5.	BSG-PtSn4	4	1.0
6.	BSG-PtSn8	8	0.8

ASG series of catalysts exhibit an increasing trend in residual Chloride content with Sn:Pt ratio. Since Chloride (as HCl) used in preparation of the catalysts was kept constant at 2 wt% on the weight of the final catalyst the difference in chloride content could either be due to contribution from the precursor salt of Sn i.e. $SnCl_2.2H_2O$ or the ability of the Sn incorporated Al_2O_3 to retain relatively higher chloride.

The BSG series too show an increase in residual chloride content with Sn:Pt increase from 2 to 4, but appears to level off or decrease slightly thereafter. The contribution to differential chloride within the series has to be from $SnCl_2.2H_2O$ or the H_2PtCl_6 (Pt precursor) since no additional HCl was used in this case.

Between the series ASG catalysts have a higher residual Chloride content than the BSG catalysts of comparable Sn:Pt ratio. Possibility of Chloride loss exists in the case of BSG catalysts during drying / calcination since NH_3 was used as the base catalyst and in the event of NH_4Cl formation it may sublime during heat treatment.

In the case of monofunctional catalysts, residual chloride levels are typically less than 0.1% and the acidity observed in these catalysts are inherent.

Irrespective of the method of preparation, Sn loading and presence of residual chloride govern acidity of Pt-Sn sol-gel catalysts.

5.3.5. Temperature Programmed Reduction

This technique is used frequently to establish the reducibility/ dispersion of various metals present and to study various interactions existing among the active metals present and with support **(11, 12)**.

TPR patterns for sol gel catalysts (ASGPS X D, ASGPS X F, BSGPS X D, and BSGPS X F, where X= 0, 2, 4 and 8) bifunctional as well as mono-functional,

