CHAPTER-IV

STUDIES ON PROMOTED PLATINUM ON ALUMINA CATALYSTS

IV.1 INTRODUCTION

Paraffin dehydrogenation is one of the major petrochemical processes like ammonia synthesis, water gas shift reaction, steam naphtha reforming, catalytic reforming for gasoline/ aromatics production, selective oxidation, ammoxidation, oxychlorination, hydrogenation, polymerisation and hydrodesulphurisation. Dehydrogenation is a key step in the manufacture of a variety of industrial products like biodegradable detergents, alcohols, homopolymers and copolymers. In the detergent industry, the monoolefins obtained by the selective dehydrogenation of C_{11}-C_{14} normal paraffins are converted into the corresponding alkylates by reaction with benzene. This product, known as Linear Alkyl Benzene (LAB), is the main raw material for the manufacture of detergents.

Paraffin dehydrogenation has now gained wider applications as a viable route for the manufacture of C_3/C_4 olefins from the corresponding paraffins. However, very little published information is available on this key reaction in the literature. Supported MoO_3 and Cr_2O_3 catalysts have been used, prior to Pt/alumina catalysts (195,196). Initial research efforts were directed towards achieving better selectivity for monoolefins and suppressing other side reactions like isomerisation, cracking, cyclisation and coking.

The overall chemical composition of a dehydrogenation catalyst resembles that of a typical reforming catalyst except for the presence of alkali metals in the latter (99). Reforming catalyst is bifunctional where the major reaction is dehydrogenation catalysed by the dispersed Pt species along with isomerisation, aromatisation and cracking accelerated by the acidic alumina support. The acidic properties of alumina and hence, these side reactions can be controlled by incorporating suitable alkali metals/halogens (99). In dehydrogenation catalyst the side reactions are suppressed by neutralising the acidity with alkali metals.

Temperature is another factor governing the activity, selectivity and stability of catalysts. The thermodynamics that prevail for dehydrogenation of higher normal paraffins require the use of relatively higher reaction temperatures in the order of 673-773 K to achieve significant levels of conversion (197). Eventhough, the undesired side reactions can be suppressed by modifying the properties of the support, even the best catalyst uncovered to date tends to catalyze many side reactions and leads to excessive coke deposition when operated at higher conversion levels. This makes it necessary to identify means other than high temperature, to achieve better activity.

As a general rule, an increased dispersion of the active species improves the catalytic activity. A better dispersion can be achieved by the choice of proper support and appropriate method of preparation and pretreatments. But this method of improving activity is associated with some inherent drawbacks. It is a wellknown fact that the more the dispersion, the more the catalyst is prone to sintering and growth of crystallites leading to decreased activity (198). Moreover, the predominantly paraffinic nature of monoolefins in the range of C_{11} to C_{14} permits sequential dehydrogenation to occur readily, leading to the formation of di and triolefins, aromatics and coke. This effect will be more pronounced in the case of catalysts with higher initial activity and they tend to deactivate faster.

Stability and resistance to sintering of a highly dispersed catalyst depends on the extent of interaction of the active species and support which is usually generated by the pretreatments. Other than this, as mentioned earlier, addition of other elements, which by themselves may be catalytically inactive, were found to have favourable effect on the activity, selectivity and stability of catalysts. The mode of action of these elements, known as promoters, varies significantly from system to system. Some modify the properties of the support (150) or combine with it to form new phases which stabilise the active species against sintering (167). In some other systems, promoters modify the active species through what is usually referred to either as ensemble effect (167) or ligand effect (189). In many of the known systems, all these effects are found to be operating simultaneously and to various extents. Considering all these aspects of this reaction and the catalyst, it is necessary to design the catalyst in such a way that the optimum activity, maximum selectivity and better stability/life are achieved. Since methods of preparation, pretreatments and use of promoters are the factors governing the performance of the Pt/alumina catalyst, these topics are reviewed briefly in the following sections.

IV.1.1 Methods of preparation of Pt/alumina catalysts

The principal catalyst preparation involves two stages namely (a) Incorporation of the active species onto the support in a finely devided form and (b) Drying/Calcination/Reduction (199). The first step can be accomplished by various techniques like impregnation, equilibrium adsorption, ion exchange, coprec-cipitation or deposition precipitation. Of these, the most widely used methods for the preparation of Pt/alumina catalysts are:

(i) Dry impregnation (Pore filling method)
(ii) Wet impregnation (Equilibrium adsorption)
(iii) Ion exchange.

The impregnation methods use mostly chloroplatinic acid solutions whereas ion exchange is generally carried out with cationic platinum ammino complexes. The high affinity of $(PtCl_6)^{2-}$ ions towards hydroxyl groups of alumina controls the dispersion and location of platinum during impregnation. It has been shown by Castro and coworkers (123) that the impregnation of aqueous chloroplatinic acid results in a shell type catalyst with high Pt concentration on the outer shell of the pellet whereas solutions containing chloride as a competing ion give uniform distribution. There are various reports about the use of different competing ions and molecules during the impregnation process specially meant for modifying the distribution of active species in the catalyst (17,124-130).

Benesi et al (126) have reported a method of preparing Pt/alumina catalyst with a high degree of dispersion by the cationic exchange of Pt as $Pt\ (NH_3)_4^{2+}$ with alumina. Another method known as photo-catalytic deposition was reported by Hermann et al (131) for the preparation of Pt/alumina and is claimed to be superior to impregnation.

Bimetallic and multimetallic catalysts containing platinum are prepared by coimpregnation or successive impregnation of the suitable salt solutions on-to the support. Various combinations like Pt-Sn, Pt-In, Pt-Re, Pt-Ir, Pt-Pb, Pt-Ga etc on alumina have been reported in literature (152-160). Other than these, methods like molecular deposition for Pt-Sn/alumina (132), electrochemical metal adsorption for Pt-Pd/alumina (133) etc have also been reported. Kern-Talas et al (134) have proposed a method to prepare Pt-Sn/alumina catalyst with Pt-Sn interaction and direct Sn-alumina interaction. Exhaustive and complete review of most of the published papers on catalyst preparation are available in texts (135,136).

IV.1.2 Pretreatments

The second stage in the catalyst preparation is the thermal treatment, usually carried out in stages. Thermal treatments upto 423 K are mainly to remove water and further between 423 to 873 K, are to decompose the adsorbed species to the metal or metal oxide. The latter stage, usually performed in oxygen atmosphere, is called calcination.

$$H_2PtCl_6 \text{ -------> } PtCl_4 + 2HCl$$

$$Pt\ (NH_3)_4^{2+} \text{----- > } Pt$$

Thermal treatments alone to form metal lead to crystallite growth (137,138) and in some cases metal relocation (137).

Pt/alumina reforming catalyst prepared by impregnation, drying at 393 K and calcination at 798 K in air followed by reduction at 773 K was found to have a dispersion of 80-85 %. This is believed to be because of the interaction of Pt with gamma alumina occuring during calcination (**139,140**). Blanchard et al (**141**), for samples dried at 383 K obtained, similar TPR patterns as that of calcined samples and hence postulated that the interaction occurs at the drying stage. Moreover, a treatment of Pt/alumina catalyst in O_2 below 873 K is reported to increase the dispersion (**142**). The effect of chloride on the O_2/H_2 treatments at different temperatures on Pt/alumina catalysts have been studied by Lieske and co-workers (**143**). They identified two surface oxides (α-PtO_2) and ($\beta$$PtO_2$) and two chlorocomplexes ($Pt(OH)_x Cl_y$) and (PtO_xCl_y) on the surface of chloride free and chloride containing catalysts and concluded that redispersion of Pt is possible only in the presence of chloride.

The final thermal treatment performed in hydrogen atmosphere is known as reduction and is meant to convert the active species to the metallic form. Reduction of Pt/alumina above 773 K is reported to decrease the chemisorption capacity drastically as if a large fraction of Pt is inaccessible to hydrogen (**144**). It is proposed that the platinum hydride is highly mobile on the surface and forms alloy with aluminium from the support. Heating and slow cooling of a catalyst is reported to decrease the dispersion whereas quenching in liquid nitrogen induce the reverse effect (**145**). Effect of thermal treatments in different atmospheres and at various temperatures have been reported by many other authors also (**146-149**).

IV.1.3 Use of Promoters

Since platinum is highly active in hydrocarbon conversions, the deactivation of such monometallic catalysts is also faster. This usually becomes a constraint when life and stability of the catalyst are considered. Hence, various promoters are used which are capable of enhancing the activity of platinum and slow down the deactivation, thus increasing the life of the catalyst. Structural breakdown of the support occuring during prolonged high temperature operations can also lead to faster deactivation of the catalyst. Boehmite derived gamma alumina,eventhough stable in the temperature range of 673 to 873 K, undergoes sintering and loss of surface area on prolonged use. Incorporation of ions like Li^+, K^+ or Mg^{2+} are known to control the acidic properties of alumina and at the same time have a stabilization effect on the support structure (150).

Various elements like Sn, I~~n~~r, Re, Ge, Bi, Ga, Rh, Pd, Pb, Cu, Au, Ag etc have been used along with platinum for different applications. Sn, Re and I~~n~~r are the elements most commonly used for naphtha reforming and dehydrogenation catalysts. Coq and Figueras (151) studied the conversion of methyl cyclopentane on Pt-Sn/alumina catalyst, containing 1% Pt and 0.6 to 4 % Sn. Sn was found to increase the activity and stability of the catalyst. On increasing Sn content, hydrogenolysis to hexanes and aromatisation go through a maximum while dehydrogenation remains constant. The enhancement in activity and stability were interpretted in terms of the "ensemble effect", i.e. the division of the surface platinum into small ensembles of platinum atoms diluted by Sn atoms. Like dehydrogenation, aromatisation also proceeds on single atom site and the inhibition of aromatisation at high Sn content is attributed to some electronic modification of Pt by Sn. Eventhough many elements are known to increase the activity of the catalysts when used along with Pt, the state of their existence and mode of action is not well understood. For example, Pt-Sn/alumina system has been extensively investigated by many authors and the informations revealed sometimes are contradictory.

It is well known that Pt and Sn, when supported on non-reactive supports (on reduction) get reduced to the zero valent state and form solid solutions/alloys (**161**). The situation may be different when they are supported on reactive supports like alumina. A comparative study of n-hexane conversion was carried out by Hoang Dang Lanh et al (**162**) on Pt-Sn alloy and Pt-Sn/Al_2O_3 and they observed similar trends in both cases. The promoting action was attributed to alloy formation and was concluded that even on supports like alumina, Sn is reduced to Sn(0) so that alloys could be formed. Lieske and Volter (152) performed TPR and adsorption experiments on Pt-Sn/alumina catalysts and observed partial reduction of Sn(IV) to Sn(0). The presence of chloride was also found to influence the reduction of Pt and Sn when supported on alumina (**163**).

Burch and Garla (**164,165**) are of the opinion that even after reduction at high temperatures and for prolonged periods, the average oxidation state of Sn in Pt-Sn/alumina is not less than (II) and the possibility of alloy formation is thus ruled out. Zhdan and coworkers (166) through the study of the interaction of Pt-Sn complexes with hydroxyl groups of alumina, concluded that tin ions bonded to the support are not reduced to metal and the oxidic species inhibit the agglomeration of Pt. More recent studies on Pt-Sn/alumina by TPR, ESCA and model reactions are reported by Adkins and Davis (167) and Sexton etal(153). It was observed that Sn exists in the (II) state only and no bulk tin oxide was detected even at 10 % (w/w) loading. They attribute the stabilisation effect to the formation of eggshell of tin aluminate on alumina support with Pt(0) supported on the tin aluminate phase. Moreover, it was shown that on supports like silica, zero valent tin and Pt-Sn alloys exist.

Even in the case of the latest and most promising naphtha reforming catalyst, Pt-Re/alumina, there are different and conflicting opinions about the state of existence and the role of Re (160,168-173). There are many reports in the literature about surface properties, dispersion and activity towards different reactions of systems like Pt-Pd, Pt-Ru, Pt-Cu, Pt-Pb, Pt-Au, Pt-Ga, Pt-Rh, on alumina (155-159,174-182). Use of B, Zr, Ge and Co (183), and rare earth elements (La, Ce, Nd, Gd, Yb, Lu) (184,185) as promoters have also been reported.

Thus, it is evident from the above discussion that promoters/additives used in Pt/alumina systems are meant to modify the support or/and the active species. Specifically in dehydrogenation catalysts, acidity of the support is one major factor governing the selectivity and life. Alumina catalyses the typical acid catalysed reactions like cracking, isomerisation and cyclisation thus decreasing the selectivity. This fact is supported by the observation that the intrinsically non-acidic BeO supported Pt was found to show better selectivity than Pt/alumina for dehydrogenation (186). Incoporation of alkali metals on to alumina is reported to decrease the number of electron acceptor centers characterising Lewis acidity of alumina by the "neighbouring centre effect" (99,187). Indium and Thallium are also reported to have similar effect on alumina (188). Thus, by modification of alumina by alkali metals (control of acidity) the selectivity and life of catalysts could be improved.

The second type of promoters are used to modify the active species in a useful way. Many elements have been reported but most important are Sn, Re and I~~n~~r. These elements can act in two different ways, (a) by separating the atoms of active species and stabilising them (increased dispersion,i.e., ensemble effect) (b) by an electronic modification of the Pt atoms and preventing deactivation (ligand effect).

In many systems both the effects operate together, as exemplified by Kogan et al (189). It was observed that addition of tin to Pt/alumina catalyst system results in an increase in the dehydrogenation activity and retardation of coke deposition on Platinum. From IR spectroscopic studies of CO on Pt, they showed that Sn reduces the strength of CO adsorption and favours the formation of an energetically homogeneous surface of the metallic component. Moreover, the observed decrease in Pt surface area in presence of Sn was attributed to the blockage of Pt surface by the promoter. Thus, the increase in specific activity of Pt towards dehydrogenation and prevention of coking are interpretted in terms of the decrease in the adsorption bond strength between Pt and the reactant. Similar effects on Sn and In promoted systems are reported by other authors also (190-192). The use of Re as a promoter along with Li in Pt/alumina catalysts was also shown to increase the selectivity for monoolefin formation without reduction in activity (193).

