CHAPTER 7

INFLUENCE OF PREPARATION METHODS ON THE PROPERTIES AND PERFORMANCE OF CATALYSTS

7. Influence of Preparation Methods on the Properties and Performance of Catalysts

This Chapter details the influence of catalyst preparation methodology on its final performance. Activity, selectivity & stability are the three major attributes focused upon. Attempts have been made to correlate the catalytic performance with metal dispersion, deactivation, etc.

7.1. Role of preparation methods

The major attributes of an ideal catalyst are activity, selectivity, stability, regenerability and mechanical and thermal stability. In the case of supported metal catalysts in general and especially for application in dehydrogenation of paraffins, (when chemical composition and dehydrogenation process conditions are optimized and fixed), these attributes emanate from a set of desired properties of the catalysts as described below:

Table 7.1 Major attributes and properties of supported metal catalysts

Attributes	Properties
Activity	Metal dispersion, M-M and M-S interactions
Selectivity	M-M and M-S interactions, acidity, pore structure (for facile diffusion of reactant and products)
Stability/resistance to deactivation	M-M and M-S interactions, acidity, pore structure (to minimize coking)
Thermal and mechanical stability	Crystalline phase of support, porosity, resistance towards sintering

(M- metal, S-support)

All the desired properties of the catalysts are acquired during preparation and hence preparation forms the origin of any type of basic or applied research in catalysis. While the correlations between preparation- properties –performance help in establishing basic concepts/theories that help to understand catalysis in a better perspective, they also form the basis for the design and development of superior catalyst formulations that are so vital for the chemical industry as a whole.

7.2. Preparation Vs Properties

Detailed studies on preparation and characterization of catalysts as described in Chapters 5 and 6 have brought out several distinguishing features in the characteristics between the catalysts prepared by conventional impregnation and sol-gel methods (Table 7.2). Sol-gel catalysts have been grouped together though the subtle variations in preparation conditions like pH during hydrolysis (acidic or basic) and mode of removal of solvent after the formation of gel, either by distillation (D) or filtration (F), lead to changes in the properties.

Table 7.2: Properties of Pt-Sn/Al_2O_3 catalysts prepared by conventional and sol-gel methods

Property	Conventional catalysts	Sol-gel catalysts
Nature of crystalline phase	γ-alumina with better crystallinity, larger crystallite size	Highly amorphous γ-alumina, smaller crystallite size
Textural Characteristics	SA- 160-170m^2/g, PV-0.6-0.7 ml NTP/g, MPR- 80-90Å, meso porous, broad size distribution	SA-200-300m^2/g, PV- 0.4-0.9ml NTP/g, MPR-40-70Å, micro+ meso porous, narrow size distribution
Acidity	0.4-0.7 millimole/g of ammonia	0.4-0.8 millimoles/g of ammonia
Active phase Composition	No loss during preparation	Measurable loss during preparation
Metal dispersion	Better dispersion (50-100%) Increases with Sn content	Less dispersion (30-75%) Does not depend on Sn content
M-M and M-S interactions-TPR	M-M (Pt-Sn) interactions more prominent	M-S (Sn-S) interactions more prominent

(SA-surface area, PV-pore volume, MPR-mean pore radius, M-metal, S-support)

ASG series of catalysts obtained by distillation routes offer better textural characteristics, metal dispersion and Pt - Sn interactions while corresponding BSG series offer better attenuation of acidity and higher level of interaction between tin and support. Variations in mode of solvent removal by distillation (D) route leads to improved textural characteristics and minimum loss of active metals compared to filtration (F) route. Invariably such changes in the properties are bound to affect the performance of these catalysts for the proposed model reaction, i.e.., dehydrogenation of n-decane

7.3. Evaluation of catalytic activity for dehydrogenation of n-decane

7.3.1. Methodology

Details of experimental conditions for evaluation of catalysts are given in Chapter.3 Evaluation studies have been carried out with the aim of collecting activity and selectivity data and following the deactivation patterns for all the catalyst systems. Variations in n-decane conversion and selectivity for formation of mono olefins, di olefins, aromatics and cracked products with respect to time on stream (TOS) have been followed by the GC analysis of the product stream. Besides overall conversion and selectivity, TOS data are used to compute initial conversion (expressed as mole% of n-decane converted after one hour stabilization period), Turn Over Frequency (TOF). (a parameter that represents intrinsic activity per site per second), and deactivation rate constants based on Voorhie's equation **(1)**. To elucidate further the aspects of deactivation, analysis of spent catalyst samples for total coke laid down and location of the coke (on the metal/ support sites) have been carried out by TGA. The parameters that represent the performance are then correlated with the relevant properties that are in turn related to various preparation methods/parameters

7.3.2. Correlations with activity

Catalytic activity of all catalysts (expressed as mole % conversion of n-decane after one hour stabilization) is directly related to the respective platinum dispersion value as shown in Fig. 7.1 and 7.2.

Since the dehydrogenation catalysts under goes continuous deactivation the initial n-decane conversion data has been considered to represent catalytic activity. As can be seen from the figures initial conversion and Initial n-decane conversion and platinum dispersion follow more or less the same trend (Table 7.3). A striking feature of this correlation is that it holds good for all the catalysts investigated here, mono or bifunctional and irrespective of variations in preparation methods, ASG/BSG of D/F. This is would mean that activity depends little on the type of the active sites, but directly on the number of available sites. This trend is typical of a structure insensitive reaction and dehydrogenation of paraffins fits in to this category.