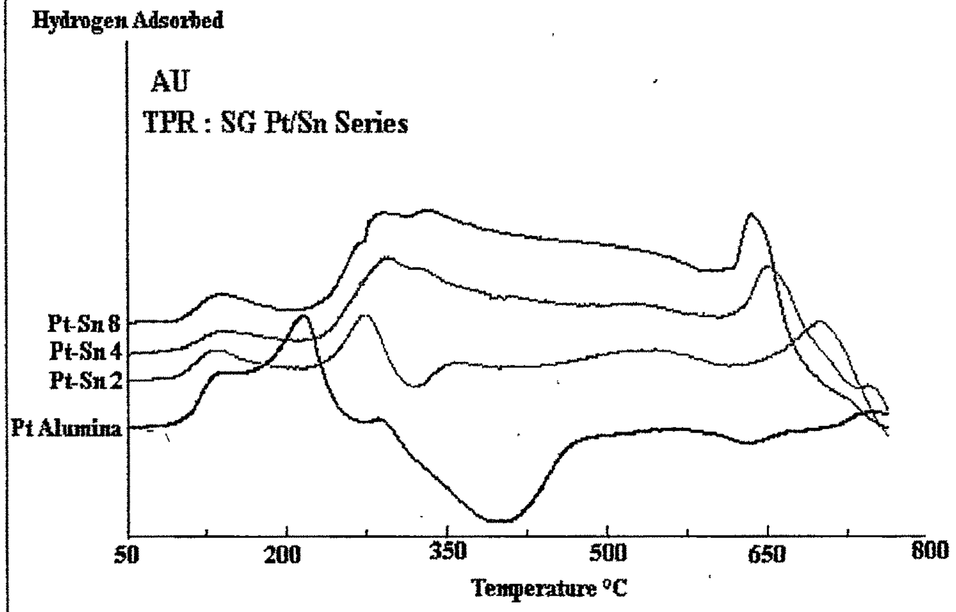


Figure 5.12 a : Temperature Programmed Reduction profiles of Bifunctional A SG D

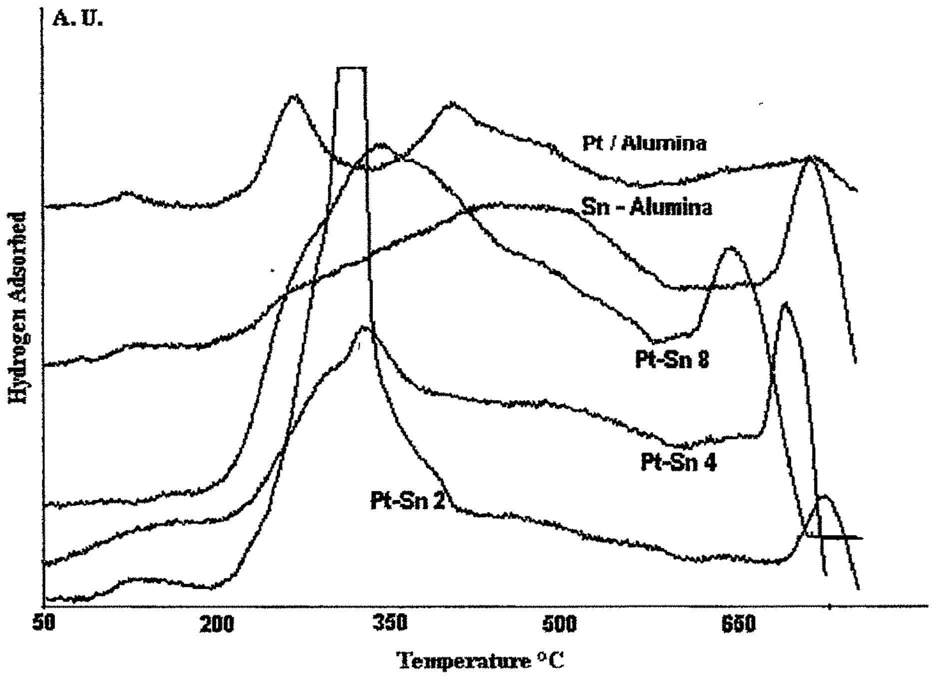