IV.2 AIM AND SCOPE OF THE INVESTIGATION

Eventhough, the objective of the study was to correlate the catalytic behaviour with properties of catalysts, the orientation is towards a specific reaction and a suitable catalyst system namely, dehydrogenation of n-dodecane and alumina supported Pt catalysts. Various means of improving catalyst performance have been revealed by different authors in the literature namely, modification of preparatory methods, pretreatments and use of promoters. Invariably all the catalyst systems studied so far contain one or more elements apart from Pt. The role played by the other elements is far from clear. Addition of modifier or promoter is expected to,

(a) Alter the electronic structure of the primary metal:

Ligand effect

(b) Change or reduce the number of adjacent primary surface atoms:

Ensemble effect

(c) Create additional active centers:

Alloying effect

To what extent, either individually or collectively, these factors contribute towards improvement of the catalyst is to be resolved.

The second aspect is concerned with the state of existence of these modifiers, i.e., in what state do they exist (metallic or oxidised or mixed) in the catalyst under reaction conditions. Unless they exist in suitable state, they may not exhibit the desired effect. Hence the study was undertaken with an intention to identify the fundamental characteristics like dispersion, reduction behaviour, electronic states and deactivation that are modified by the promoters and to correlate with activity and selectivity for dehydrogenating n-dodecane to monoolefins.

Plan of work

Till now there are various reports on the effect of different supports (194), effect of alkali metal additives (99, 187), and effect of various promoters (188-192) on Pt/alumina systems. Further studies on this system were planned so that information could be gathered which can supplement the existing knowledge and help in clarifying some of the controversial issues. The work was planned as follows.

(i) Preparation of Pt/alumina catalysts promoted separately by Ag, In, Sn and Sb with a constant Pt and Li loading of 0.45 and 0.6 % (w/w) respectively and promoter to platinum atomic ratio 2. Since the main interest was to study the modification of the surface structure and electronic states of Pt caused by the promoters, it was decided to prepare and treat the catalysts under identical conditions.

(ii) Physico-chemical characterisation of samples by chemical analysis, temperature programmed reduction, H_2-O_2 titration and X-ray diffraction.

(iii) Diffuse reflectance spectroscopy and ESCA studies to identify the nature of the surface species.

(iv) Evaluation of the catalysts for the activity towards dehydrogenation of n-dodecane and selectivity for the formation of monoolefins.

(v) High pressure evaluation of the catalyst under low severity and high severity conditions to compare the steady state activity and stability.

(vi) Temperature programmed oxidation studies of coke deposited on used catalysts in order to identify the nature and location of coke deposits.

IV.3 CHARACTERISATION OF LITHIUM MODIFIED GAMMA ALUMINA

The alumina used for catalyst preparation was characterised before and after Li incorporation by chloride content, acidity, apparent bulk density, attrition loss, crushing strength surface area, pore volume, pore size distribution and X-ray diffraction measurements. A comparison of the properties can be seen in Table IV.1.

X-ray diffraction patterns of alumina and Li modified alumina do not show any difference showing that Li incorporation has not induced any structural modification. But it is found to cause a small reduction in surface area and pore volume and a significant improvement in attrition resistance. The observed changes in porosity are complementary to each other and could be due to Li deposition in the pores and extented calcination. As anticipated, there is a four fold reduction in the total acidity in the case of Li modified alumina (187).

TABLE IV.1

Properties of Li Modified Alumina

Property	Alumina	Li/alumina
Apparent bulk density (g/ml)	0.33	0.33
Crushing strength (Kg)	1.70	1.80
Attrition loss (%)	10.00	2.00
Surface area (m^2/g)	148.00	143.00
Pore volume (ml/g)	0.47	0.42
Pore size distribution (%)		
Micro (<20 A°)	19.08	16.07
Meso (20-500 A°)	63.62	72.82
Macro (>500 A°)	17.30	11.11
Acidity (moles $NH_3/m^2/g$)	2.2×10^{-6}	0.5×10^{-6}
Chloride content (%)	0.35	0.33

IV.4 CHARACTERISATION OF PRECURSORS AND CATALYSTS

Dehydrogenation catalysts, namely Pt-Li/alumina, Pt-Ag-Li/alumina, Pt-In-Li/alumina, Pt-Sn-Li/alumina and Pt-Sb-Li/alumina were prepared by impregnation of respective salt solutions on-to the lithium modified alumina as described in II.3. Samples were collected at every stage like drying at **343** K, oxidation at 673 K, moisture treatment at 773 K and reduction at 748 K and were characterised by chemical analysis, dispersion, temperature programmed reduction (TPR), diffuse reflectance spectroscopy (DRS), electron spectroscopy for chemical analysis(ESCA/XPS) and x-ray diffraction (XRD). Such studies are expected to yield valuable information regarding the evolution of active phase in the catalysts. DRS, ESCA and XRD studies were performed with samples containing 2 wt % Pt and promoters in the atomic ratio 1:2 due to the sensitivity limitations. Analysis of Pt $4f_{7/2}$ and $4f_{5/2}$ lines by ESCA was not possible with certainty because they overlap with Al $2p_{3/2}$ and $2p_{1/2}$ lines and hence,had to depend on another comparatively weak $4d_{5/2}$ signal of Pt (153). At least 2 wt % loading of Pt was necessary to obtain this signal with sufficient intensity.

IV.4.1 Chemical Analysis

(a) Platinum content

U.V. spectroscopic determination of platinum (228) in the catalysts as a complex with $SnCl_2$ in HCl solution has been carried out and the results are presented in Table IV.2.

TABLE IV.2

Pt Contents In Catalysts

Catalyst	Pt content wt %	
	calculated	observed
Pt-Li/Alumina	0.45	0.425
Pt-Ag-Li/alumina	0.45	0.412
Pt-In-Li/alumina	0.45	0.426
Pt-Sn-Li/alumina	0.45	0.422
Pt-Sb-Li/alumina	0.45	0.425

The discrepancy in the calculated and observed values could be due to the loss of liquid occuring during impregnation. Lithium, silver, indium, tin and antimony contents in finished catalysts were checked by wet chemical analysis and Atomic Absorption Spectroscopy.

b) Chloride content

Impregnation of aqueous chloroplatinic acid solutions is known to produce non-uniform distribution of platinum on alumina pellets or spheroids (123). Hence, it was necessary to use some competing anions in the solution. In all the catalyst preparations, 10% (by weight of alumina) chloride was used so that uniform distribution of Pt could be achieved. Major part of the added chloride gets removed during the thermal treatments. But chloride present in alumina is known to increase acidity. The residual chloride is desired in reforming catalysts whereas in dehydrogenation catalysts, it is detrimental for the selectivity and life. Hence, to minimise the chloride content of the final catalyst, an additional step, known as moisture treatment, was performed in all the cases. Even then, the inherent property of alumina to retain chloride makes it impossible to remove the chloride completely under the conditions adopted in this investigation. This treatment required a careful optimization of parameters, namely, the calcination temperature, moisture content in ambient air flow and the velocity of air. Since both moisture and higher temperature could adversely affect the platinum crystallite size and the mechanical properties of the spheres, optimum conditions which invariably left behind some residual chloride were adopted. Chloride estimations were carried out before and after moisture treatment and the data are given in Table IV.3.

TABLE IV.3

Chloride Contents In Catalysts

Catalyst	**Chloride content wt %**	
	Before moisture treatment	**After moisture treatment**
Pt-Li/alumina	1.98	0.40
Pt-Ag-Li/alumina	1.48	0.39
Pt-In-Li/alumina	1.94	0.47
Pt-Sn-Li/alumina	1.99	0.46
Pt-Sb-Li/alumina	1.67	0.46

Though the chloride levels have been brought down, the residual chloride could still catalyse side reactions to some extent.

IV.4.2 Dispersion Measurements

Dispersion is a measure of ratio of the exposed platinum atoms on the surface to the total amount present in a catalyst. Catalysts with smaller Pt crystallites will have higher dispersion. Theoretically, an atomic level disribution of Pt is said to have a degree of dispersion unity. Eventhough this is practically impossible, degree of dispersion close to unity have been achieved by suitable methods (200–222). Since H_2/O_2 reversibly adsorb on Pt and are mutually titrable, dispersion can be measured by chemisorptive titration of H_2 and O_2 (203).

In this work the dynamic gas titration technique was used to determine the dispersion. This method was originally proposed by Benson and Boudart (203), according to the surface reaction scheme,

$$Pt + \frac{1}{2}H_2 \longrightarrow Pt\text{-}H, \qquad Pt + \frac{1}{2}O_2 \longrightarrow Pt\text{-}O$$

$$2\ Pt\text{-}H + \frac{3}{2}O_2 \longrightarrow 2\ Pt\text{-}O + H_2O$$

$$Pt\text{-}O + \frac{3}{2}H_2 \longrightarrow Pt\text{-}H + H_2O,$$

where Pt is an exposed platinum atom. The stoichiometry, expressed as the ratio of chemisorbed H_2 to chemisorbed O_2 to H_2 titre value (HC:OC:HT) is 1:1:3. Different stoichiometries have been proposed by other authors (204–206) but 1:1:3 ratio was reconfirmed by Prasad et al (207) to hold good irrespective of the pretreatments. However, according to a recent report by Boudart et al (227), the controversy regarding the experimental conditions to be employed for chemisorptive titration has not been solved yet. In the present work, the experimental conditions used were similar to that of Prasad et al (207), and are shown in Table.II.1. The results were calculated on the basis of 1:1:3 titration stoichiometry and are tabulated in Table IV.4.

TABLE-IV.4

Pt Dispersion In Catalysts

Catalyst	Dispersion %				
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Pt-Li/alumina	44.50	44.05	43.03	41.88	41.48
Pt-Ag-Li/alumina	11.85	12.35	13.30	13.07	15.13
Pt-In-Li/alumina	14.21	13.00	13.23	12.80	11.26
Pt-Sn-Li/alumina	18.53	11.40	11.13	10.85	10.55
Pt-Sb-Li/alumina	7.43	7.62	6.95	8.98	7.35

Overall dispersion observed for Pt/alumina catalysts for a number of consecutive cycles of H_2-O_2 treatments were consistent. Fairly good dispersion could be achieved in the case of unpromoted catalyst. All the promoted catalysts invariably show a drastic reduction in overall dispersion. The observed reduction in dispersion in the case of promoted catalysts could be due to, (1) reduction of the number of adjacent platinum atoms, perhaps due to the formation of bimetallic clusters (ensemble effect); and (2) inhibition of chemisorption capacity of Pt atoms by promoter due to electronic modification or alloy formation. The suppression of hydrogen chemisorption has been observed in monometallic Pt/alumina catalysts also but only after high temperature reduction (144). The reason attributed to this was alloy formation with aluminium from the support. In bimetallic catalyst systems, many authors have reported such drastic reduction in chemisorption capacity (169,205,208), which was explained on the basis of alloy formation/electronic modification and ensemble effect.

Pt atoms are known to chemisorb hydrogen in a dissociative manner requiring atleast a pair of adjacent atoms of Pt. Platinum, when coimpregnated with promoter, would be expected to have fewer contiguous platinum atoms than a normal Pt crystallite i.e., one would expect fewer pairs of Pt atoms in Pt-promoter clusters. This factor can considerably reduce the chemisorption capacity of bimetallic clusters eventhough the individual Pt atoms are active. None of the promoter elements are known to individually chemisorb hydrogen. The only possible mode of H_2 chemisorption is via a spillover of hydrogen from Pt. Since the observed hydrogen consumption values were less in promoted Pt catalysts in comparison with the unpromoted Pt, H_2 spillover appears to be highly unlikely, under the experimental conditions employed for chemisorptive titration. The second aspect is more complicated. The Pt atoms may become inactive towards chemisorption due to alloy formation with promoters or the strength of the adsorption bond between Pt and adsorbate may be decreased due to electronic modification. But a discrimination between these explanations is not possible with the help of dispersion studies alone. The dehydrogenation activity data (IV.5) on these catalysts show that all of them promote the activity of Pt but to varying extent. Although the dispersion value of Pt-Sn-Li/alumina was found to be very low it showed maximum activity making it obvious that the Pt atoms are still active towards chemisorption. TPR and DRS results presented in IV.4. 3&4 on promoted catalysts present strong evidence for the interaction between Pt and promoters, which could perhaps alter the electronic levels of Pt and thereby the reactivity towards hydrogen chemisorption (209,210).

Recent EXAFS studies reported by Meitzner et al (222) on Pt-Sn/alumina show extensive co-ordination of Sn atoms to oxygen and only a small degree of co-ordination to other tin atoms or platinum atoms. These data coupled with absorption edge data, provided evidence for the fact that Sn is largely present as Sn(II) Moreover, by analysing the EXAFS data, it was found that Pt-Pt co-ordination in Pt-Sn/alumina is only 3.2 compared to 7.2 in Pt/alumina catalysts indicating that Pt-Sn pairs are perhaps more significant in number than Pt-Pt pairs, due to ensemble effect. Hence, it can be concluded that the observed reduction in the dispersion values determined by H_2-O_2 titration is mostly due to the reduction in the number of adjacent Pt atoms (ensemble effect) eventhough the possibility of ligand effect cannot be ruled out. However, dispersion measurements on bimetallic catalysts investigated are thus incomplete. Chemisorption of hydrogen or chemisorptive titration of H_2 and O_2 are not suitable in the present systems.

IV.4.3 Temperature Programmed Reduction Studies (TPR)

TPR is a relatively new and highly sensitive technique and does not depend on any specific property of the catalyst other than the reducibility of the species under study. Particularly in Pt/alumina systems where low loading and high dispersion of Pt exist TPR has proved to be very useful in identifying the surface species. The reaction between metal oxide (MO) and hydrogen to form metal (M) and water vapour can be represented as,

$$MO + H_2 \longrightarrow M + H_2O$$

When a metal oxide is subjected to thermal treatment in presence of a reducing gas mixture, it undergoes reduction to metal/low valence state in single or multiple steps. The identification of these stages and quantification of the hydrogen consumption can provide valuable information about the species present and their valence states. The reduction of an oxide, when supported may be hindered or favoured depending on their mutual interaction.

