

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 The Effect of Promoters on Activity at 500 °C

Dilution of catalytically active Pt atom with a catalytically inactive atom has been employed as a means of studying the intrinsic activity of ensembles of contiguous Pt atoms of different size. For this work the activity data are obtained in quartz tube reactor. The activity is compared in terms of the conversion of propane dehydrogenation and the selectivity to propylene on the different type of catalysts. Figure 4.1 presents the conversion of propane dehydrogenation at 500 °C as a function of reaction time.

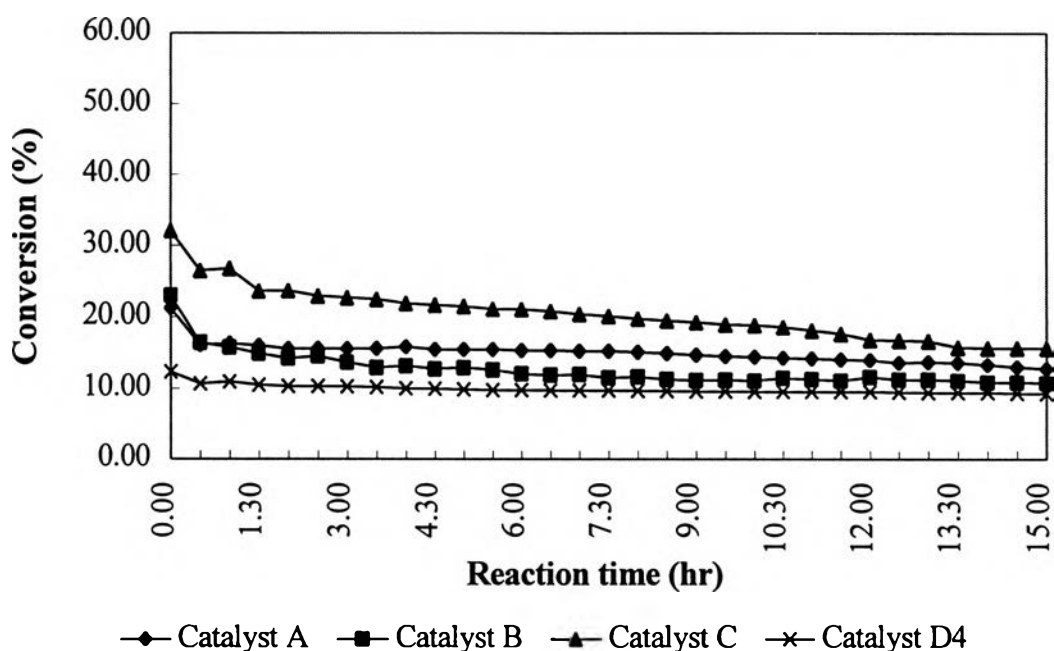


Figure 4.1 The conversion of the propane dehydrogenation at 500 °C as a function of reaction time on alumina-supported catalyst.

The effect of promoters, tin (Sn) and lithium (Li), on activity are observed at 500 °C. From Figure 4.1 illustrates the addition of Li into Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and it is found that the Pt-Li/Al<sub>2</sub>O<sub>3</sub> exhibits decreasing dehydrogenation activity and gives less cracking products but increases the selectivity for propane dehydrogenation as shown in Figure 4.2, in agreement with results reported elsewhere (Cortright and Dumesic, 1995), when compare to the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