Figure 5.12 b : Temperature Programmed Reduction profiles of Bifunctional B SG D

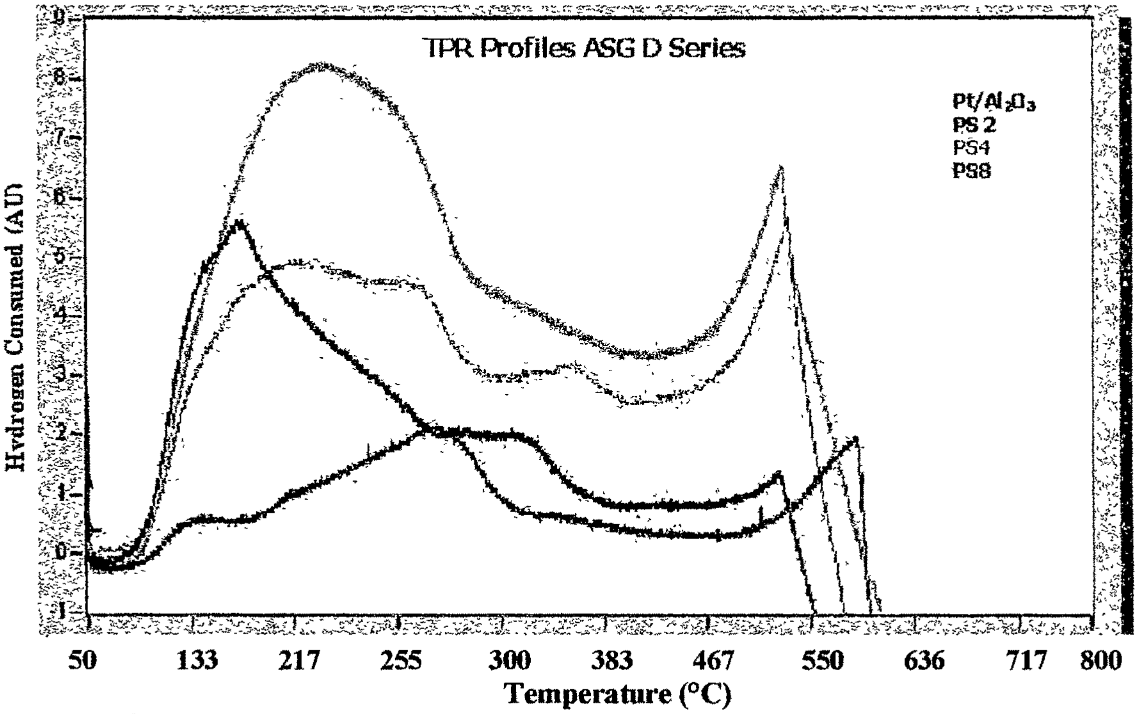


Figure 5.13 a : Temperature Programmed Reduction profiles of Monofunctional A SG D series