Mc Nicol (211) has shown that unsupported PtO_2 gets reduced to Pt(0) in two stages with T_{max} at 298 and 348 K whereas Pt oxide on alumina undergoes single stage reduction to Pt (0) with T_{max} at 553 K (140). Moreover, it has been shown by Lieske et al (143) that the T_{max} of Pt reduction increases in general with temperature of calcination and especially so in chloride containing catalysts.

In promoted catalysts, the TPR patterns will be modified owing to the mutual interaction between the oxides or surface species present. It is therefore vital to characterise the state of components in such catalysts, to determine the role of the promoters and also to establish factors influencing the catalyst performance. There have been a number of investigations on bimetallic systems like Pt-Ru (141), Pt-Re (140,169), Pt-Ir (208), Pt-Ge (212,213), Pt-Sn (31,153,167,209,214,215) supported on alumina. In Pt-Re and Pt-Ge systems, alloy formation during reduction have been established. Only a small portion of the promoter is said to reach the zero valent state and undergo alloying with platinum (212,213).

TPR experiments were performed on all the monometallic and bimetallic catalysts after calcining them in air at 673 K for 3 h and the reduction profiles are compared (Figures IV.1 &2).

The TPR pattern of Li/alumina does not show any major reduction peak except for the two small maxima at 510 and 605 K, probably due to reduction of impurities in alumina. Pt-Li/alumina exhibits a single major reduction peak with T_{max} at 518 K. However, there is a small shoulder at 633 K which can be attributed to some strongly bound species getting reduced at higher temperature. The Pt reduction peak in this system appears at a slightly lower temperature (518 K) than the reported temperatures (533 K) for similar catalysts (143). This might be due to comparatively lower calcination temperature adopted in this study. Moreover, in separate experiments it was observed that the T_{max} shifts to the higher temperature region when pretreated at higher temperatures. In the present case, supported Pt species on alumina appears to be one of the type $Pt(IV)OH_xCl_y$ or $Pt(IV)O_xCl_y$ as reported by Lieske et al (143). Some distinction between these two species by DRS is possible (Sect. IV.4.4). The TPR pattern of Ag/alumina was found to be complicated with two strong reduction maxima at 500 K and 700 K. Paryjczak et al (216) have also observed a complicated pattern for Ag/alumina system with three maxima, two of them close to 400 K and third one at 850 K.

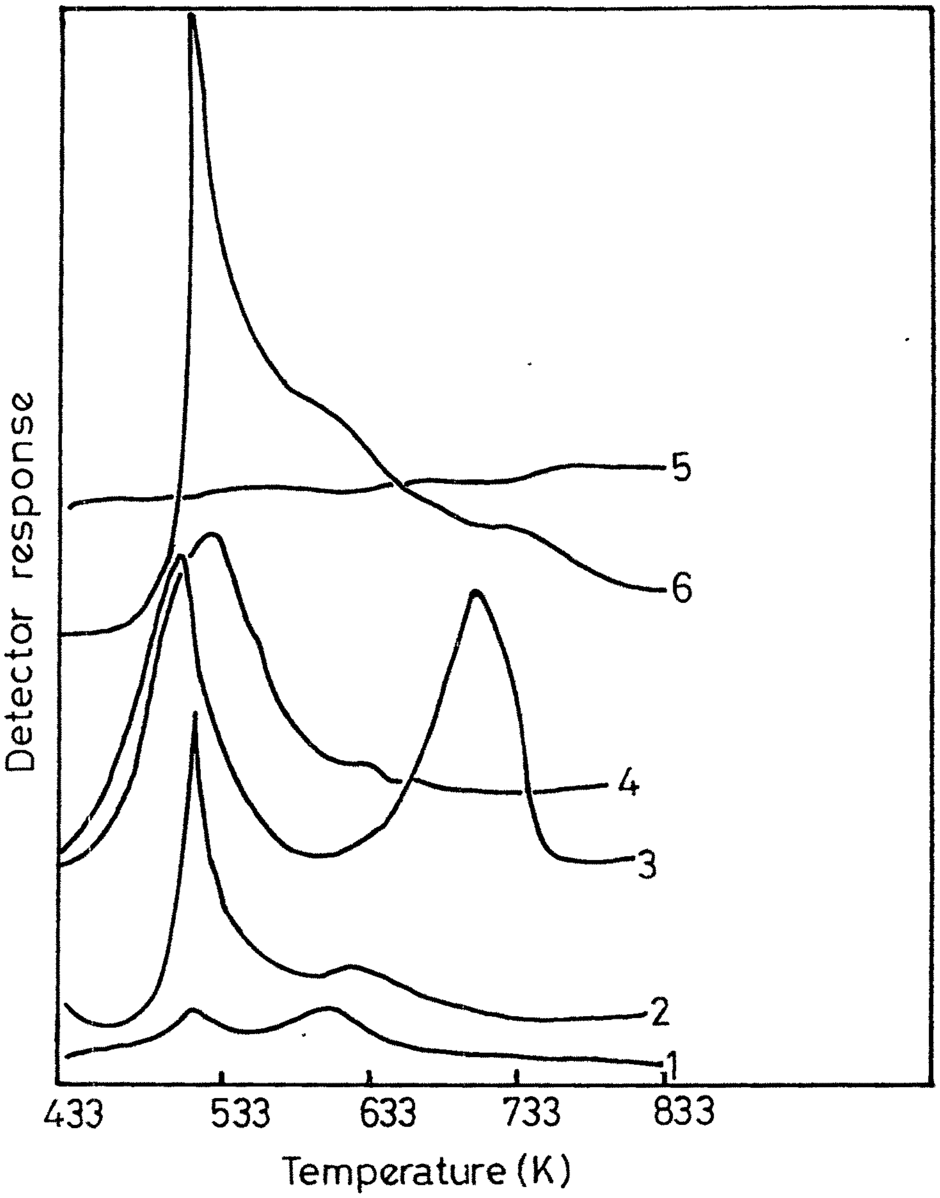

Fig. IV.1 TPR Patterns of catalysts calcined at 673K
1. Li/Al_2O_3, 2. Pt-Li/Al_2O_3, 3. Ag-Li/Al_2O_3,
4. Pt-Ag-Li/Al_2O_3, 5. Sb-Li/Al_2O_3, 6. Pt-Sb-Li/Al_2O_3

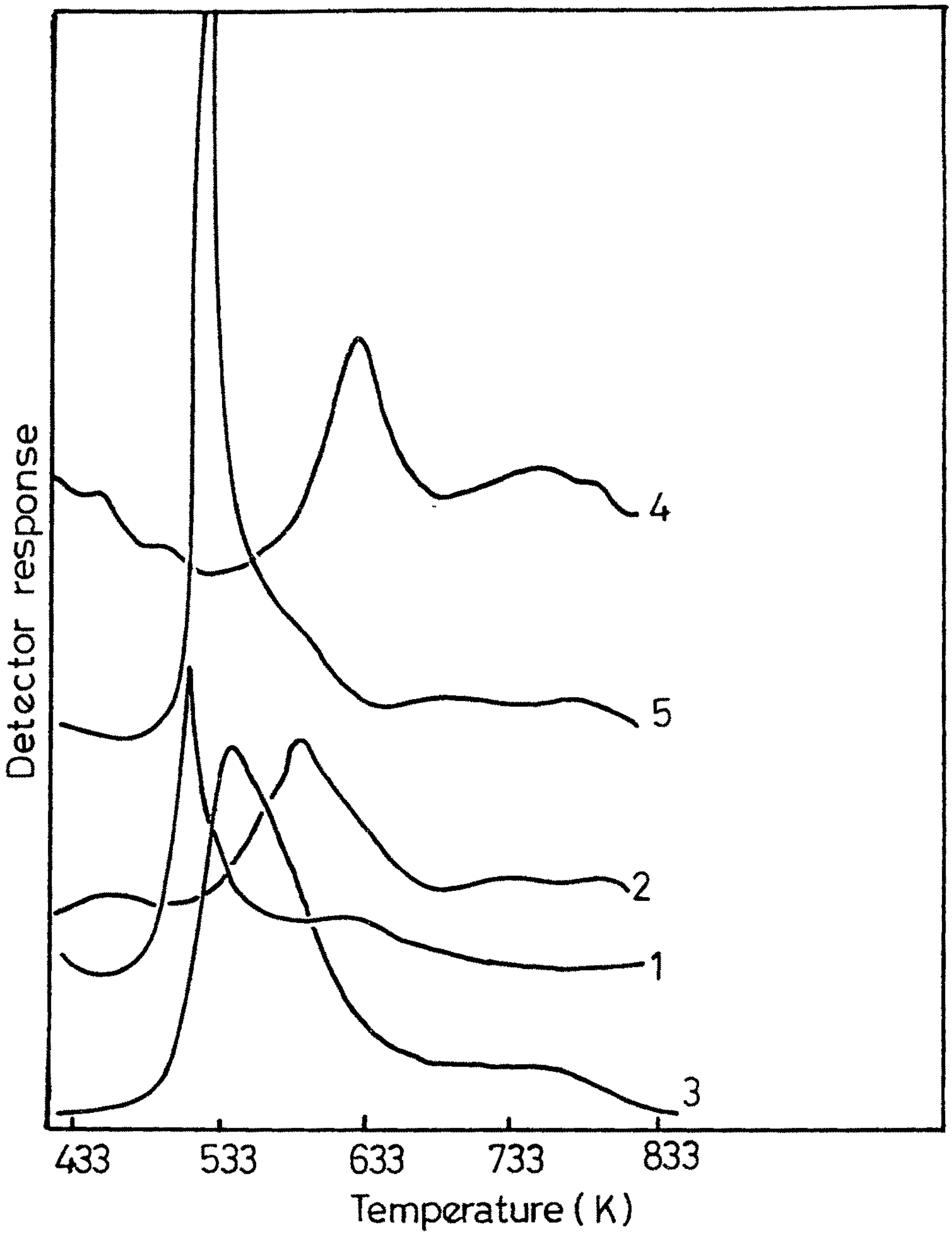

Fig. IV. 2. TPR Patterns of catalysts calcined at 673 K.

1. Pt-Li/Al_2O_3 2. Sn-Li /Al_2O_3

3. Pt-Sn-Li/ Al_2O_3 4. In-Li /Al_2O_3

5. Pt -In-Li/Al_2O_3

They ascribed the individual maxima to intermediate oxide species formed during reduction and suggested hard reducibility of a part of supported silver caused by strong metal-support interactions. Moreover, Ag is well known for its ability to form non-stoichiometric oxidic species. Sub-surface oxygen have been detected in silver catalysts (218). Silver nitrate used as the source of Ag in this preparation is known to decompose above 623 K to metallic silver. But separate XRD studies with 2% Ag on alumina revealed the presence of metallic silver as well as Ag_2O on the surface, after calcination at 673 K. Thus, the presence of a mixed phase led us to the conclusion that the low temperature reduction peak may be due to the reduction of absorbed/subsurface oxygen present in the metallic phase. Consequently, the high temperature reduction peak is assigned to the Ag_2O/alumina. In-Li/alumina exhibits a major sharp reduction peak at 625 K and a broad peak in the range of 583 to 813 K. Sn-Li/alumina shows a single broad reduction peak in the range of 533 to 683 K with T_{max} at 590 K. Though two differently bound tin species on alumina have been reported by other authors (152,164) in the present case the single stage reduction could be due to two factors;(a) lower calcination temperature and (b) presence of Li (0.6% by wt) in the support. The above two factors could perhaps effectively reduce the interaction of Sn with the support and consequently a single stage reduction at a lower temperature occurs. Monometallic Sb-Li/alumina was not found to get reduced in the temperature range of 273 to 873 K.

The TPR patterns of the promoted catalysts exhibit interesting behaviour. Pt-Ag-Li/alumina has a broad reduction peak in the range of 483-633 K which appears to be a combination of two sharp peaks merged together. The initial part of the peak appears to be that of Pt reduction and is immediately followed by Ag reduction. Eventhough the catalytic effect of Pt on Ag_2O reduction could be clearly seen, the reduction of Pt oxide is not found to be influenced by the presence of Ag. The TPR patterns of Pt-In and Pt-Sb on Li/alumina also exhibit single reduction peak whose T_{max} matches with that of Pt reduction. The peak intensities are very high, probably due to the simultaneous reduction of Pt and promoters. Obviously, Pt catalyses the reduction of the oxides of promoters. Moreover,the appearance of some high temperatue reducing species (at the tail of the main peaks) in In and Sb promoted catalysts could be regarded as evidence for the formation of some interaction compounds. This was found to be more pronounced in Pt-Sb than in Pt-In system. Pt-Sn-Li/ Al_2O_3 also exhibits only one combined reduction peak but the T_{max} was found to be significantly shifted to the higher temperature region with respect to Pt reduction. Similar observations in TPR of Pt-Sn system has been reported by Lieske and Volter (152). The decrease in the tin reduction temperature shows the catalytic effect of Pt on tin reduction and the increase in Pt reduction maximum clearly indicate a strong interaction between Pt and Sn species.

It can therefore be concluded that In, Sb and Sn interact with platinum and the extent of interaction increases in the order In <Sb <Sn. However, no evidence for interaction of Pt with Ag could be obtained from TPR studies.

IV.4.4 Diffuse Reflectance Spectroscopic Studies (DRS)

DRS is a technique generally used for the characterisation of heterogeneous catalyst surfaces. Unlike ESCA or EXAFS which utilizes high energy sources for excitation, this technique utilizes radiation in the UV-Vis range as the probe. Since most of the catalyst surfaces are opaque, this technique measures the intensity of the reflected radiation from the surface. A clear understanding of ligand field theory in conjunction with a knowledge of the possible surface species can lead to the identification of the actual surface species in DRS studies.

DRS has been extensively used for the characterisation of supported Pt catalysts at various stages of preparation, like drying, calcination, reduction and redispersion. Pt and Pt complexes are reported to absorb energy in the wavelength range of 200-600 nm corresponding to charge transfer (C.T.) from Cl->Pt and electronic transitions (d-d) (219). A number of surface Pt species with characteristic absorption maxima have been identified. However, most of the studies are confined to monometallic Pt catalysts. Pt-Sn is the only bimetallic catalyst system to be studied in detail by DRS (219). The surface oxo and chloro complexes of Platinum are also reported to absorb in the wave length range of 200-600 nm (220).