Within IMP (mono or bifunctional) series, activity increases with Sn loading, while there is no clear trend in SG catalysts. Possible reason for this may be the different levels of interaction of Sn with support and between Pt and Sn

IMP series exhibit better activity compared to ASG/BSG series. Within SG series ASG displays better activity. No clear trend again with respect to catalysts obtained by distillation or filtration route. This may due to the differences in the levels of Pt retained by different catalysts.

To summarize, mono or bifunctional nature, variations in Sn/Pt ratio and preparation methods (ASG/BSG and D/F) ultimately reflect in Pt dispersion, which emerges as the sole factor responsible for activity

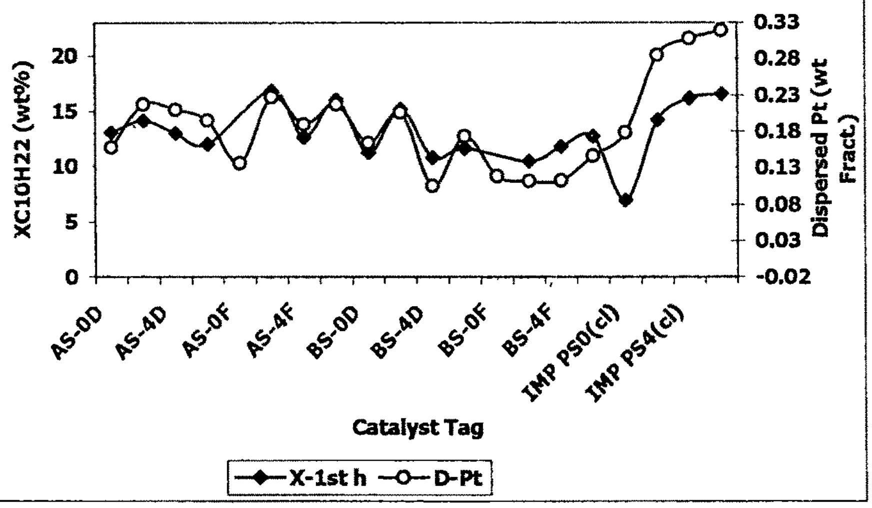


Figure 7.1 Correlation of catalyst activity with Pt dispersion (Monofunctional catalysts)

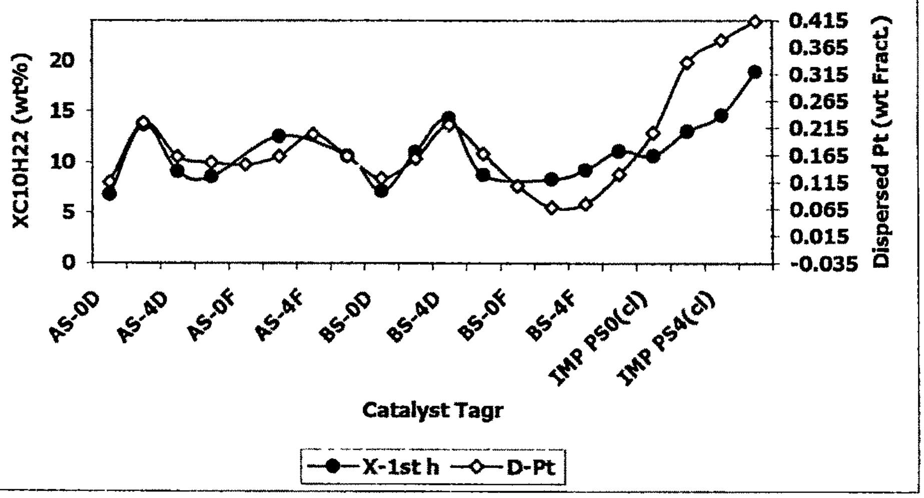


Figure 7.2 Correlation of catalyst activity with Pt dispersion (Bifunctional catalysts)

Table 7.3 First hour activity data for the catalysts prepared by various routes

Monofunctional		**Bifunctional**	
Catalyst	Ist h activity	Catalyst	Ist h activity
ASG PS 0D	13.02	ASG PS 0D	6.77
ASG PS 2 D	14.14	ASG PS 2D	13.69
ASG PS 4 D	12.98	ASG PS 4D	9.08
ASG PS 8 D	11.99	ASG PS 8D	8.55
ASG PS 2 F	16.84	ASG PS 2F	12.54
ASG PS 4 F	12.63	ASG PS 4F	
ASG PS 8 F	15.99	ASG PS 8F	10.60
BSG PS 0 D	11.22	BSG PS 0D	7.13
BSG PS 2 D	15.19	BSG PS 2D	10.98
BSG PS 4 D	10.78	BSG PS 4D	14.31
BSG PS 8 D	11.61	BSG PS '8D	8.74
BSG PS 2 F	10.46	BSG PS 2F	8.28
BSG PS 4 F	11.79	BSG PS 4F	9.21
BSG PS 8 F	12.71	BSG PS 8F	11.08
IMP PS0	6.94	IMP PS 0	10.60
IMP PS2	14.17	IMP PS 2	13.00
IMP PS4	16.16	IMP PS 4	14.60
IMP PS8	16.56	IMP PS 8	18.90

Activity is mole % conversion of n decane

Based on the first hour conversion data, platinum content as estimated in the finished catalyst, reaction conditions and Pt dispersion values, Turn Over Frequency (TOF) for all the catalysts were calculated and plotted against Sn/Pt ratios for different preparation methods. Such trends are shown in Fig.7.3 and 7.4 for mono and bifunctional catalysts. TOF for sol-gel catalysts are slightly higher than their impregnated counter parts indicating that the type of active sites in SG catalysts are different from those in conventional catalysts.