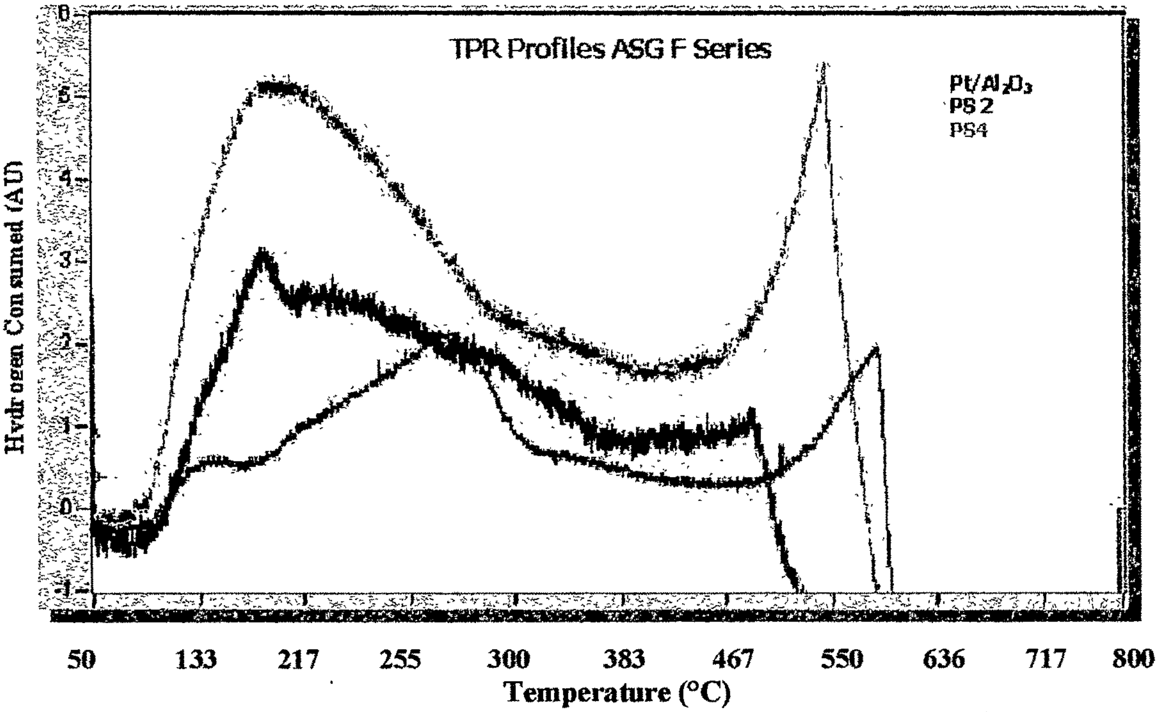
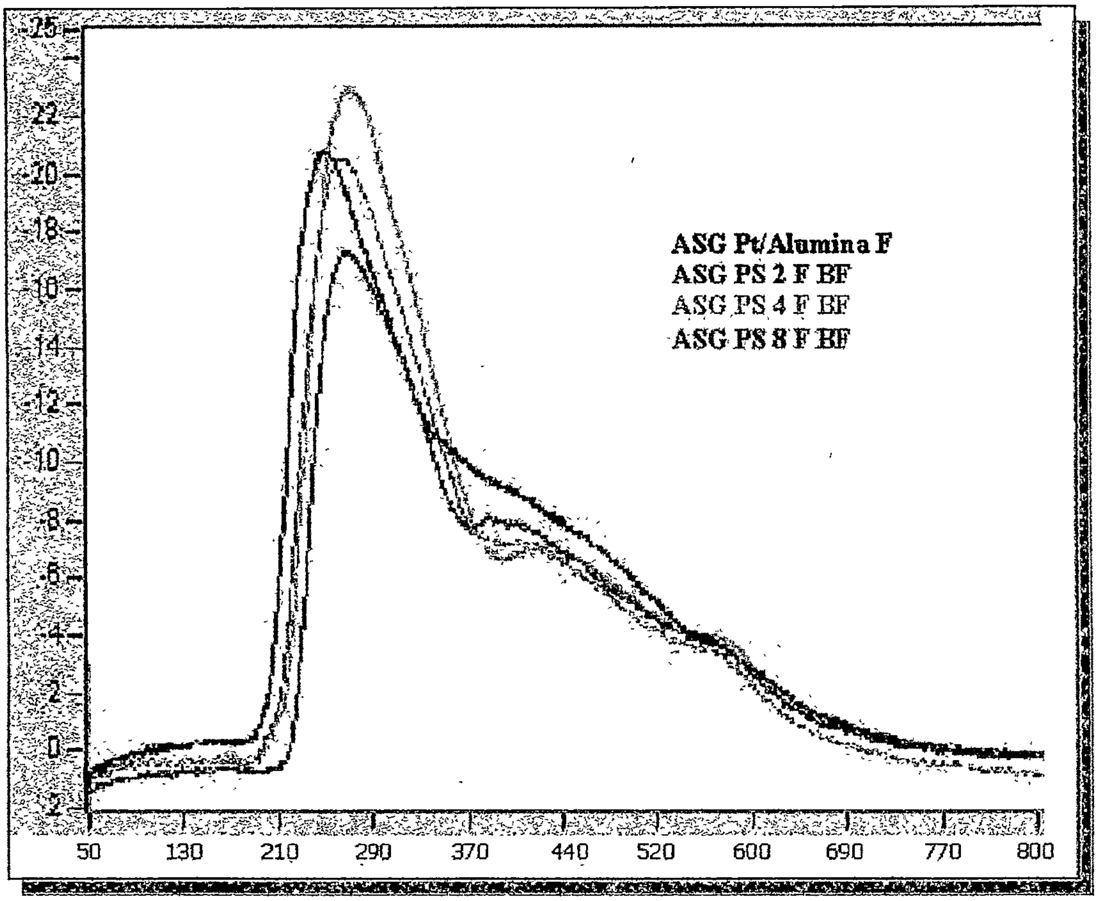