In this investigation, a systematic DRS study has been attempted on bimetallic catalysts, at three different stages, namely drying, calcination and reduction, with a view to elucidate the possible rolė of promoters in modifying the electronic levels of platinum. The DRS of dried (343 K, 3 h) samples of H_2PtCl_6 + HCl on alumina and H_2PtCl_6 + $SnCl_2$ + HCl on alumina are given in Fig.IV.3. The former exhibits three maxima at 270,370 and 465 nm. Nearly the same bands are known from the spectrum of H_2PtCl_6 in aqueous solution with d-d transitions at 353 and 450 nm and a charge transfer band resulting from an electron transfer from Cl to Pt at 262 nm (220). The shift in the positions of the bands may be due to the interaction with alumina support. The changed d-d transitions probably indicate distortion of the octahedral complex when adsorbed on alumina. The spectrum of H_2PtCl_6 + $SnCl_2$ + HCl/alumina show maxima at 215, 260, 330, 390 and an unclear band at 460-480 nm. The 215 nm band is due to $SnCl_4$ (219) and bands at 330, 390 and 480 nm could be assigned to $PtCl_4$ species (220). Since H_2PtCl_6 and $SnCl_2$ solutions were taken in a Pt:Sn atomic ratio 1:2, the formation of the complex of Pt and Sn was anticipated according to the reaction (223),

$$SnCl_2 + Cl^- \text{ ----> } SnCl_3^- \qquad \text{---- (1)}$$

$$PtCl_6^{2-} + SnCl_3^- + Cl^- \text{ ----> } (PtCl_4)^{2-} + SnCl_6^{2-} \qquad \text{---- (2)}$$

$$PtCl_4^{2-} + 2(SnCl_3)^- \text{ -------> } [PtCl_2(SnCl_3)_2]^{2-} + 2Cl^- \qquad \text{---- (3)}$$

$$SnCl_6^{2-} \text{ ------> } SnCl_4 + 2Cl^- \qquad \text{---- (4)}$$

This complex is reported to have an absorption band at 275-280 nm due to charge transfer from $(SnCl_3)^-$ ligands to Pt (224). But in the spectrum this band was absent and instead a weak band at 260 nm was observed which could be attributed to the presence of Pt(IV) species (220) on the surface. These observations indicate that no complex was formed when the solutions of Pt and Sn were mixed. Such a situation can arise only when the $SnCl_2$ content in the tin solution is not sufficient to reduce the Pt(IV) to Pt(II) and then form the complex. Hence, it appears

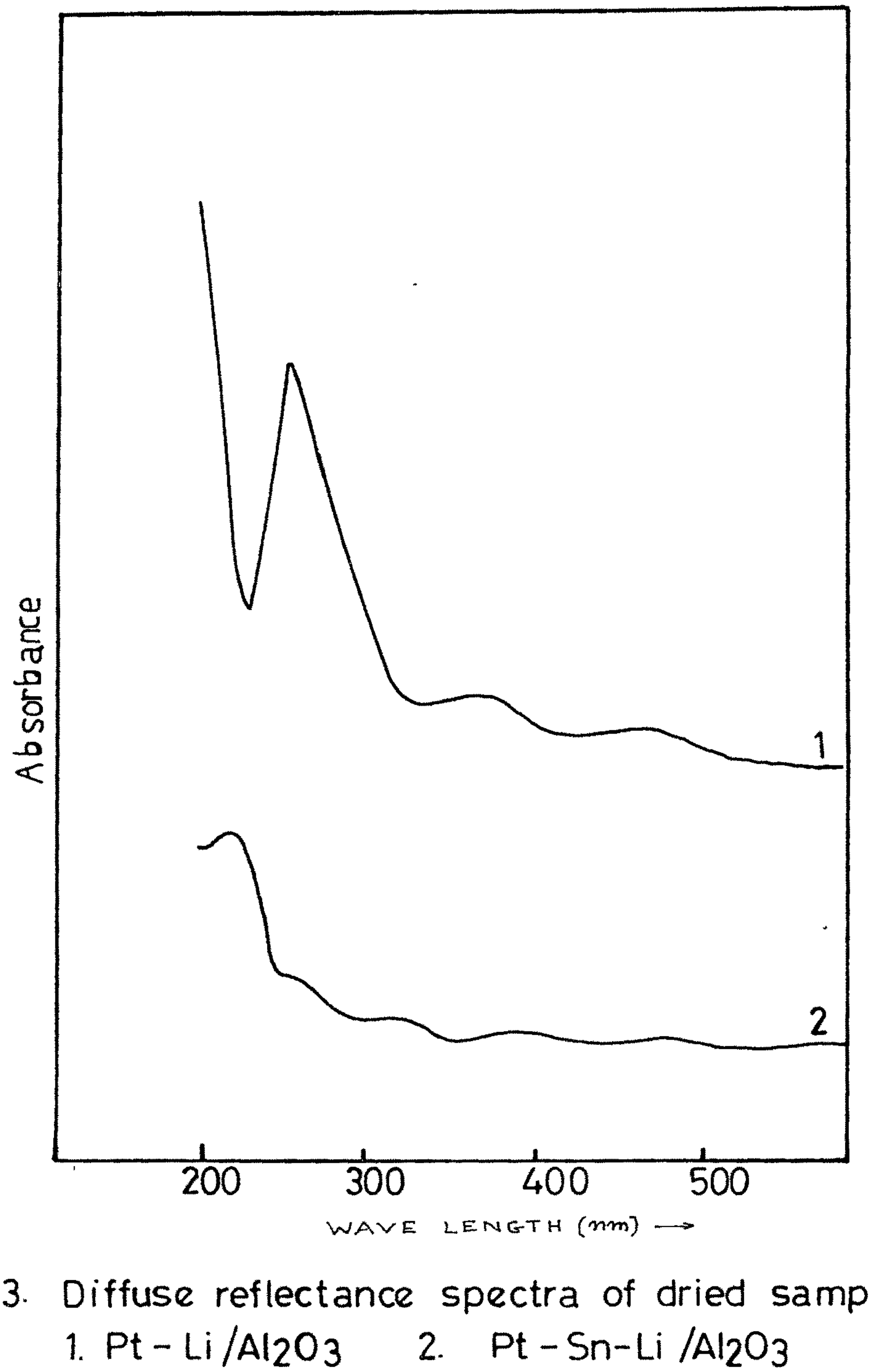

Fig. IV.3. Diffuse reflectance spectra of dried samples.
1. Pt - Li /Al_2O_3 2. Pt - Sn-Li /Al_2O_3

that the amount of $SnCl_2$ present in the solution was not even sufficient to reduce Pt(IV) to Pt(II) completely and no complex formation had occured. The other bimetallic dried samples did not show any absorption bands other than those for H_2PtCl_6 in the spectral range studied.

DRS of all the mono metallic and and bimetallic samples in oxidised and reduced states are presented in Fig.IV. 4 & 5. Pt-Li/alumina oxidised at 673 K exhibits bands characteristic of the surface species $Pt(IV)O_xCl_y$ in accordance with the reports of Lietz et al(220) (Curve 5 in Fig.IV.4, bands at 260, 340 and 450 nm). The 260 nm band corresponds to the charge transfer from Cl->Pt. The bands at 340 and 450 nm correspond to d-d transitions. They are broad and unclear due to adsorbed moisture. In, Sn and Sb on alumina in the oxidised state were not found to have any considerable absorption of energy in the range studied. But Ag/alumina exhibits bands at 260 and 400 nm. Since our earlier experiments have proved that Ag/alumina after calcination contain Ag in metallic as well as oxidised state, the bands could be assigned to silver species containing adsorbed oxygen on the surface. DRS of Pt-Ag-Li/alumina and Pt-In-Li/alumina in the oxidised state (curves 7&9 in Fig.IV.4) show bands characteristic of oxidised Pt species only. Even the Ag peaks observed in the mono metallic catalyst disappear probably as a result of the successive impregnation method adopted in the preparation of Pt-Ag catalyst. Curve 8 shows a more intense band at 375nm probably due to some interaction compound formed between Pt and Sb oxides. Correspondingly, even the C.T. bands undergo a shift but in the opposite direction. Pt-Sn-Li/alumina also exhibits a much more intense

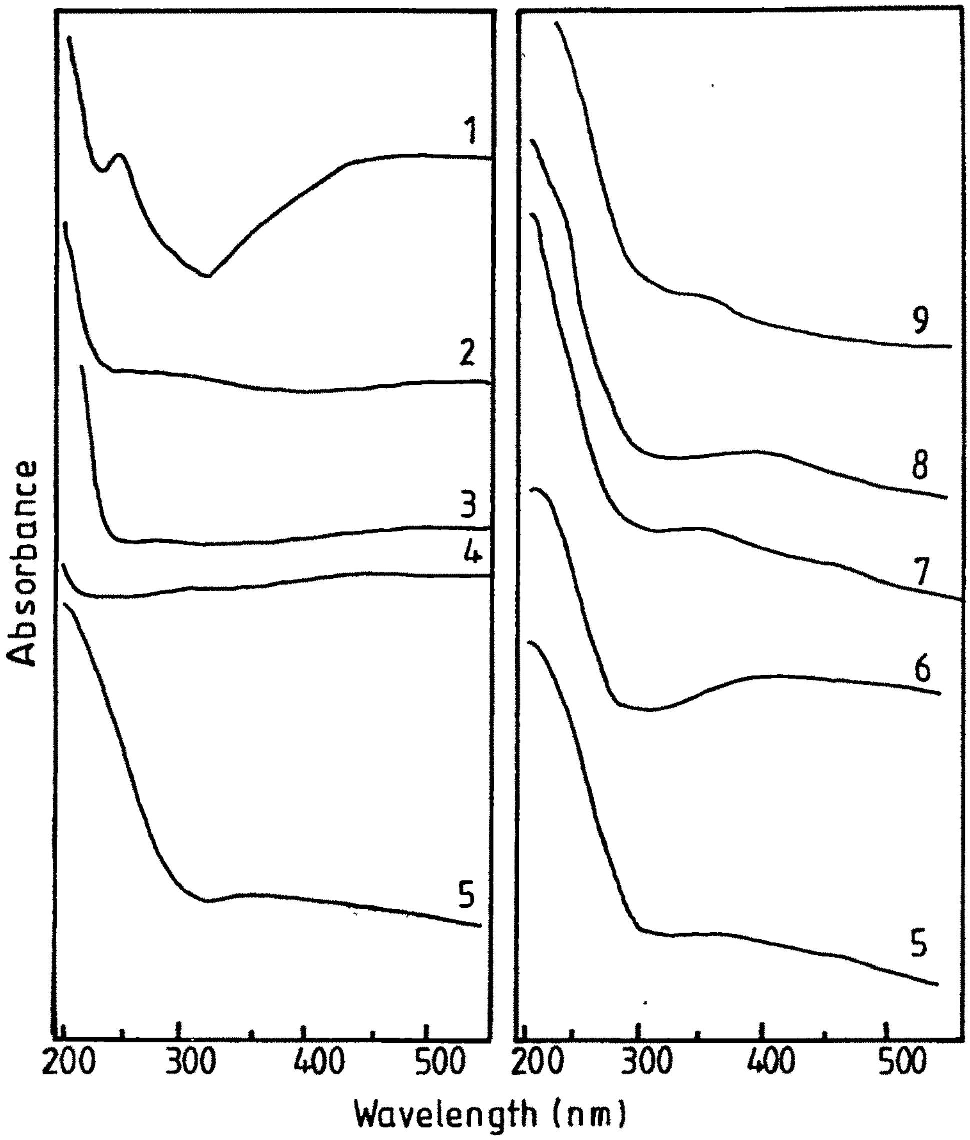

Fig. IV.4. Diffuse reflectance spectra of catalysts oxidised at 673 K.

1. $Ag-Li/Al_2O_3$, 2. $Sb-Li/Al_2O_3$, 3. $In-Li/Al_2O_3$,
4. $Sn-Li/Al_2O_3$, 5. $Pt-Li/Al_2O_3$, 6. $Pt-Ag-Li/Al_2O_3$,
7. $Pt-In-Li/Al_2O_3$, 8. $Pt-Sb-Li/Al_2O_3$,
9. $Pt-Ag-Li/Al_2O_3$.