TOF

Figure 7.3: Turn Over Frequency: Monofunctional Catalysts

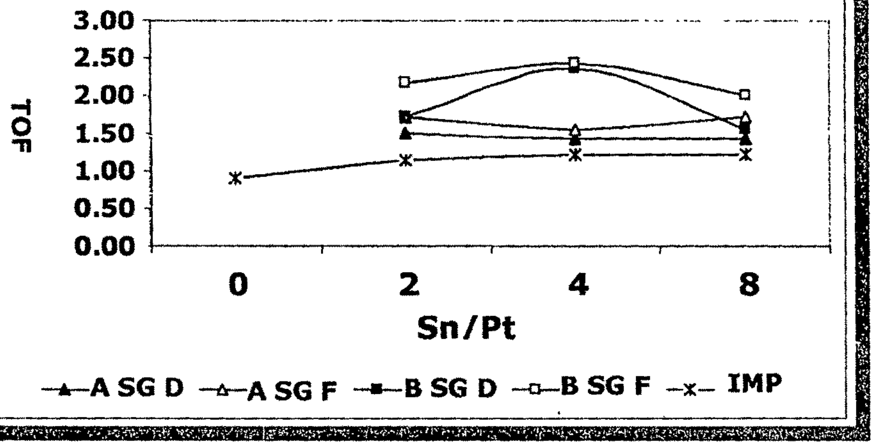
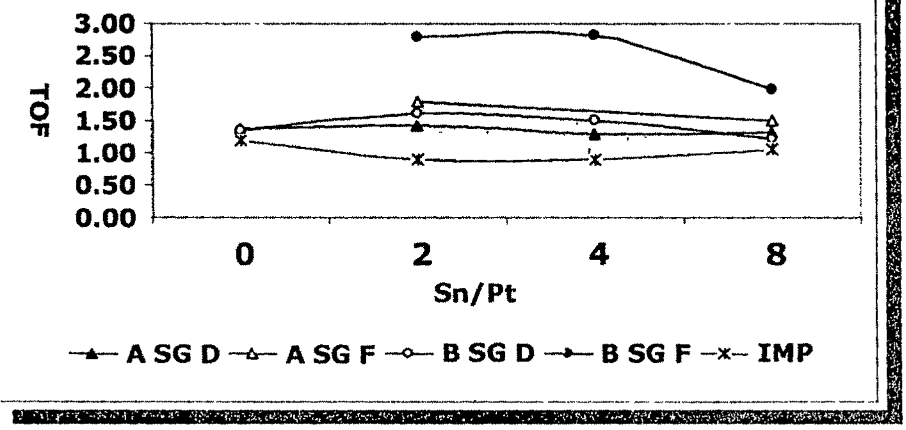


Figure 7.4 Turn Over Frequency: Bifunctional catalysts



Some differences in the type of sites could be noted within SG catalysts too. For monofunctional catalysts, the order is:

IMP<ASGD< ASGF<BSGD <BSGF

The trend for bifunctional catalysts is:

IMP<ASGD<BSGD<<ASGF<BSGF

Thus within SG, ASG series has higher TOF and amongst D and F routes catalysts through distillation route show better perfomance

It is to be noted that the variations observed in the TOF values are quite small compared to those reported (TOF of 26 for SG catalyst Vs 7 for conventional one) by Gomez et al **(2)** for n-heptane dehydrocyclization on Pt-Sn/Al_2O_3 catalysts. Gomez et al **(3)** have also reported similar increase in TOF (from 3 to 28 for SG catalyst) for cyclohexane dehydrogenation, while on the same catalyst, TOF for SG was 0.16 against 19 for conventional catalyst for toluene dealkylation.

As discussed earlier, Gomez et al have adopted two-step SG method while in the present work single step SG method has been used. According to Lopez et al **(4)** single step method leads to encapsulation of platinum by the support causing a reduction in exposed platinum. This is also supported by Bettcher et al **(5)**, who observed better dispersion for Pt-Sn/Al_2O_3 catalysts, obtained by two-step method (Table.7.4).

The pertinent point to be noted here is that in spite of having nearly 50 % less dispersion compared to two step method, TOF (for isobutane dehydrogenation) for catalysts prepared by single step method is just twice that observed for catalysts obtained by the other route. This is in line with the findings of current investigation, wherein SG catalysts with less dispersion compared to IMP series show higher TOF.

Table 7.4 Influence of SG method of preparation on Pt dispersion/TOF

Catalyst Components (wt%)	SG method	Pt dispersion (%)	TOF (mole/Pt_ss)
0.45 Pt, 1.1 Sn, 0.65 Cl / Alumina	Preparation of Sn/Al_2O_3 by SG method + Pt impregnation Two step method	70	23
0.44 Pt, 1.0 Sn, 1.0 Cl / Alumina	Introduction of Pt and Sn precursor at hydrolysis stage Single step method	38	46

Such observations indicate that SG method actually alters the nature of active site, vis-à-vis sites available in catalysts obtained by conventional method.

According to Bettcher et al **(5)**, there is no difference in exposed Pt and isobutene conversion or deactivation rate for catalysts prepared single step or two-step SG method. A more recent work by Sault et al **(6)** for propane dehydrogenation on SG and conventional $Pt\text{-}Sn/Al_2O_3$ catalysts also supports the view that both conventional and SG methods yield similar performance. However, the authors have claimed that SG catalysts exhibit lower deactivation rate.

While there is a general agreement that SG methods do modify the nature of active sites, controversy still exists as to what extent this modifications affect the overall activity.