Figure 5.13 b : Temperature Programmed Reduction profiles of Monofunctional A SG F series



5.14 a : TEMPERATURE PROGRAMMED REDUCTION PROFILES OF BIFUNCTIONAL A SG F SERIES

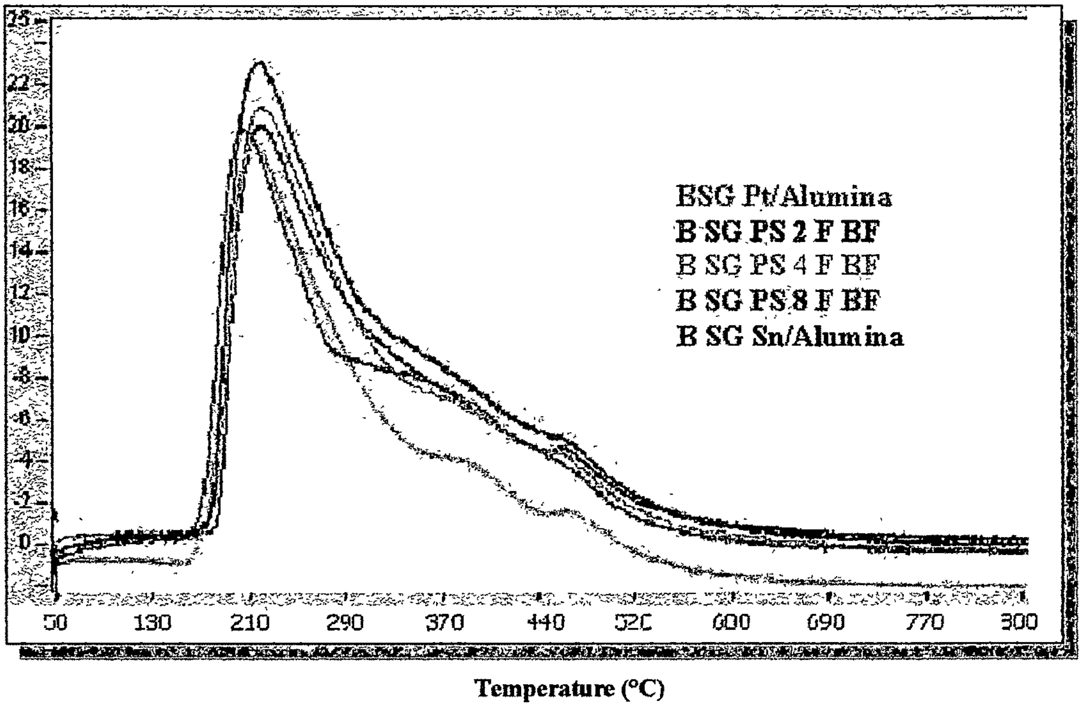


Figure 5.14 b: TEMPERATURE PROGRAMMED REDUCTION PROFILES OF BIFUNCTIONAL B SG F SERIES

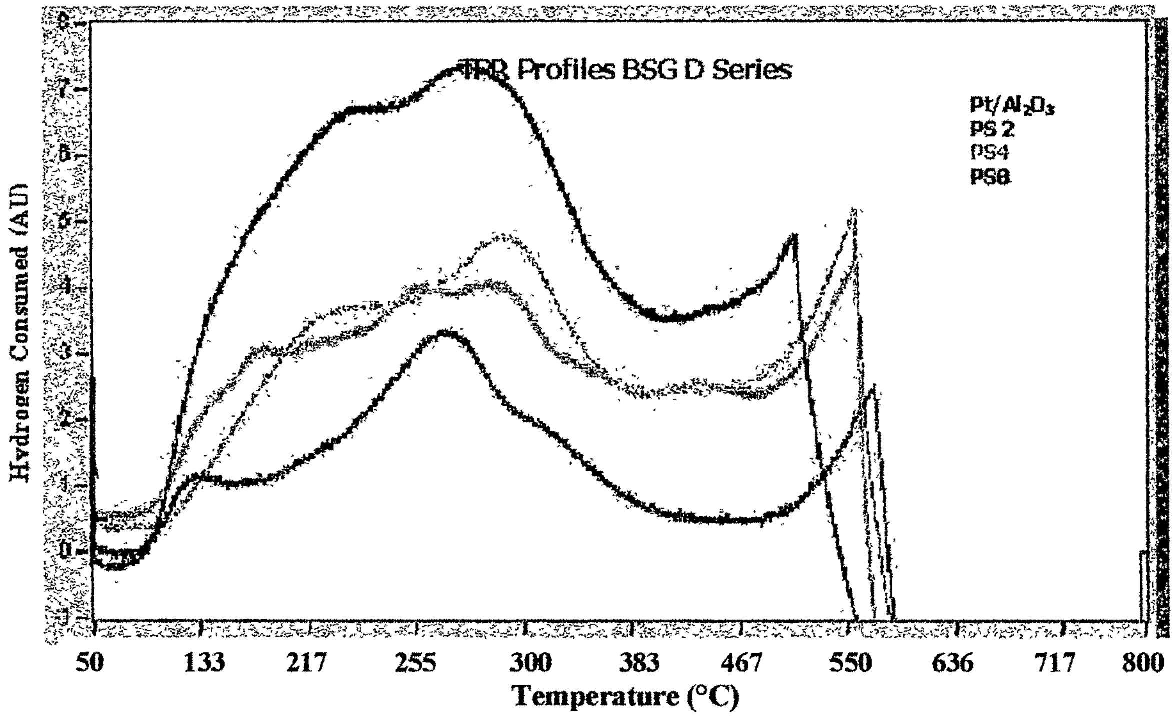


Figure 5.15 a : Temperature Programmed Reduction profiles of Monofunctional b SG D series