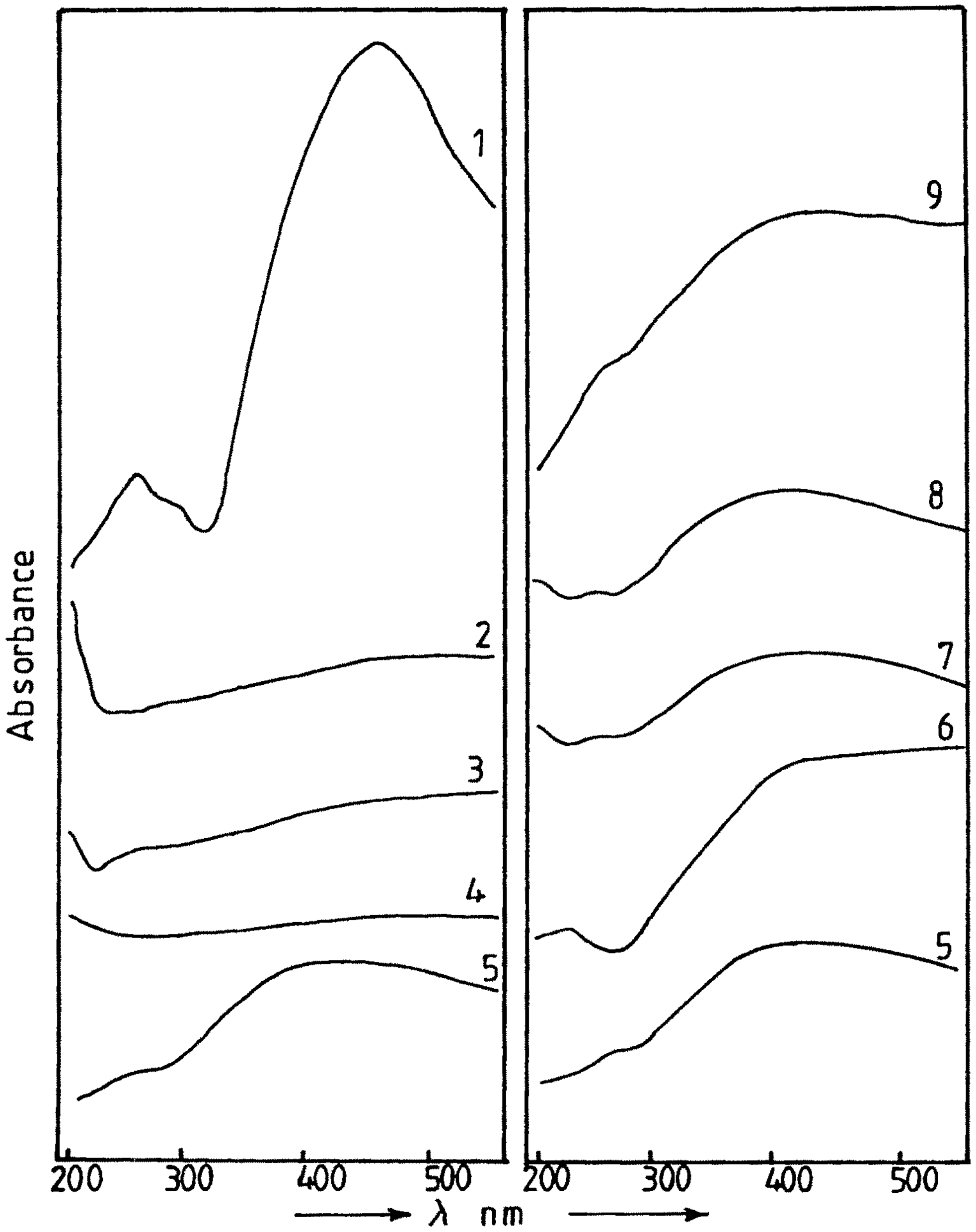

Fig. IV.5. Diffuse reflectance spectra of catalysts reduced at 748 K.

1. Ag-Li /Al_2O_3 , 2. Sb-Li / Al_2O_3, 3. In-Li /Al_2O_3,
4. Sn-Li /Al_2O_3 , 5. Pt-Li /Al_2O_3 , 6. Pt-Sn-Li/Al_2O_3,
7. Pt-In-Li /Al_2O_3, 8. Pt-Sb-Li/Al_2O_3 ,
9. Pt-Ag-Li/Al_2O_3

and broad band in the region of 325-500 nm indicating a stronger interaction between Pt and Sn oxides. The nature and structure of the interaction compounds proposed could not be established with DRS results alone. However, it is clear from the DRS results that the interaction between Pt and promoters occur in the oxidised state itself.

Pt-Li/alumina reduced at 748 K exhibits band at 260 nm which corresponds well with the C.T. transition, Cl->Pt. This band was present in all the Pt containing catalysts in the reduced state. Since the catalysts contain sufficient amount of chloride and there is a possibility for the existence of electron deficient Pt in such systems (225), a charge transfer is quite likely. Reduced Pt-Li/alumina exhibits another broad band centered around 375 nm. It has been reported that dispersed Pt on acidic alumina exhibits a broad band at 325 nm characteristic of a molecular charge transfer complex between oxidising sites of alumina and molecularly dispersed Pt (220). Moreover, this band was found to be absent in the spectrum of reduced Pt supported on silica (220) and it appears as a broad band in the range of 300-500 nm. The results have been interpreted in terms the acidity of the support and it is proposed that silica owing to its lower acidity is unsuitable for the complexation. Similar pattern was observed in our catalysts also and the broad band at 375nm is attributed to the dispersed Pt on alumina. The shift from 325 to 375 nm is possibly due to decreased acidity of the alumina caused by the modification by lithium. On reduction, Ag/alumina exhibits more intense bands at the same position as observed in the oxidised state, indicating the presence of more reduced Ag species.

Curves 6,7 and 8 in Fig. IV.5. indicate some modification of the charge transfer complex of Pt with alumina due to the presence of promoters. Pt-Sn-Li/alumina shows a clear & distinct behaviour. The C.T. band around 260 nm is shifted to the higher energy region and the d-d transition band to lower energy region along with considerable broadening and intensity increase. Similar effect can be observed in the case of Sb and In modified systems also. Moreover, extent of modification by Sb is more than that by In. Pt-Ag-Li/alumina shows an entirely different behaviour. The bands characteristic of reduced Ag have diminished and the bands corresponding to Pt cannot be clearly observed. It appears that what is observed is the resultant of bands of Ag & Pt. The absorption of energy in the lower energy region observed in the case of Sn, Sb and In modified catalysts indicates a homogenisation of energy levels due to mutual interaction. The extent of interaction is maximum in Pt-Sn system. In Pt-Ag system it appears that Pt catalyses the reduction of Ag, as indicated by TPR results accompanied by a possible electron transfer.

Hence, the DRS patterns of the reduced catalysts indicate the presence of dispersed Pt on the surface. Eventhough the state of the promoters are not exclusively proved the data so far discussed indicate a modification of the electronic structure of Pt, very significant in the case of Sn and less pronounced in the cases of Sb and In. Indium, antimony and tin induce a high energy shift in the C.T. band of Pt whereas Ag shifts the band towards the low energy region. The d-d transition bands of Pt are also shifted accordingly though the extent of shifts are not clearly visible due to the broad nature of the band. Thus it appears that all the elements modify the electronic environment of Pt which is bound to affect the adsorption-desorption behaviour of the reactants and products on the catalyst surface during reaction. Accordingly, the results of our activity studies discussed in the following sections reveal that except Ag all other elements used as promoters in this study promote the activity considerably but stabilisation of the catalyst differs from element to element. Sn promotes and stabilises the catalyst to the maximum extent whereas Sb and In promote to equal extent but the stability is much better in the case of Sb when compared to In. Generally, promoting action in Pt/alumina catalyst is explained on the basis of geometric/ensemble effect (increased dispersion and fewer number of contiguous platinum atoms)and electronic/ligand effects (modification of electronic environment of Pt including formation of alloys or interaction compounds). In reality, both the effects are expected to be operative. In order to obtain a better idea about the changes in the electronic environment of platinum caused by the promoters, XPS studies have been conducted.

IV.4.5 Electron Spectroscopy For Chemical Analysis (ESCA/XPS)

XPS measurements were carried out on all the reduced monometallic and bimetallic catalysts. The shift in binding energy of platinum, in presence of promoters, could give an indication about the nature of modification of electronic environment of platinum by the promoter elements. In the case of platinum, determination of binding energy of 4f electrons was not possible with accuracy due to the masking by Al 2p XPS lines. Hence, $4d_{3/2}$ and

$4d_{5/2}$ lines of platinum which are weaker had to be used. Similarly, the major XPS line in the case of Sb ($3d_{5/2}$) is masked by the presence of $1s_{1/2}$ line of oxygen from the support. Typical XPS patterns for Pt-Li/alumina, Sn-Li/alumina and Pt-Sn-Li/alumina in the reduced state are given in Figures IV.6 & 7. The observed binding energy values (with an accuracy of ±0·1 eV are presented in Table IV.5. For reduced Pt-Li/alumina the $4d_{5/2}$ line is observed at 314.7 eV. This value of binding energy is close to those reported by Bouman and Biloen (235) for Pt/alumina (314.6 eV) reduced in hydrogen at 923 K. In comparison with the reported binding energy values for Pt(0) state a positive shift is observed. Our own measurements on Pt(0) system gave a value of 314.4 eV. These observations support the fact that Pt when supported on alumina exists as electron deficient species. Apart from the modification caused by the support, promoters also are expected to contribute towards changes in the electronic environment of platinum. This fact is well established when the binding energies of Pt in promoted catalysts are compared with that for unpromoted Pt catalyst. As can be seen from Table IV.5 both the magnitude and direction of shifts are different for different promoter elements. In presence of silver the electron density of Pt increases (relatively more electron sufficient in comparison with Pt-Li/alumina) while both Sn and Sb cause mutually opposite effects i.e., Sn tends to decrease the electron density around Pt atoms while Sb tends to increase the electron density around Pt. Indium on the other hand, apparently does not register any noticeable change in the binding energy of Pt. The XPS data are in accordance with the observations recorded by DRS

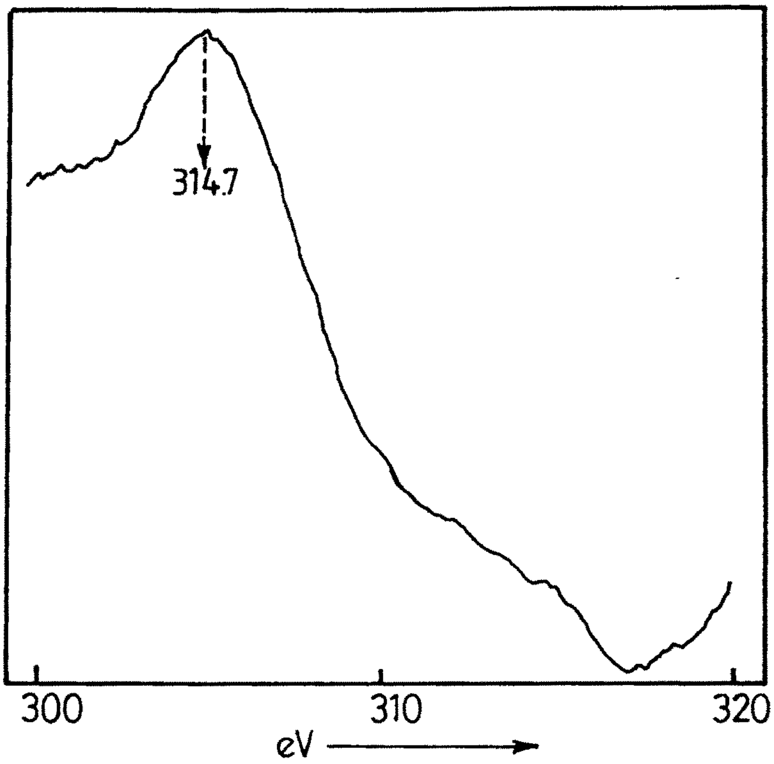

Fig. IV.6. XPS $4d_{5/2}$ line of platinum in Pt-Li/Al_2O_3 (Reduced)

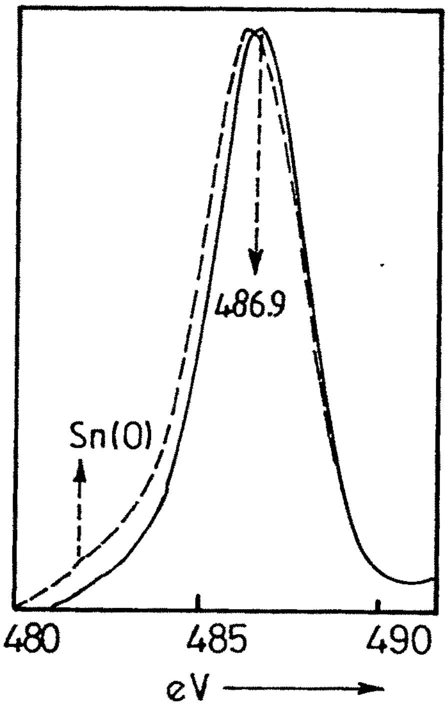

Fig. IV.7. XPS $3d_{5/2}$ line of tin species

1. (– – – –) Pt - Sn-Li / Al_2O_3 (Reduced)
2. (———) Sn - Li - Al_2O_3 (Reduced)

TABLE IV.5

Binding Energies For Reduced Catalysts From XPS Studies

Catalyst	Binding Energy (eV)	
	Platinum	Promoter
Pt-Li/alumina	314.7	
Pt-Ag-Li/alumina	314.2	
Pt-In-Li/alumina	314.7	445.3
In-Li/alumina		445.3
Pt-Sn-Li/alumina	314.9	486.7
Sn-Li/alumina		486.9
Pt-Sb-Li/alumina	314.5	

and TPR techniques. Sn exhibits a distinct behaviour when compared to other promoter elements. Sn was found to have a strong interaction with Pt and induce a good amount of shift in Pt reduction maximum. Ag was not found to influence the Pt reduction significantly but the generation of some high temperature reducing species was observed in the case of In and Sb. DRS also revealed shifts in both charge transfer and d-d transition bands of Pt, strongly indicating the changes in electronic environment of Pt brought out by promoter elements.

XPS data on some typical reduced monometallic catalysts, viz, In-Li/alumina and Sn-Li/alumina have also been collected. Reduced Sn-Li/alumina shows the presence of Sn in oxidised state (+2 or +4) only, in accordance with the observations by other authors (152,153,167). An indication of the presence of Sn as Sn(0) is seen in the XP spectrum of reduced Pt-Sn-Li/Al_2O_3 (Fig. IV.7). Except for Pt-Sn system, others were not studied with a view to establish the oxidation states of promoter elements and only the changes in Pt levels were monitored. As can be seen from the XPS results, significant changes in electronic levels of Pt are registered by different promoter elements. These changes invariably affect the activity, selectivity and stability of the catalysts, as discussed in subsequent sections.

IV.5 ACTIVITY EVALUATION

The ultimate aim of a catalyst researcher is to prepare a catalyst with optimum activity, stability and the best selectivity towards the desired product. A better understanding of the catalyst properties vis-a-vis its performance, could be useful for formulating scientific bases for catalyst preparation which will finally achieve the shape of a generalised comprehensive theory. Hence, a correlation of the catalyst characteristics with its activity and selectivity becomes a necessity.

Thus the series of promoted catalysts were subjected to a performance evaluation test as described in Chap.II.10. Two different types of catalyst testing were carried out and the results are discussed separately in the following sections.