7.3.3. Correlations with selectivity

In the case of monofunctional IMP catalysts, mono olefins selectivity is directly related to n-decane conversion, increases with Sn content and aromatics formation is retarded (Fig.7.5). Similar trend is observed for bifunctional IMP series also. In the case of SG catalysts no specific trend is observed due to various levels of interaction of Sn with the support and differences in Pt levels due to losses during preparation. Such losses have made the comparison between conventional and sol-gel catalysts unrealistic (7). Irrespective of the method of preparation or changes in preparation parameters, and Sn/Pt ratio, selectivity towards diolefins formation is not affected to any significant extent.

7.3.4. Correlations with deactivation

Pt-Sn/Al_2O_3 catalysts during dehydrogenation process undergo continuous deactivation due to coke deposition on active sites. Though deactivation through sintering of Pt crystallites is possible, sintering rates being slow, normally it is the coking process that needs to be tackled in order to extend the life of dehydrogenation catalysts.

It is well known that acid sites present in the catalysts promote coke-forming reactions like cracking and consequently one can visualize a relationship between coke formation and acidity.

Figure 7.5: Product Selectivity of Monifunctional IMP Catalysts

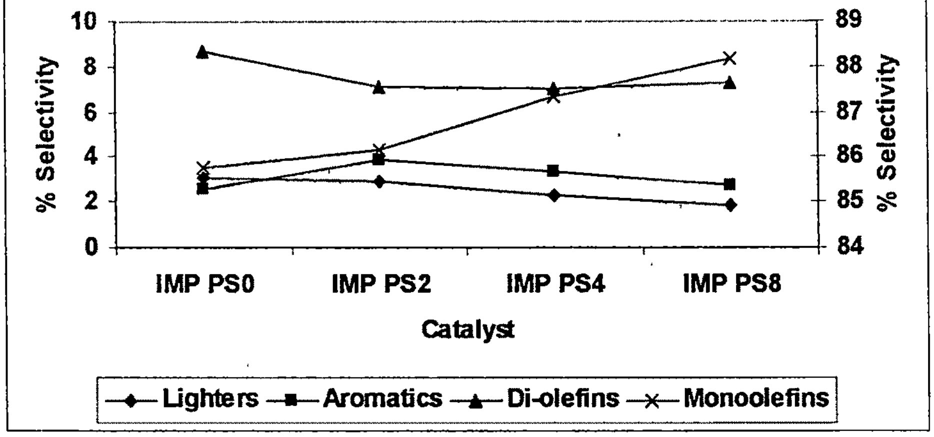


Table 7.5: Nature of coke on Pt-Sn/Alumina catalysts

Bifunctional

Catalyst	Coke on metal (%)	Coke on support (%)	Total Coke (%)	Fraction of coke on metal
BSG 2D	4.5	5.1	9.6	0.5
BSG 4D	3.9	3.8	7.7	0.5
BSG 8D	5.4	4.5	9.8	0.5
BSG 2F	4.4	4.1	8.5	0.5
BSG 4F	3.7	3.7	7.4	0.5
BSG 8F	3.7	4.6	8.3	0.4
ASG 2D	2.9	4.9	7.8	0.4
ASG 4D	4.9	4.6	9.4	0.5
AGS 8D	5.2	4.8	10.0	0.5
ASG 2F	5.2	5.2	10.4	0.5
ASG 4F	5.3	4.6	10.0	0.5
ASG 8F	5.8	4.4	10.2	0.6
		Monofunctional		
BSG 2D	2.6	6.9	9.6	0.3
BSG 4D	2.7	5.0	7.7	0.3
BSG 8D	3.0	6.8	9.8	0.3
BSG 2F	2.8	3.1	6.0	0.5
BSG 4F	2.5	3.1	5.6	0.4
BSG 8F	2.3	2.4	4.7	0.5
ASG 2D	2.8	3.1	6.0	0.5
ASG 4D	3.1	3.2	6.3	0.5
ASG 8D	2.9	2.7	5.6	0.5
ASG 2F	2.7	3.0	5.7	0.5
ASG 4F	3.0	3.0	6.0	0.5
ASG 8F	3.0	2.9	5.9	0.5
IMP MF 2	2.8	2.0	4.8	0.6
IMP MF 4	3.0	2.9	5.9	0.5
IMP MF 8	3.2	2.7	5.8	0.5

Fig 7.6 shows the relationship between acidity of monofunctional catalysts (expressed as millimoles of ammonia/g of catalyst) and coke formation. Trends for acidity and coke laid down follow the same pattern along ASG/BSG and D and F series. Similar trends are observed for bifunctional catalysts too. Table.7.5 gives total coke formed on spent