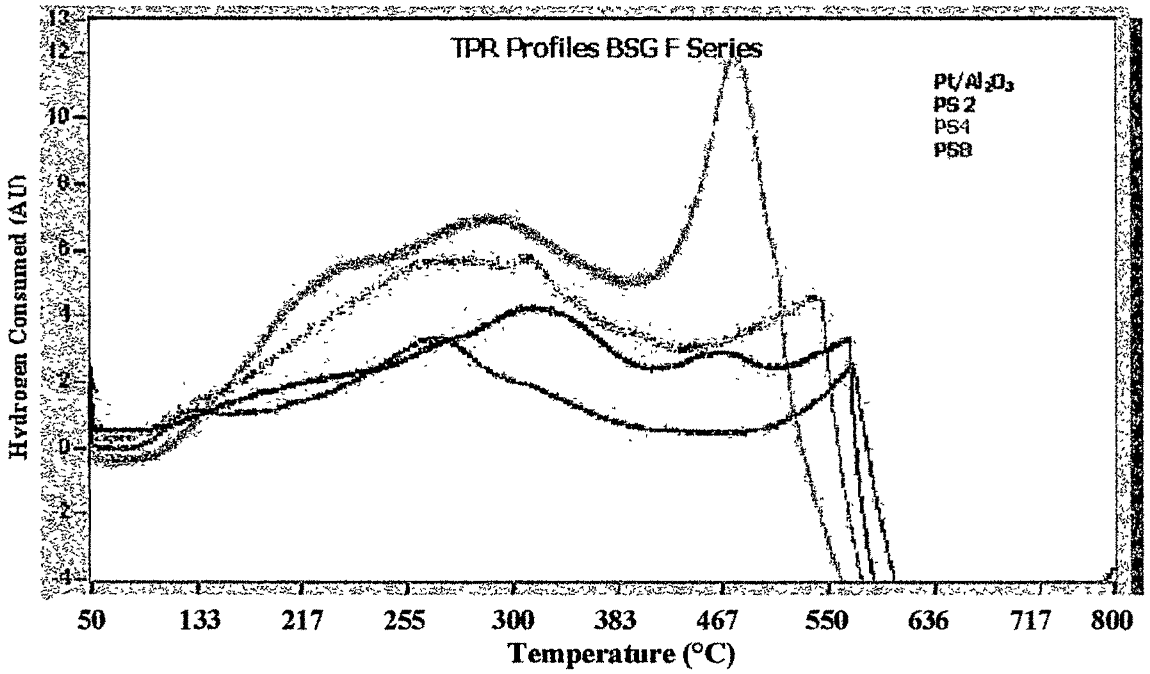


Figure 5.15 b : Temperature Programmed Reduction profiles of Monofunctional b SG f series

as presented in Fig 5.12 to 5.15 are broad in nature, indicating the presence of several reducible phases. Reduction peaks corresponding to free Pt oxide (in the temperature range 100-200^{0}C and indicative of poor interaction with the support), simultaneous reduction of well dispersed Pt and Sn (200-400^{0}C) and Sn bound to alumina (400-700^{0}C) are observed. While the reduction peak corresponding to Pt oxides does not shift significantly with respect to different samples, other two peak maxima show considerable shift from case to case. Within the assigned temperature range of 200-400^{0}C for simultaneous Pt and Sn reduction, a shift towards higher temperature is indicative of weaker Pt-Sn interaction, while a shift towards lower temperature, relatively stronger interaction. Similarly variations in T_{max} in the range 400-700^{0}C for reduction of alumina bound Sn, is also an indication of the extent of Sn – support interaction.

In the case of ASGPSXBD series it is observed that that interaction of Sn with the support is stronger than with Pt **(13)**. The existence of free platinum oxide as well as Sn bound to support, are indicative of this phenomenon. While the intensity of the peak due to alumina bound Sn increases with Sn content, T_{max} values shift towards lower temperature indicating that at higher Sn loading the interactions between Sn and alumina are perhaps weaker.

In BSGPSXBD series, the presence of platinum oxide is at moderate level. But the extent of Sn – Al_2O_3 interaction is relatively high. As seen in the case of ASGPSXBD series, in this case too, the nature of interaction of Sn with alumina, as indicated by T_{max} and intensity, varies with Sn content. Both series of catalysts display TPR maxima due to simultaneous reduction of Pt and Sn, whose intensity increases with Sn. Significance of a sharp peak due simultaneous reduction of Pt and Sn at Sn/Pt=2 is not known at present.