V.5.1 Activity Evaluation At Atmospheric Pressure Conditions

The experimental conditions like temperature, hydrocarbon and hydrogen flow are detailed in Chap.II.10. The activity of the catalysts were evaluated for selective dehydrogenation of n-dodecane to C_{12} monoolefins. The product streams were analysed by gas chromatographic analysis. The initial activity was measured from the sample collected for the first five minutes after the introduction of the feed and then changes in the product concentration were monitored with time on stream by analysing samples collected for 5 min at the end of every hour. The total conversion data for the first six hours of time on stream for all the catalysts studied are given in Table IV.6. (FigIV 8)

TABLE IV.6.

Conversion Versus Time On Stream Data For Promoted Pt Catalysts

Catalyst weight	50 mg	Particle size	0.5-0.8 mm
Reduction temp.	748 K	Hydrogen flow	0.5268 mole/h
Reaction temp.	723 K	Hydrocarbon flow	0.088 mole/h

Catalyst	**Total Conversion %**						
	IN	**1 h**	**2 h**	**3 h**	**4 h**	**5 h**	**6 h**
Pt-Li/alumina	6.46	4.18	3.56	3.43	3.33	3.27	3.20
Pt-Ag-Li/alumina	7.60	5.57	4.98	4.50	4.10	4.00	3.90
Pt-In-Li/alumina	13.84	8.68	7.32	6.55	6.00	5.60	5.30
Pt-Sn-Li/alumina	16.45	12.82	11.55	10.69	9.96	9.36	9.20
Pt-Sb-Li/alumina	13.64	10.40	8.80	7.76	6.68	6.40	6.10

The data presented in TableIV.6 show clearly that all the elements including Ag, promote the activity and stability but to varying extents. Ag promotes the initial activity by hardly 1.2 % and the activity after 6 h on stream is 0.7 % more than that of unpromoted catalyst. Within the experimental errors this enhancement is not a significant one. In and Sb promoted catalysts show a very significant enhancement in initial activity and almost to equal extent. Pt-Sn system showed a still higher initial activity. Moreover, the deactivation during the first hour, which is an indication of the coke deposition, was found to be maximum

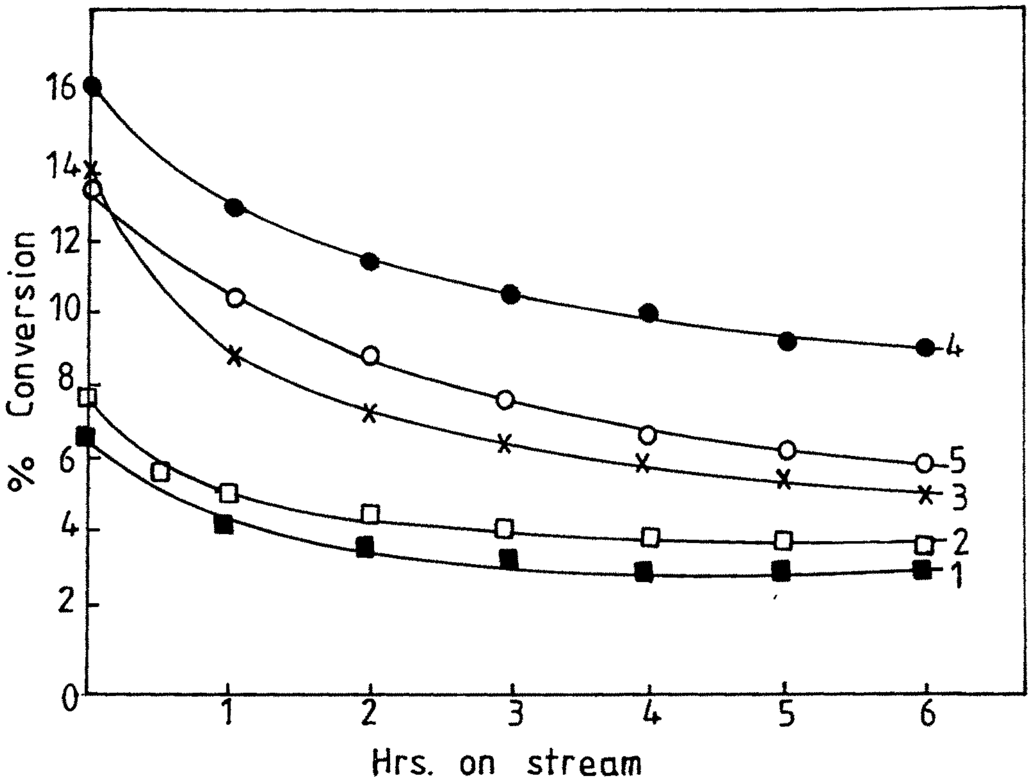

Fig. IV.8. Activity curves of promoted and unpromoted platinum catalysts.
1 Pt - Li /Al_2O_3 , 2. Pt -Ag- Li /Al_2O_3 ,
3. Pt-In-Li/ Al_2O_3 , 4. Pt - Sn-Li /Al_2O_3,
5. Pt -Sb-Li / Al_2O_3

in the case of Pt-In and much less and equal for Pt-Sb and Pt-Sn systems. Pt-Sb-Li/alumina shows only a 3.24 % decrease in conversion during the same period of time. The initial conversion of Pt-Sn catalyst is about 3 % more compared to Pt-In or Pt-Sb catalysts. But the deactivation during the first hour corresponds to only 3.6% drop in conversion. Thus it can be observed that the extent of stabilisation is maximum in Pt-Sn system and is in the order Pt-Sn>Pt-Sb>Pt-In.

IV.5.2 High Pressure Reaction Studies

Catalysts used in high temperature hydrocarbon conversions behave quite differently under high pressure conditions when compared to atmospheric pressure conditions. The decline in activity is significantly less and the life of the catalyst (stability) increases tremendously. Considering the thermodynamic equilibrium of the reaction,

$$\text{PARAFFIN} \rightleftharpoons \text{OLEFIN} + \text{HYDROGEN}$$

there is an increase in the number of moles for the forward reaction. The presence of hydrogen which is one of the products of the reaction itself retards the activity towards olefin formation. Similarly an increase in the system pressure will favour the backword reaction which involves a reduction in the number of moles. The equilibrium would shift more to the paraffin side and hence a decrease in the activity is possible. Moreover, coke deposition on the metallic surface, which mainly is responsible for the deactivation of the catalysts will also be less owing to the lower activity. The increased system pressure also has an additional favourable effect on the hydrogenation activity and removal of coke precursors and thus clear the surface continuously during the reaction. Comparison of stability of the catalyst against deactivation would be realistic when a decoking atmosphere persists. Hence, a comparative study of these catalysts on a long run under high pressure conditions was undertaken. The catalysts were tested for a total duration of 48 h out of which first 24 h under comparatively low severity conditions and rest under high severity conditions. Low severity conditions include a pressure of 30 psi, temperature 723 K, and LHSV 30 h^{-1}. After testing the catalyst for 24 h, the conditions were changed over to 15 psi pressure, 748 K temperature and 20 h^{-1} LHSV on the same catalyst charge, which are more severe in nature.

The data for high pressure testing of the catalysts are presented in Fig.IV.9. Only the percentage conversion to monooelefins are considered. Under the low severity conditions all the catalysts show comparatively good performance but Pt-Sn-Li/alumina proves to be better with practically no deactivation over the first 24 h. Pt-Li/Al_2O_3 and Pt-Sb-Li/Al_2O_3 show a slight fall in activity corresponding to 1% reduction in total conversion. Pt-Ag-Li/Al_2O_3 exhibits a three percent reduction in total conversion at the end of the low severity run.

Under high severity conditions also a similar trend was observed. In the case of Pt-Sn-Li/Al_2O_3 the conversion increases to 18 % whereas in the case of Pt-Sb and Pt-In catalysts it reaches 10 to 13 % at the start of the high severity run. Pt-Ag catalyst showed a very poor performance and it gave just 8 %

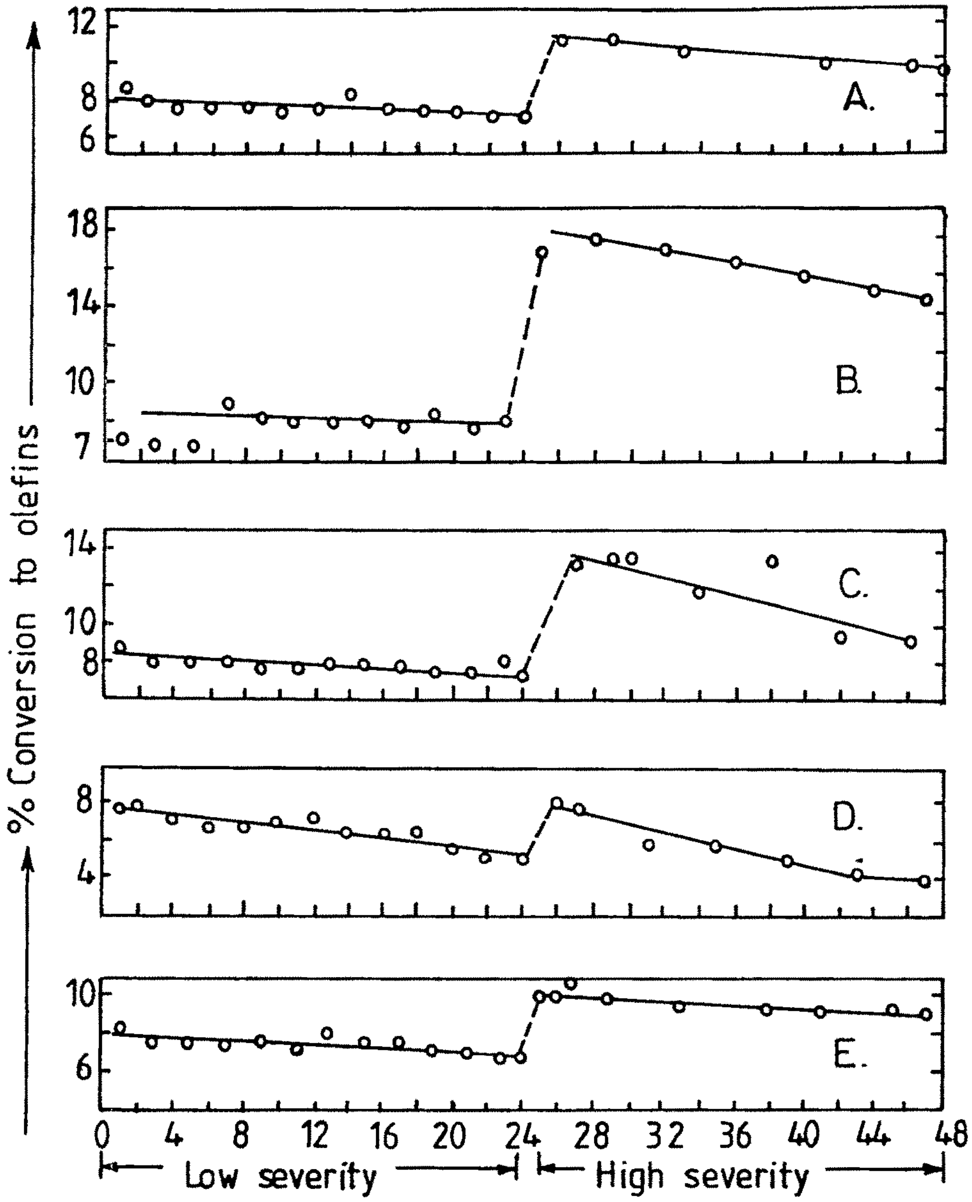

Fig.IV.9. High pressure activity evaluation of promoted catalysts.

A. Pt-Sb-Li/Al_2O_3 B. Pt-Sn-Li/Al_2O_3

C. Pt-In-Li Al_2O_3 D. Pt-Ag-Li/Al_2O_3

E. Pt-Li/Al_2O_3

conversion at the start of the high severity run. This shows that this catalyst has undergone sufficient coke coverage compared to other catalysts. The possible reason for this could be the increase in electron density of Pt due to the presence of Ag which in turn can increase the adsorption bond strength of olefin. Consequently, the residence time of olefin on the surface is increased thereby leading to the irreversible deposition of coke on platinum surface. In spite of the decoking atmosphere prevailing, the differences in the performance of the promoters are very clear and trends similar to the atmospheric pressure evaluation are followed.

IV.5.3 Studies On Selectivity of The Catalysts For Different Products

The reactions which accompany the dehydrogenation of higher normal paraffins and change the selectivity of the catalysts are cracking, bond isomerisation, sequential dehydrogenation to poly-olefins and cyclisation. The activity evaluation of catalysts was carried out at 723 K where the thermal cracking was not observed. Even during the catalytic runs, no cracked products were found in the reaction products except for some negligible amount in the initial stages. The usual packed coulmn analysis mainly showed 5 well separated components other than the unreacted paraffin. With the help of capillary column GC-MS analysis these peaks were further split and identified as clusters of 1,2,3-monoolefins, 4-monoolefins, (5+iso)olefins, diolefins and aromatics respectively.

The overall selectivity of these catalysts towards the formation of monoolefins was calculated after clubbing up all the monoolefins together. Pt-Sn showed the maximum and unpromoted Pt showed the minimum selectivity. The actual values are presented in Table IV.8.

TABLE IV.8

Overall selectivity of Catalysts For Monoolefin Formation

Catalyst	Selectivity
Pt-Li/alumina	88 %
Pt-Ag-Li/alumina	90 %
Pt-In-Li/alumina	90 %
Pt-Sn-Li/alumina	93 %
Pt-Sb-Li/alumina	92 %

The changes in the yield ratios of the different products were calculated as a function of time on stream and with respect to total conversion according to the method described below:

If the total conversion at any 'time on stream' "t" is "x_t" and the product distribution, $x_t = x_1 + x_2 + x_3 + x_4 + x_5$ the yield of 1 at time "t" is given by the equation:

$(yield_1)_t = (x_1)_t / x_t$ where x_t is the total conversion at time "t"

Yield ratio of "1" at time "t" is calculated as,

$$\frac{(yield_1)_t}{(yield_1)_0}$$

Similarly, yield ratios for other products can be calculated as,

$$\frac{(yield_2)_t}{(yield_2)_0}, \quad \frac{(yield_3)_t}{(yield_3)_0}, \quad \frac{(yield_4)_t}{(yield_4)_0} \quad \text{etc.}$$

The yield ratio plots are presented in Figures.IV.10 to 14.