Figure 7.6: Co - relation of coke with acidity of catalyst

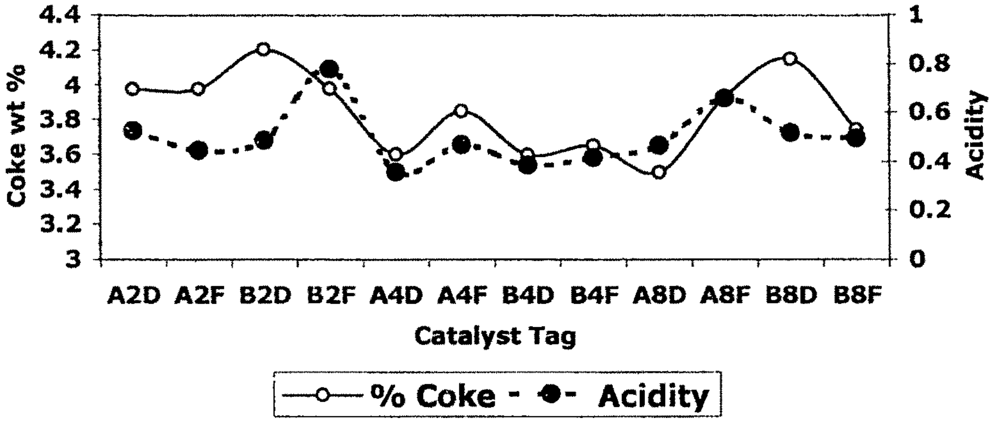
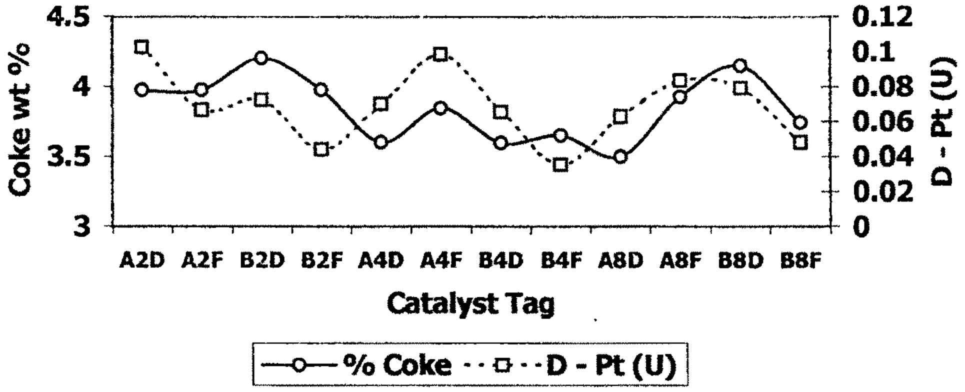


Figure 7.7: Co - relation of coke with dispersion of unalloyed platinum



mono and bifunctional catalysts as determined by TPCO/TGA. It can be clearly seen that irrespective of the method of preparation (ASG/BSG) or mode of solvent removal (D/F), spent bifunctional catalysts contain more coke compared to monofunctional ones. Higher levels of residual chloride in bifunctional catalysts induce strong acid sites, which in turn catalyze coke-forming reactions. This explains relatively higher levels coke observed for bifunctional catalysts. Coke deposits on IMP series are moderate in spite of the high activity displayed and do not vary significantly with Sn/Pt ratio. Similarly in the case of SG series, total coke contents carry little with respect to Sn/Pt ratio. In general coke contents in SG catalysts are higher than those observed for IMP series of catalysts

Sn as a promoter in Pt-Sn bimetallic catalysts is expected to play several roles, like:

- Formation of Pt-Sn ensembles and increase Pt dispersion
- Modify the electronic levels of Pt and change (olefin) adsorption-desorption process
- React with support and attenuate acidity and/or form tin aluminate phase

Of the above three aspects, the effect of changes in Pt dispersion due to addition of Sn has been discussed earlier. In Table 5.7, which summarizes the dispersion data, the total dispersed Pt has been classified into alloyed (with Sn) and unalloyed fractions. These two fractions differ in their olefin adsorption- desorption characteristics. It is known **(8)** that alloying with Sn/ligand effect due to added Sn modifies the electronic level of Pt and consequently adsorption strength of olefins is weakened. On the other hand unalloyed part displays strong adsorption tendency for olefins. Such sites could retain olefins, which ultimately form coke. Presented in Fig.7.7 is the relationship between unalloyed Pt measured in various monofunctional catalysts and coke laid down on these. Extent of coke formation and unalloyed Pt content follow the same trend across the series of catalysts. This correlation clearly brings out the effect modification of electronic level of Pt by Sn and its effect on strength of adsorption of olefins and ultimately the tendency to form coke.

In order to analyze the nature of coke formed Temperature Programmed Coke Oxidation studies on spent catalysts have been carried out by TGA. Typical thermograms in the case of monofunctional catalysts are given in Fig 7.8 and 7.9. In all cases two major coke oxidation peaks could be observed. One in the range 200-400^{0}C and the other in 400-800^{0}C range. As explained in Chapter.3 the low temperature peak corresponds to coke deposited on metal (Pt) and the high temperature one on support. Table 7.4 gives coke content in these two ranges for all the catalysts. It can be clearly seen that the total coke as well as the fraction of coke on metal is less in the case of monofunctional catalysts while it is relatively higher for bifunctional catalysts. The influence of such coking patterns on the deactivation of catalysts could be understood from the data on deactivation kinetics for various catalysts, which is presented in the section below.

7.3.5. Deactivation patterns: sol-gel vs. conventional catalysts

The data on n-decane conversion with respect to time presented in Fig 7.10 and 7.11 for monofunctional catalysts have been analyzed on the basis of Voorhie's equation **(1)**. The conversion versus time on stream data were fitted to an exponential equation and extrapolated to time on stream zero to determine the initial conversion. Relative activity (at time t a_t) was calculated as the ratio of conversion at time t and the initial conversion. The extent of deactivation was calculated using the Voorhies equation $\mathbf{\log(a) = \log A - k_d \log(t)}$ where a= relative activity, k_d = slope which is proportional to the magnitude of deactivation. K_d values for mono and bifunctional IMP series of catalysts are presented in Fig 7.12 and 7.13. Deactivation rates for bifunctional catalysts are higher than that for monofunctional catalysts. Higher levels of chloride in bifunctional catalysts induce cracking and coking leading to faster deactivation. This is