Bifunctional catalysts ASGPSXBF and BSGPSXBF, obtained through filtration process (F) possess less free Pt oxides compared to respective monofunctional ones. It is known that residual chloride retards the reduction of Pt and this facilitates reaction between Pt and Sn resulting in relatively less free Pt oxide. This would also mean less of Sn is available for interaction with support. It should also be kept in mind that the loss of Pt and Sn through filtration is more than that observed for catalysts prepared via distillation route. However, overall reducibility does not change with Sn/Pt atomic ratio.

In the case of monofunctional ASG and BSG series, as expected, presence of free Pt oxide and increase in reducibility with Sn/Pt atomic ratio are the common features. With respect to the reduction peak for Pt in corresponding monometallic catalysts, in BSG, simultaneous reduction of Pt and Sn occurs at higher temperature, while in ASG series, it is observed at lower temperature. This would mean that Pt-Sn interactions are stronger in the ASG series.

Bettcher et al **(5)** have studied the TPR of Pt-Sn/Al_2O_3 catalysts prepared by single step and two step SG method and have concluded that the patterns are complex. The catalyst composition (Pt, Sn and residual chloride contents) as well as preparation methods have been varied simultaneously. It appears that free Pt oxide content is relatively higher in two-step method (A). While only one low temperature peak due to Sn on alumina is seen with single step method (B), an additional high temperature peak is observed with two-step method (A), which incidentally has higher Sn content too. Considering the levels of residual chloride content (0.45 and 0.65%) the catalysts could be considered as bifunctional. In spite of such differences, the overall TPR patterns observed in the present work are similar to those reported by Bettcher et al **(5)** for SG catalysts.

Thus TPR studies clearly establish the complex relationship between preparation methods and interactions within the active phase and that with the support.

5.3.6. Metal dispersion

Results on metal dispersion measurements carried out by H_2-O_2 titration at 25°C and at 150°C on all the catalysts are tabulated in Table 5.7 According to the method developed by Rajeshwer et al **(14)** alloyed and unalloyed components of Pt and Sn computed separately are presented in the table.

Table 5.7: Platinum Dispersion results

Catalyst	Sn/Pt mole ratio	Bifunctional				Monofunctional			
		% Pt(T)	% Pt (U)	% Pt (A)	% Sn (A)	% Pt(T)	% Pt(U)	% Pt (A)	% Sn(A)
ASG PS 0 D	0	33	33	0	0	45	45	0	0
ASG PS 2 D	2	66	32	36	16	68	30	40	18
ASG PS 4 D	4	44	20	21	11	60	28	31	15
ASG PS 8 D	8	41	18	20	6	56	28	23	10
ASG PS 0 F	0	40	40	0	0	39	39	0	0
ASG PS 2 F	2	51	22	26	18	75	32	36	18
ASG PS 4 F	4	60	30	29	13	58	30	21	13
ASG PS 8 F	8	48	26	20	8	68	38	20	8
BSG PS 0 D	0	34	34	0	0	48	48	0	0
BSG PS 2 D	2	53	25	26	14	71	30	40	15
BSG PS 4 D	4	69	31	35	11	50	28	31	12
BSG PS 8 D	8	42	21	23	5	46	28	23	8
BSG PS 0 F	0	31	31	0	0	36	36	0	0
BSG PS 2 F	2	30	20	10	13	51	20	30	16
BSG PS 4 F	4	36	16	17	11	57	18	36	13
BSG PS 8 F	8	48	19	28	8	58	17	40	10
IMP PS 0	0	53	50	0	0	46	48	0	0
IMP PS 2	2	86	42	44	21	75	40	45	25
IMP PS 4	4	95	42	53	13	80	39	51	26
IMP PS 8	8	106	38	68	8	82	34	69	32

It is observed that all SG catalysts, mono or bifunctional, D or F display less metal dispersion compared to those prepared by conventional impregnation method and using oil drop alumina (IMP series).

While there is no clear trend in dispersion with increase in Sn/Pt atomic ratio for all SG catalysts, IMP series catalysts display regular increase in dispersion with Sn/Pt. Sn (A), alloyed Sn component is less in the case of SG catalysts indicating that most of Sn has interacted with the support. Consequently the availability of Sn for forming small Pt ensembles is less and hence the dispersion of Pt. In the case of bifunctional catalysts, ASG series, D or F display better dispersion compared to BSG series. In the case of monofunctional catalysts, both ASG and BSG series of catalysts exhibit comparable Pt dispersion.