Fig.IV.10 shows the yield ratio plots as a function of time on stream, of 1, 2 and 3-monoolefins for the set of catalysts studied. The selectivity for this particular product remains

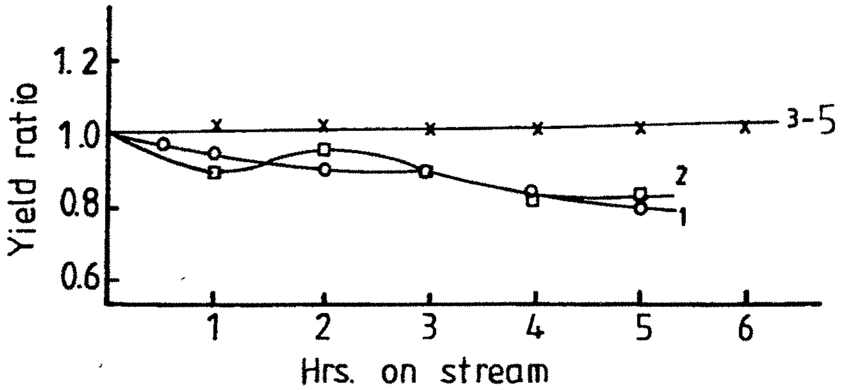

Fig. IV.10. Yield ratio plots for 1,2,3-mono-olefins

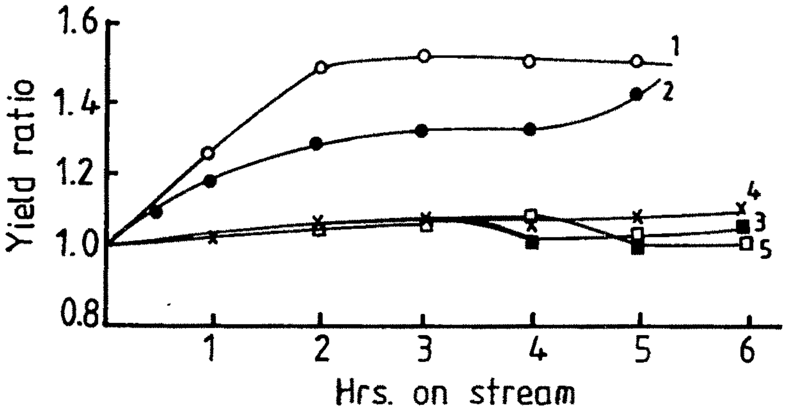

Fig. IV.11. Yield ratio plots for 4-mono olefins.

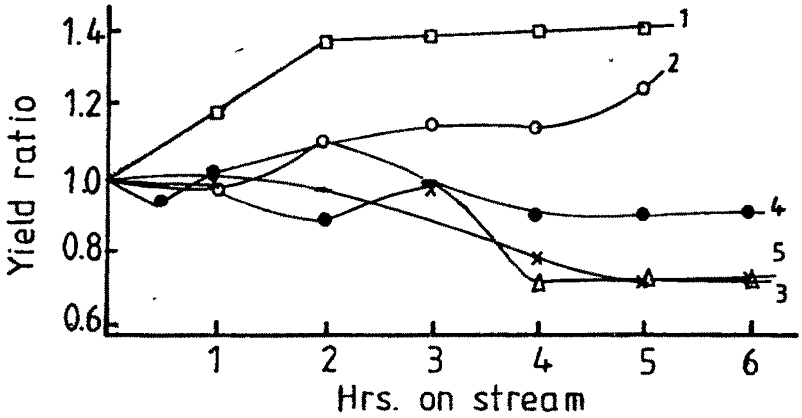

Fig. IV.12. Yield ratio plots for (5 + iso) olefins.

1. Pt-Li/Al_2O_3, 2. Pt-Ag-Li/Al

3. Pt-In-Li/Al_2O_3, 4. Pt-Sn-Li/Al_2O_3

5. Pt-Sb-Li/Al_2O_3.

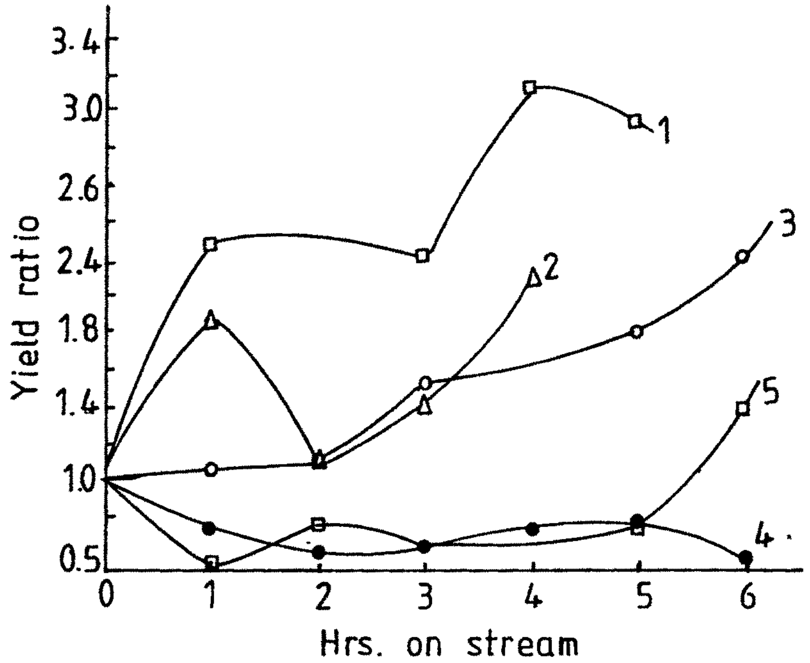

Fig. IV. 13. Yield ratio plots for diolefins.

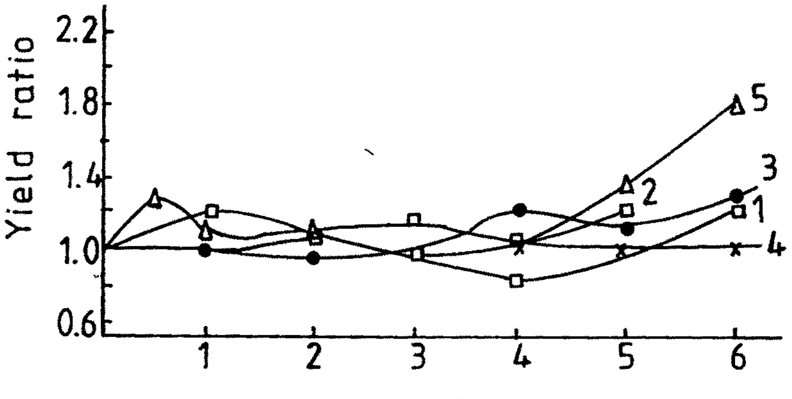

Fig. IV.14. Yield ratio plots for aromatics.

1. Pt-Li /Al_2O_3 , 2. Pt-Ag-Li /Al_2O_3,
3. Pt-In-Li /Al_2O_3 , 4. Pt-Sn-Li /Al_2O_3,
5. Pt-Sb-Li /Al_2O_3 .

almost same throughout the run for Sb, Sn and In promoted catalysts whereas it decreases by 20% for the Ag promoted and unpromoted catalysts. The yield ratio plots for 4-monoolefins are presented in Fig. IV.11. The selectivity for the 4-mono olefins is found to be continuously increasing with hours on stream for unpromoted and Ag promoted catalysts whereas it is more or less steady for the other catalysts. The changes in the yield ratio of (5 mono + iso) olefins depicted in Fig.IV.12 also shows a similar behaviour for Pt and Pt-Ag catalysts but it shows a downward trend for Sn, Sb and In promoted catalysts.

These observations of change in selectivities appear to be complementary to each other. The unpromoted and Ag promoted catalysts show a decrease in the yield ratios with time on stream for 1, 2 and 3-monoolefins and an increase for 4, 5 and isoolefins. The changes occuring on the surface of the catalyst when exposed to the hydrocarbon feed appear to favour the formation of isomeric products thereby decreasing the selectivity for 1, 2 and 3-monoolefins. More specifically, the bond isomerisation and skeletal isomerisation are favoured for Pt and Pt-Ag catalysts. This is probably because of the modification of the surface by the initial coke deposition occuring on exposure to the hydrocarbon feed. The changes in selectivity observed in Sn, Sb and In promoted catalysts are less significant indicating less pronounced modification of the surface. Thus it can be inferred that the coke deposition is slower on Sn, Sb, and In promoted catalysts when compared to Ag promoted and unpromoted catalysts. This faster coke deposition on Pt-Ag and Pt/alumina catalysts may be the consequence of a stronger adsorption bond between the Pt atoms and adsorbate molecules which is directly dependent on the electron density of Pt. The selectivity for diolefins (Figure.IV.13) increases to a higher extent for Pt-Li/Al_2O_3 than that for Ag promoted catalyst, with time on stream. The formation of diolefins can occur either by sequential dehydrogenation or multipoint adsorption of the same molecule (i.e. flat orientation of the molecule). The observation that diene formation is more favoured on unpromoted platinum catalyst, may be due to multipoint adsorption which require more than one Pt atom in close proximity. This depends on the number of atoms in an ensemble of Pt. The chances of finding ensembles containing more number of atoms of Pt is higher in the case of unpromoted catalyst, than in a promoted catalyst. This may favour multipoint adsorption and increase the selectivity for dienes. Indium promoted catalyst shows an initial slower increase and then more pronounced increase towards the selectivity for diolefins. Similarly, Sb promoted catalyst shows an initial decrease and then an increase after 5th hour on stream whereas Sn promoted catalyst shows a steady decline throughout. The extent of interaction of these elements with Pt are also in the same order as observed in TPR and DRS data. However, the fact that these measured quantities are very small and hence the points are scattered is acknowledged.

Finally, the selectivity patterns for aromatics formation (Fig. IV.14) shows an initial stability and then increase in the case of Sb and In catalysts and initial increase and then fall in the case of unpromoted and Ag promoted catalysts. The aromatics yield ratios of the latter set was expected to increase as indicated by the initial increase and analogous to diene selectivity trend, but the catalysts appear to be sufficiently deactivated already, which makes it unable to accomplish the triene formation and resultant aromatisation.

IV.5.4 Temperature Programmed Oxidation Studies

The observations discussed above indicate that the stability and constancy in selectivities of Sn, Sb & In promoted catalysts are mainly because of the electronic modifications by the promoters which restrict the coke formation on the active sites. This effect renders sufficient number of exposed (uncoked) Pt atoms on the surface in order to maintain the activity. Also one can anticipate that the coke deposition on the metal species for the same duration of time in all the catalysts would be similar and almost to the same extent in spite of the higher initial activity in some cases. The deactivation and selectivity changes observed in Pt and Pt-Ag catalysts could be mainly due to the coke deposited on the metal (but not on the support) which happens within the initial 2 hours time. Since the activity after 2 h for these catalysts are very low, the coke deposited on the support is also expected to be low. It can also be predicted that the long term deactivation of Sn, Sb and In promoted catalysts excluding the initial fast deactivation will be mostly due to the slow accumulation of coke on the support. Also, more amount of coke on the support compared to the less active catalysts is expected because of their considerable activity even at the end of the run. Since the activity of Sn, Sb and In promoted catalysts are much higher at any moment compared to Pt or Pt-Ag catalysts, the arguement that more number of exposed (uncoked) Pt is available on the surface (less coke coverage of the metals) is justified. In order to understand the nature and coverage of coke on the catalysts, with an intention to provide supplementary evidence for the above conclusions, a temperature programmed oxidation of coke on used catalysts was carried out, results of which are presented in the following paragraphs.

Irrespective of the reaction, whether hydrogenation or dehydrogenation or reforming, hydrogen is used as the carrier gas without which the catalyst gets completely deactivated within a short span of time. Hydrogen is reported to continuously hydrogenate the coke precursors or prevent excessive dehydrogenation by maintaining the equilibrium always shifted to the left hand side. Since the mechanism of dehydrogenation follows a sequential process (Paraffin to monoolefin, then diolefin and then triolefin and so on) the reason for the coke formation could be the formation and oligomerisation of the polyolefins which undergo further dehydrogenation to coke. The C:H ratio is generally very high in coke. Coke deposits are classified into two types, soft coke and hard coke, depending on the temperature of its oxidation. Hard coke, which is more of the graphitic form gets oxidised at very high temperatures (229). The C:H ratio will be small in the case of soft coke and higher in hard coke. Moreover, coke deposited on the metallic species usually gets oxidised at a lower temperature than the coke on the support due to the catalytic effect of the metal. A temperature programmed oxidation study of the coke deposited on the catalysts, could reveal the nature and distribution of coke in the catalyst system. TPO experiments on catalysts exposed to hydrocarbon feed under identical conditions and time were carried out.

In order to avoid any mass transfer limitations due to diffusion, separate TPO runs were carried out with the same used sample in the powdered form and as spheroids. The curves overlap as shown in Fig.IV.15 indicating that this process is free of mass transfer constraints under the conditions employed.

The actual TPO curves for the series of used catalysts under investigation are presented in Figure IV.16. Care was taken during the coking reaction to avoid any loss of coke by hydrogenation. This was achieved by changing over from hydrogen to helium, after the run for flushing,which removes any weakly adsorbed hydrocarbon. The oxidation of coke proceeding with temperature was followed by monitoring the CO_2 content of the effluent gas by gas chromatographic analysis at definite intervals.