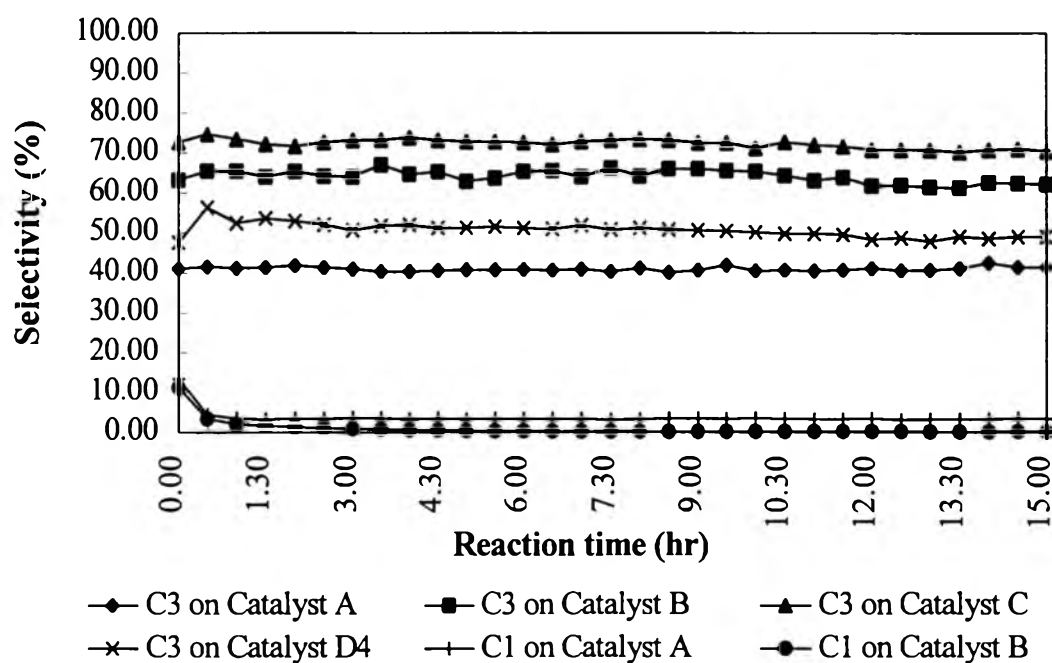


Figure 4.2 The selectivity of propane dehydrogenation at 500 °C as a function of reaction time on alumina-supported catalyst.

This effect can be explained in that Li can neutralize the acidity of the support reducing the cracking reactions that may occur. In addition, Li may donate electrons of alkali metal to the Pt. When hydrocarbons adsorb on this structure, the Pt-C bond is stronger and the C-H bond weaker than on the

unpromoted catalyst. Therefore it is more selective to propylene but non-selective to hydrocracking reaction.

The influence of tin on the performance of supported Pt catalyst can be seen in Figure 4.1. Addition of Sn to Pt/Al<sub>2</sub>O<sub>3</sub> catalyst markedly increases dehydrogenation activity for propane. It furthermore, follows that not only the activity but also the selectivity of the Pt function is modified by addition of tin (Dautzenberg et al., 1980). Particularly the formation of cracking products is suppressed because of the hydrocarbon cracking reaction requires larger ensembles of surface Pt atoms than dehydrogenation reaction. So when Sn is added into Pt/Al<sub>2</sub>O<sub>3</sub> catalyst it will decrease the ones requiring ensembles with relatively large numbers of adjacent Pt atoms on the surface. The literature suggests that dehydrogenation reaction can proceed on small ensembles of surface Pt atoms (Cortright and Dumesic, 1995 and Resasco et al., 1994). We can say that Sn has more positive effect in promoting the activity and selectivity of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst than Li at these moderate conditions by decreasing the size of Pt surface ensembles. Sn has a significant effect on metal sites whereas Li has little effect on metal sites, so Pt-Li/Al<sub>2</sub>O<sub>3</sub> can not give higher activity as can be seen in Figure 4.1.

With the addition of two promoters (Sn and Li) into Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, it is found that only the selectivity for propylene can be modified whereas the activity of propane dehydrogenation is reduced and it shows the steady behavior on activity and selectivity. In addition, there is reduced cracking products. This poorer results of the promoted catalyst in reducing its activity is observed under moderate conditions. Lin et al., 1980, studied cyclohexane dehydrogenation and they reported a poisoning the dehydrogenation reaction

may occur by promoting catalyst under the mild conditions. This implies that the activity of trimetallic catalyst depends on the operating conditions.

#### 4.2 The Effect of Promoters on Activity at 600 °C

When the reaction temperature is raised to 600 °C the effect of Sn and Li on the Pt catalyst plays a positive significant role as can be seen in Figure 4.3 and 4.4. It can be seen that under these severe conditions, the influence of Li or Sn on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst exhibits the same behavior as the reaction is operated at 500 °C. However, it gives the higher selectivity and activity than when it is operated at lower temperature. In contrast to the results at moderate reaction temperature, the Pt-Sn-Li/Al<sub>2</sub>O<sub>3</sub> catalyst shows higher in activity and selectivity than Pt/Al<sub>2</sub>O<sub>3</sub>, Pt-Li/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst.