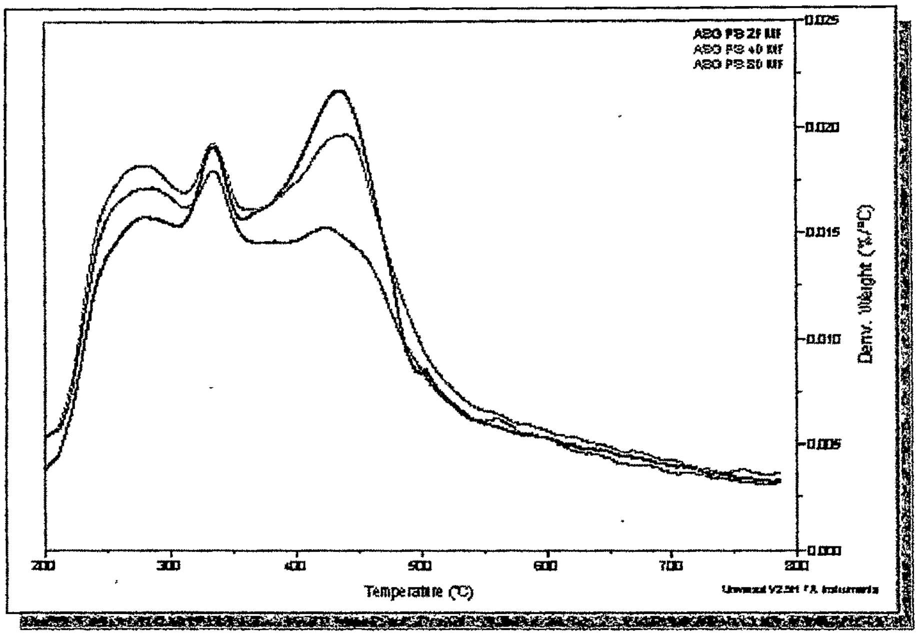


Figure 7.8a: TPCO Curves of ASG F Monofunctional catalysts

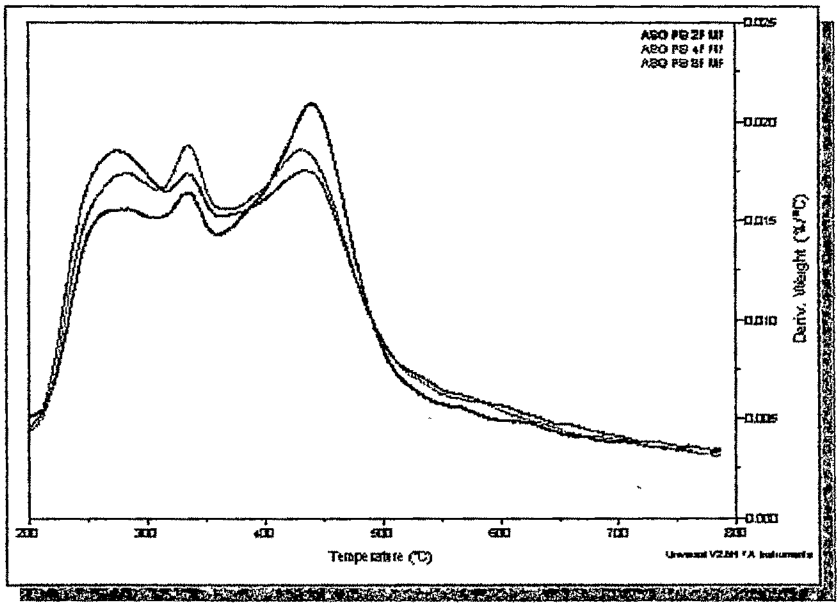


Figure 7.8b: TPCO Curves of ASG D Monofunctional catalysts

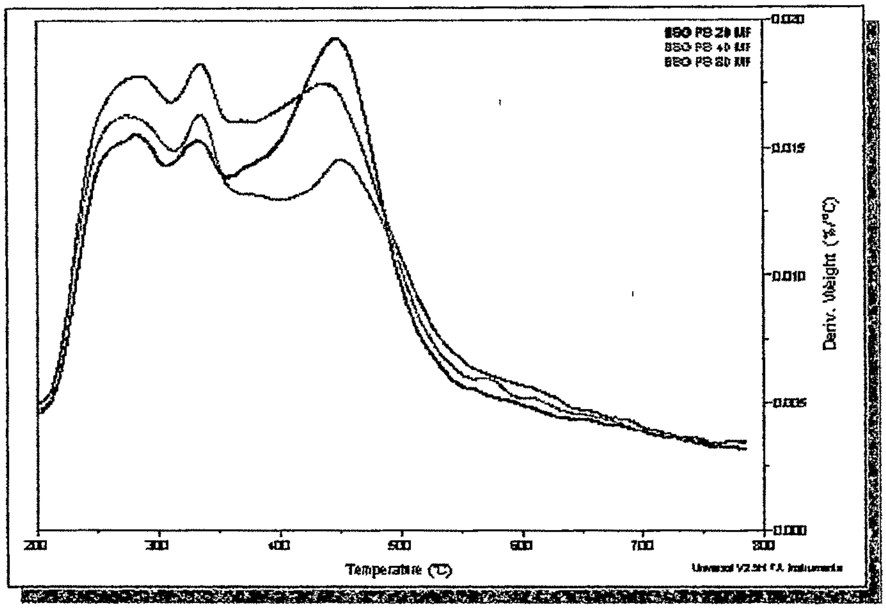


Figure 7.9a: TPCO Curves of BSG D Monofunctional catalysts

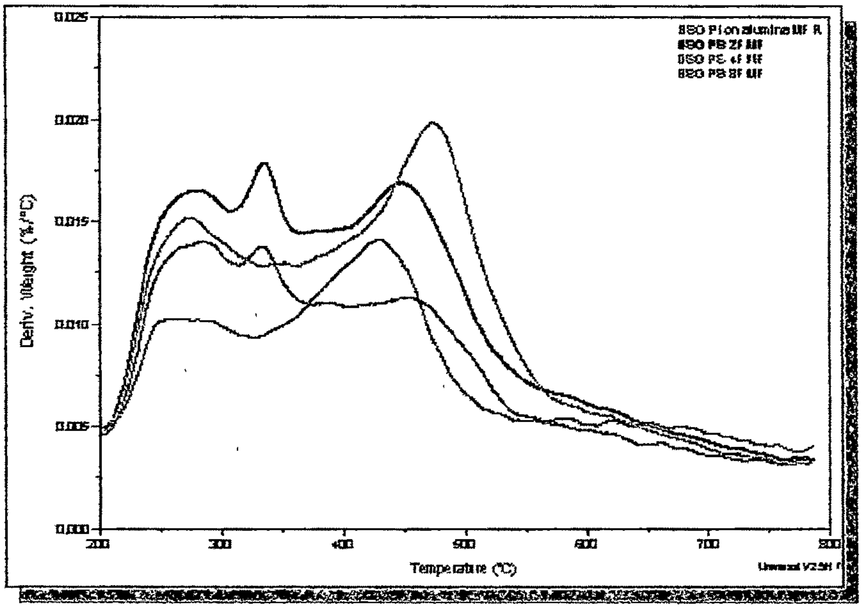


Figure 7.9b: TPCO Curves of BSG F Monofunctional catalysts