The results of TPO experiments show exactly the same behaviour as anticipated in the previous section. The pattern of coke oxidation shows that coke deposited on the metal (oxidisable upto 623 K) is relatively less in all the cases irrespective of the initial activities or total coke deposit. Coke oxidation starts at lower temperatures in all promoted catalysts, when compared to unpromoted catalyst indicating that,in general, the coke

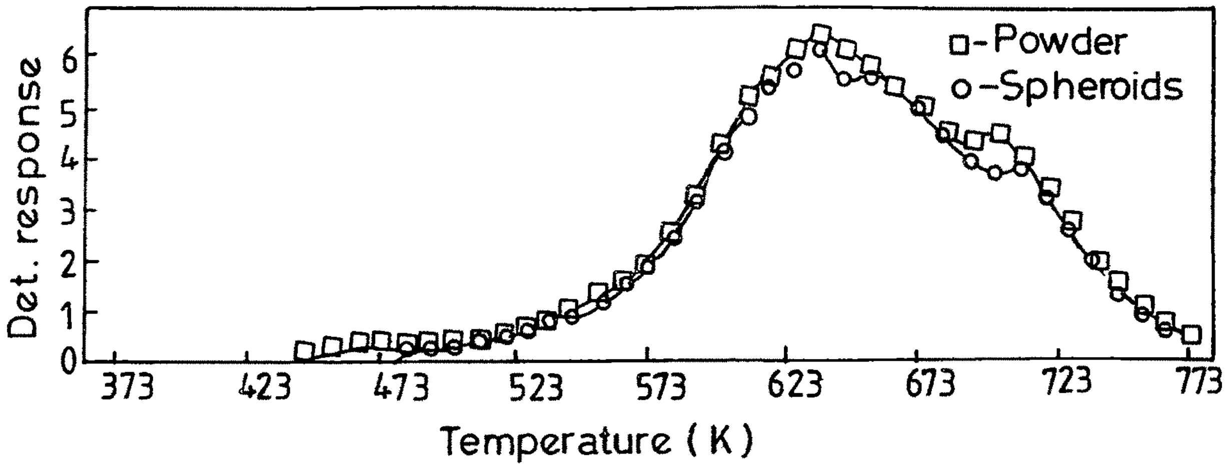

Fig.IV.15. Mass transfer behaviour of coked catalysts.

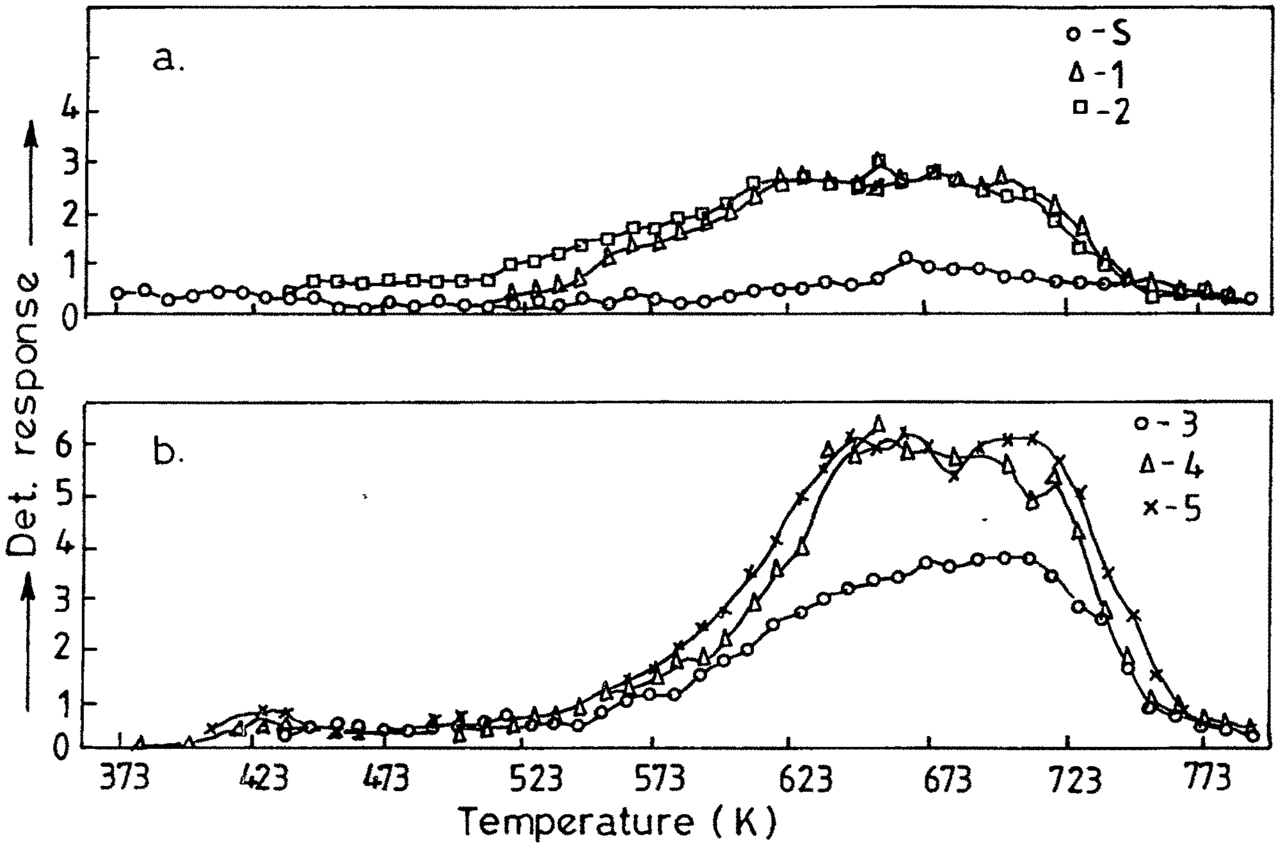

Fig.IV.16. TPO Patterns of coked catalysts.

a: S. Li/Al_2O_3 , 1. Pt-Li/Al_2O_3 , 2. Pt - Ag-Li/Al_2O_3 ,

b: 3. Pt - In-Li/Al_2O_3 ,4. Pt - Sn-Li/Al_2O_3, 5. Pt-Sb-Li/Al_2O_3.

on promoted catalysts are soft in nature. Majority of the coke was found to be on the alumina support which is probably the reason for the slower long term deactivation of the catalysts. The proportion of coke on the support was found to be in direct relationship with the activity and increased stability. Hence Pt-Sn-Li/Al_2O_3 was found to have the maximum coke on support and others showed a decreasing trend in the order,

Pt-Sn > Pt-Sb > Pt-In > Pt-Ag > Pt.

A close observation of the TPO patterns of Pt and Pt-Ag catalysts reveals another interesting feature. The coke on the metal on Pt-Ag is significantly higher than that on unpromoted Pt. This leads us to believe that the adsorption bond (Pt-HC) is strengthened in the case of silver promoter in contrast to Sn, Sb and In promoters.

IV.6 PROMOTED PLATINUM ON ALUMINA CATALYSTS: CORRELATIONS BETWEEN PROPERTIES AND PERFORMANCE

As seen in the earlier sections, among all the catalyst systems studied, Pt-Sn combination displays better performance in terms of activity, selectivity and stability for the dehydrogenation of n-dodecane even under highly severe conditions. TPO results clearly indicate that coke deposition is mainly restricted to the alumina support, leaving the metal sites still exposed for catalysis. The changes in selectivity for different products during the reaction is also minimum with Pt-Sn system.

The physico-chemical properties investigated by metal dispersion, TPR, DRS and XPS measurements can now be used to explain the beneficial effect of tin on platinum relative to the other promoted catalysts studied to arrive at a comprehensive idea about the promoter action of the various elements on platinum.

As mentioned earlier, a promoter brings about changes in the nature of the primary metal by (1) Ligand effect (2) Ensemble effect and (3) Alloying effect. Metal dispersion measurements by H_2-O_2 chemisorptive titration have revealed that hydrogen chemisorption is severely inhibited in the case of promoted catalysts. TPR studies have shown that maximum metal-promoter interaction is observed in the case of Pt-Sn system, followed by Pt-Sb and Pt-In, in that order. XPS studies explicitly indicate the direction of charge transfer by different promoter elements. Electron density around platinum is expected to play a major role in the adsorption - desorption process during dehydrogenation.

The mechanism of dehydrogenation of paraffins involves the following elementary steps as suggested by Biloen et al (236).

(1) Cleavage of the first C-H bond in a dissociative adsorption step resulting in an adsorbed alkyl group.

(2) Cleavage of the second C-H bond resulting in σ or π bonded olefin.

(3) Desorption of olefin.

Assuming a similar mechanism for dehydrogenation of n-dodecane, the following conclusions could be drawn: the initial adsorption of paraffin which occurs through a charge transfer from hydrocarbon to platinum would be facile when the metal is more electron deficient. Such a situation exists in Pt-Sn system due to ligand effect. However, in spite of adverse ligand effect, indium as well as antimony promoted catalysts show significant and equal improvement in activity presumably due to the ensemble effect. Higher activity of Pt-Sn system can then be ascribed to the combination of favourable ligand and ensemble effects.

Desorption of olefin from the surface which governs the coking and deactivation of the catalysts, is another important step. Mechanism of olefin adsorption on platinum is well studied by several workers (230-232). When adsorbed, olefins are reported to form sigma (σ) and pi (π) complexes with platinum (233). The formation of π complex occurs through a back donation of electron density from platinum to the vacant antibonding orbitals of olefin as shown in Fig.IV.17. The stability of such an adsorbed olefin is believed to be determined by the extent of back donation (234) by the metal. Thus, it is obvious that a decreased electron density on platinum would reduce the tendency for back donation which in turn would favour the desorption of olefin from the surface. This could be the possible reason for the extra stability shown by Pt-Sn system in both atmospheric and high pressure evaluation studies.

Another interesting observation is that Pt-Sb system shows slightly better stability when compared to Pt-In system. XPS studies show that platinum in the former is more electron rich. Therefore, the adsorbed olefin is expected to be held more firmly on the surface which should result in faster deactivation of the catalyst. Probably in this case, the initial adsorption bond between the hydrocarbon and platinum which is weaker, more than counterbalances the effect due to back donation and thus, desorption of the product is still favoured. Exceptionally lower dispersion value exhibited by Pt-Sb system lends further support

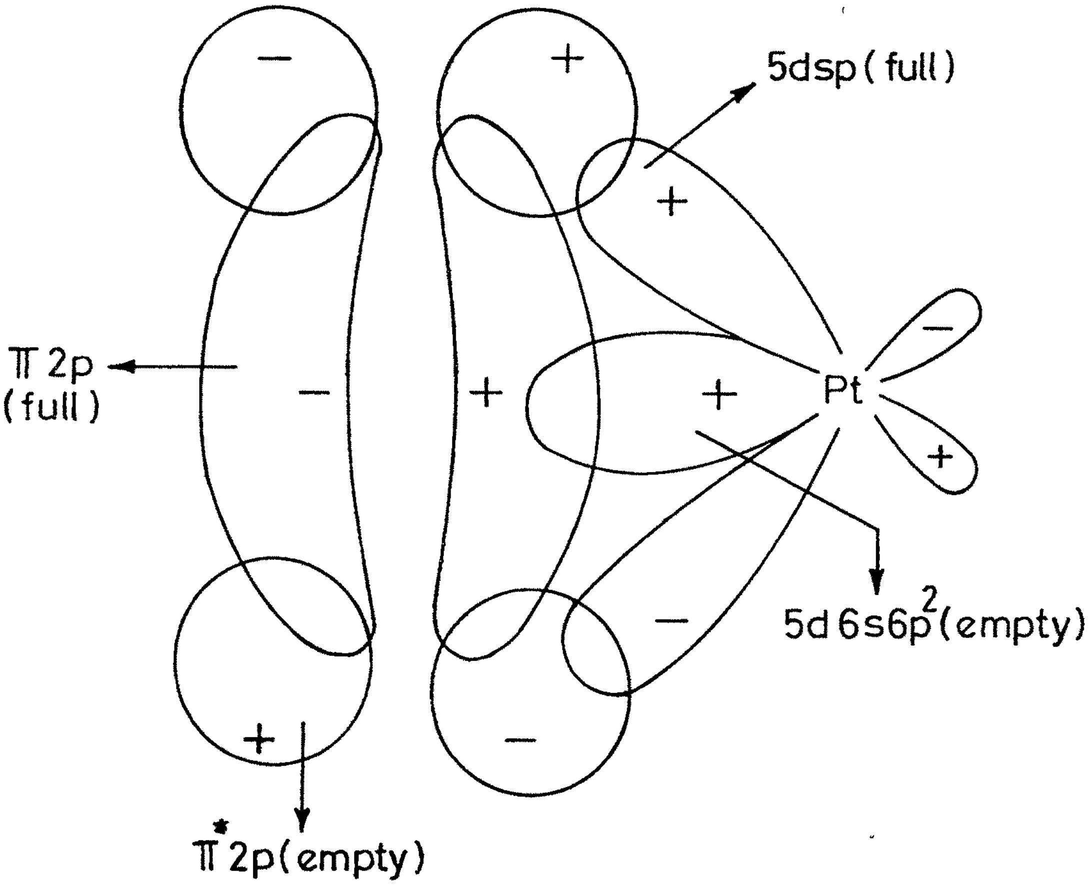

Fig. IV. 17. Ethylene - Platinum π complex to this arguement. In the Pt-Ag system, due to the possibility of significant back donation caused by increased electron density and poor ensemble effect (due to successive impregnation) neither enhancement nor stabilization are manifested.

Thus, the overall picture is complicated with both electronic and ensemble effects contributing towards the performance of the catalysts. Creation of additional active centers or significant alloying are ruled out because except in Pt-Sn system, where there is an indication of small amount of Sn(O), promoters were found to be present mostly in a positive oxidation state. Thus, it may be concluded that the impact of ensemble effect is manifested in the activity improvement whereas ligand effect is mainly responsible for the stabilisation of the catalyst; however, there could be an overlap. The relative contribution from the two can not be easily established. Bursian et al (226) have tried to quantify the ensemble and ligand effects in terms of shift in the vibrational frequencies of adsorbed CO and observed entirely different behaviour in the case of isoelectronic indium and thallium, in terms of direction and magnitude. Eventhough, in the present case qualitative idea about ligand effect is obtained by XPS, the techniques available are inadequate for estimating ensemble effect. Unless unambigous methods to quantify these effects are made available it is difficult to obtain a better understanding of the action of promoters. Appropriate method for this purpose appears to be EXAFS because it can measure the co-ordination numbers.