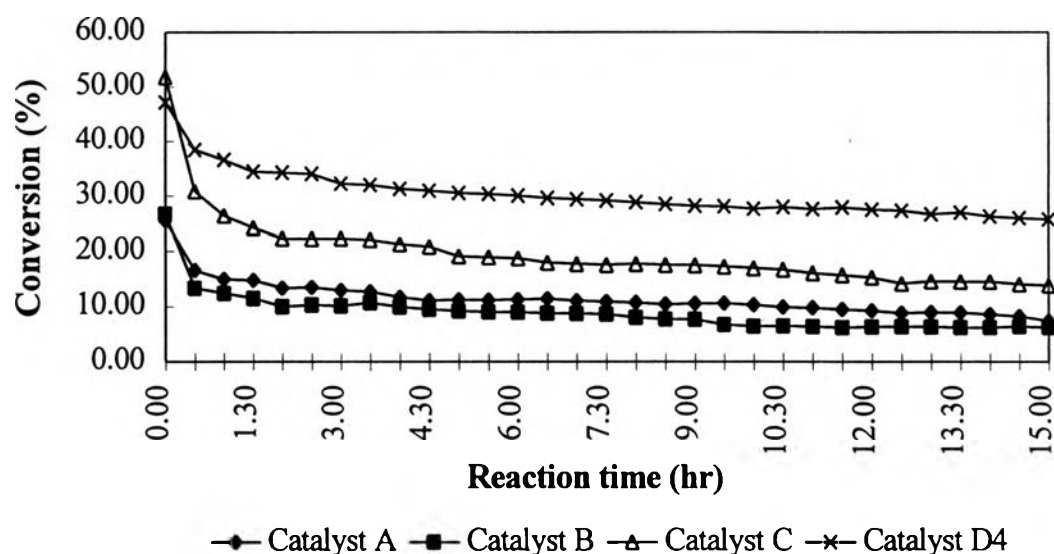


Figure 4.3 The conversion of propane dehydrogenation at 600 °C as a function of reaction time on alumina-supported catalyst.

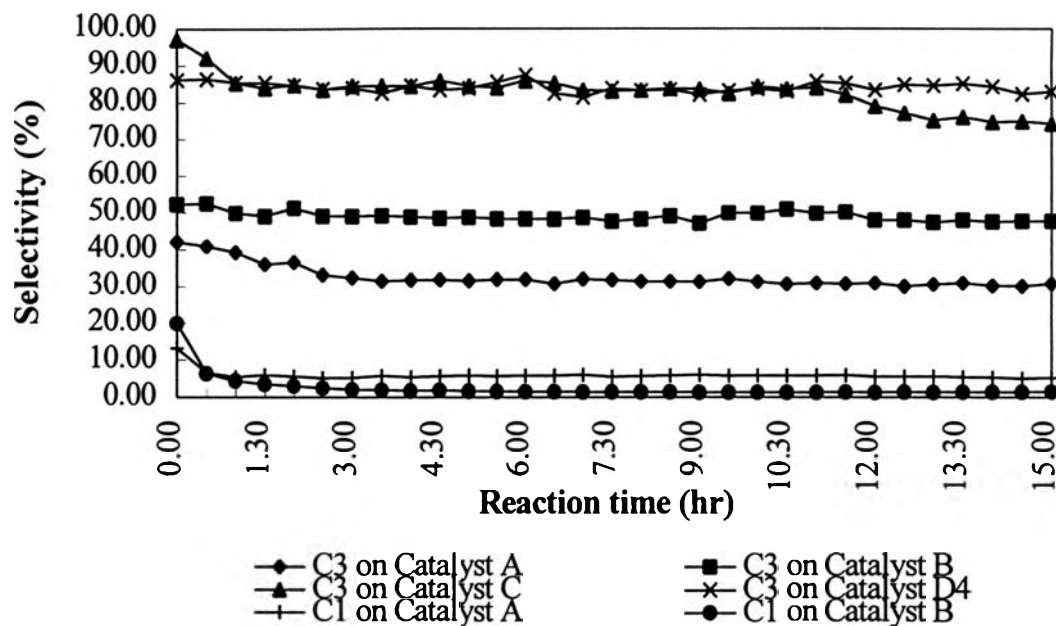


Figure 4.4 The selectivity of propane dehydrogenation at 600 °C as a function of reaction time on alumina-supported catalyst.