For the BSG series, where synthesis is base catalyzed (pH = 10), the Pt – Sn complex precursor itself will not be stable resulting into a low or no Pt – Sn interaction. This instability results into the formation of the respective hydroxides of Pt and Sn. In the ASG series, at pH = 3, the Pt – Sn complex is pretty stable and hence good interaction.

Another significant observation is that while IMP series display proportional increase in dispersion with Sn loading, in the case of SG catalysts, Sn addition does not have significant effect on Pt dispersion except for an initial addition

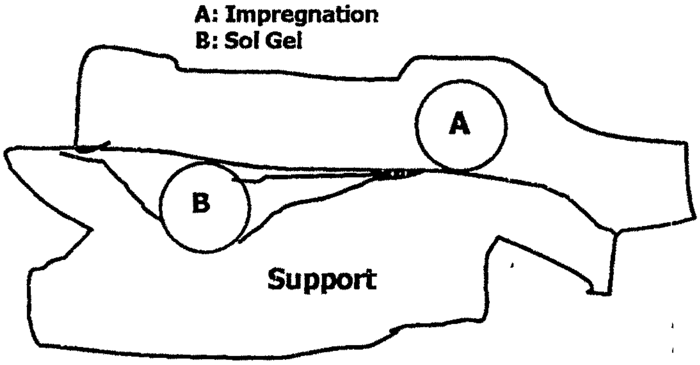


Fig 5.16: A Schematic representation of two possible configurations of the metal particles with respect to the support.

Gomez et al **(1)** observed an increase in Pt dispersion in the case of Pt-Sn/Al_2O_3 catalysts prepared by SG route, vis-à-vis catalysts prepared by the co-impregnation method. As mentioned earlier in this Chapter, Gomez et al prepared the SG catalysts by two-step method, first preparation of Sn-alumina by SG route followed by conventional impregnation of Pt on it. From the same school of research, Lopez et al **(15)** have shown that preparation of Pt/SiO_2 by single step method, i.e., addition of Pt precursor to silica precursor prior to hydrolysis, leads to encapsulation of Pt by silica resulting in less dispersion.

Balakrishnan and Gonzalez **(2)**, have also prepared the catalysts by single step SG method but have not discussed the dispersion of conventional Vs SG catalysts. Bettcher et al **(5)** have prepared Pt-Sn/Al_2O_3 catalysts by both one step and two step sol-gel methods and have observed that the two step method yields catalysts with better dispersion. However both Bettcher et al **(5)** and Sault et al **(6)** claim that Pt is accessible completely, irrespective of whether the catalyst is prepared by single or two- step method.

In the present case, catalysts have been prepared by single step method, and SG catalysts display relatively less dispersion. Encapsulation of Pt by the support as visualized in fig 5.16 and/or decoration of Pt by Sn could be responsible for the observed low dispersion. The method adopted in the current work for dispersion measurement, gas chemisorption, may not be suitable in such cases since the metal crystallite may not be completely accessible.

5.4. Summary

Sol-gel method of preparation of alumina supported Pt-Sn catalysts by single step method has been studied by varying several preparation conditions

It is observed that subtle variations in preparation methods significantly affect the textural properties of the catalysts as revealed by surface area, pore volume, pore size distribution, pore shape, and nitrogen adsorption-desorption isotherms and hysteresis loop analysis data. Catalysts prepared via distillation route offer better textural characteristics compared to those obtained via filtration route adopted for separation of gels from mother liquor

Sn/Pt atomic ratio and residual chloride levels in the catalysts play a major role in evolution of acidity of SG catalysts as investigated by butene-1 isomerisation and temperature programmed desorption of ammonia

Variations in preparation methods significantly influence the Pt metal dispersion, Pt-Sn interaction and Sn-support interactions as revealed by metal dispersion measurements by chemisorptive titration and temperature programmed reduction studies.

Pt dispersion for SG catalysts is observed to be less than those observed for catalysts obtained by conventional impregnation methods. Encapsulation of Pt crystallites by support, decoration of Pt by Sn and more favorable interaction of Sn with alumina could be the possible reasons for low dispersion values displayed by SG catalysts.

Controversy regarding the influence of SG preparation method, single step or double step on the metal dispersion remains unsolved.

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