Fig 7.10: n-Decane dehydrogenation activity of mono-functional ASG catalysts

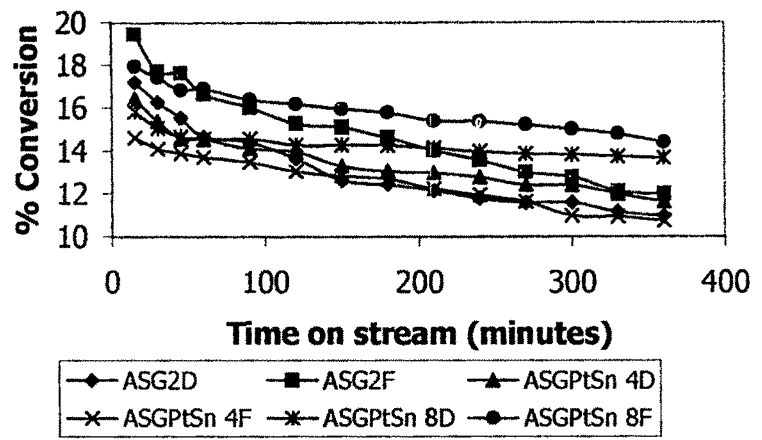
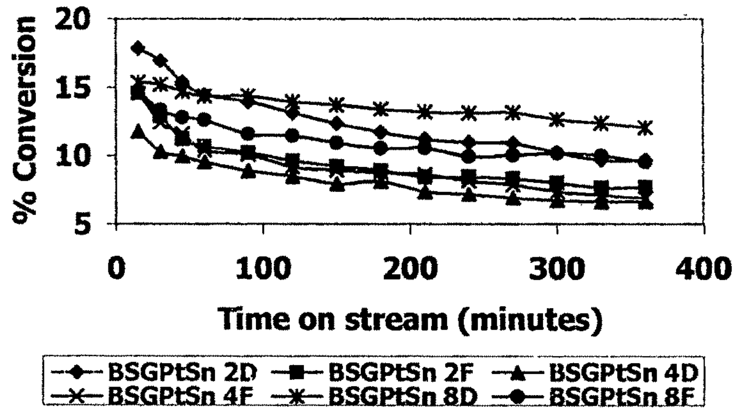


Fig 7.11: n-Decane dehydrogenation activity of mono-functional BSG catalysts



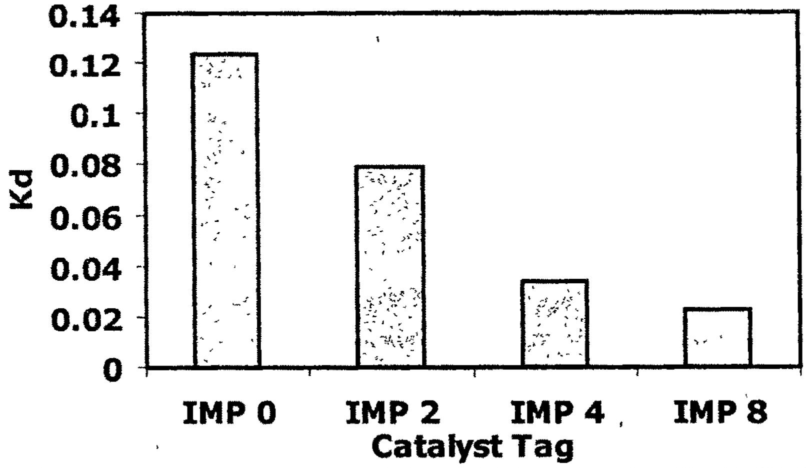


Figure 7.12: Deactivation rate constant kD for bifunctional impregnated catalysts

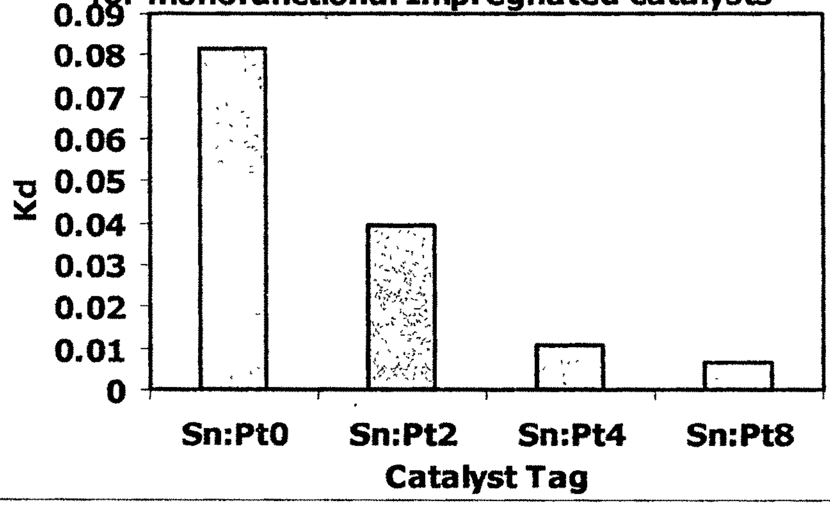


Figure 7.13: Deactivation Rate Constant kD for monofunctional Impregnated catalysts

also supported by the coke analysis data discussed above. Within mono or bifunctional catalysts, deactivation is retarded with increase in Sn/Pt atomic ratio. As discussed above, modifications in electronic level of Pt by Sn and modification of support acidity by Sn could help to bring down the deactivation rate

Fig 7.14 shows k_d values for various monofunctional sol-gel catalysts. It is observed that BSG series catalyst deactivate faster than ASG series. Better dispersion and PtSn interactions (through TPR studies) observed in the case of ASG catalysts could be responsible for ASG series stability. In the case of BSG, higher level of interaction of Sn with the support (TPR data) and relatively less dispersion could be the reasons for faster deactivation. With respect to the influence of Sn/Pt ratio in SG catalysts on deactivation the following trends emerge based on k_d data:

ASG 2 > ASG-4 > ASG-8

BSG-2 ~ BSG-4 > BSG-8

Choice of solvent removal by D or F process does not seem to affect the deactivation rate to any significant extent. It is likely that the effect of Sn/Pt ratio being strong, it masks the effect due to D or F process.

Compared to IMP series of catalysts, SG series (ASG and BSG) display higher deactivation rates. The role of two major factors, Pt-Sn interaction and Sn-support interactions come into the focus at this stage. As explained earlier, Pt-Sn interaction, which is vital for retarding coke formation/deactivation is weak in the case of SG catalysts. This could be counter balanced by increased Sn-support interaction and consequent moderation of support acidity. However, the primary step for coke formation, i.e., retention of olefins on SG catalysts proceeds unhindered, with support acidity playing secondary role.

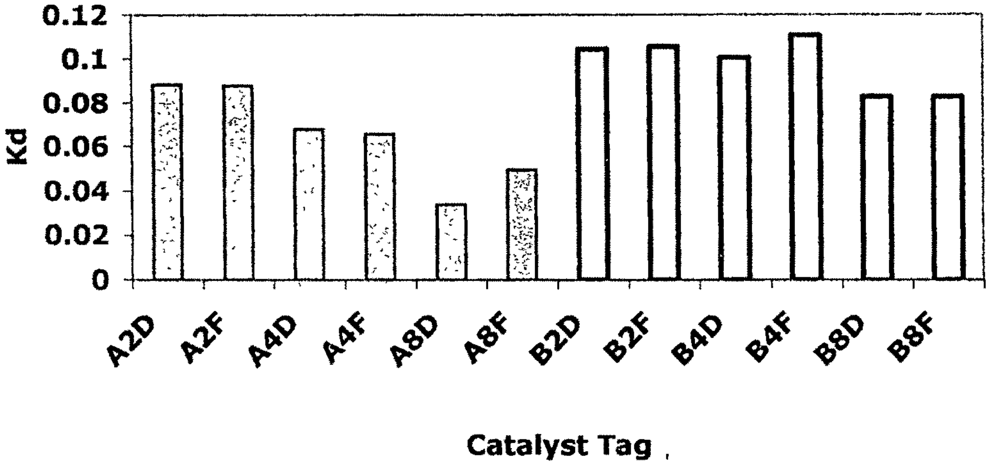


Figure 7.14: Values of Deactivation Rate Constant (kd) of different catalysts

7.4. Summary

- Pt metal dispersion emerges as the sole factor responsible for activity of the catalysts, conventional or sol-gel
- IMP series of catalysts with better dispersion display higher activity compared to SG catalysts that have relatively poor dispersion
- SG catalysts display higher TOF values compared to IMP catalysts indicating that the nature of active sites is different in SG catalysts
- TOF values for SG catalysts indicate that the nature of sites in them are different from those observed in IMP series of catalysts
- Selectivity for mono olefins formation follows regular trend with respect to Sn/Pt ratio in the case of IMP catalysts while no trend is observed for SG catalysts
- Coke contents in spent SG catalysts are higher than those on IMP catalysts.
- Deactivation rates observed for monofunctional IMP series is less compared to those observed for bifunctional IMP catalysts
- Deactivation rates for SG catalysts are higher than those for IMP catalysts, possibly due to weak Pt-Sn interactions strong Sn-support interactions
- Coke formation in SG catalysts is related to acidity as well as the fraction of unalloyed platinum
- Platinum dispersion, Pt-Sn interaction and acidity are the major factors that influence the overall performance of conventional and sol-gel type catalysts

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