Therefore it can be said that under these severe conditions only Li or Sn alone is not sufficient to promote the activity of propane dehydrogenation and the selectivity to propylene.

### 4.3 The Role of Sn on the Dehydrogenation Reaction at 600 °C

To investigate the role of Sn in more detail, the propane dehydrogenation data are observed at 600 °C with five catalysts system that employs Pt-Sn-Li/Al<sub>2</sub>O<sub>3</sub> catalyst. These catalysts consisting of Sn/Pt wt ratio from 0.5 to 2.5 while fixed the concentration of Pt and Li at 0.40 wt% and 0.45 wt% respectively. The results are compared in Figure 4.5.

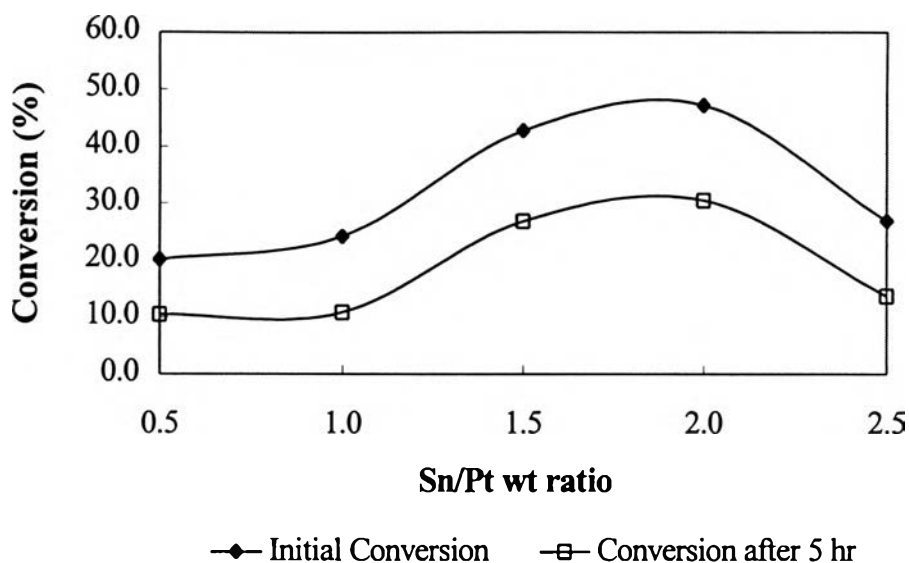


Figure 4.5 The conversion of propane dehydrogenation at 600 °C as a function of Sn/Pt ratio over 0.40%Pt-x%Sn-0.45%Li/Al<sub>2</sub>O<sub>3</sub> catalyst.

It is known that in the limit of vary high dilution, their intrinsic activity may become constant or slow down. This assumption is probably justified by vary the Sn/Pt ratio as can be seen in Figure 4.5, the conversion of propane dehydrogenation over Pt-Sn-Li/Al<sub>2</sub>O<sub>3</sub> catalyst is plotted as a function of Sn/Pt ratio, an optimum Sn/Pt ratio of 2 is proved to be the best for the Pt modified by Sn whether the data are observed at the short reaction times or after 5 hr of reaction time. These results agree with the study of Yarusov et al., 1992, in the propane dehydrogenation over Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts which suggests that the optimum Sn/Pt ratio should be greater than 2.0 for both Pt site and support modification. Therefore the trimetallic catalyst has more efficiency in improving its activity at these reaction conditions. The effect of Sn on the catalyst can be shown clearer in Figure 4.6 and 4.7 by plotted the conversion and selectivity of propane dehydrogenation versus reaction time.

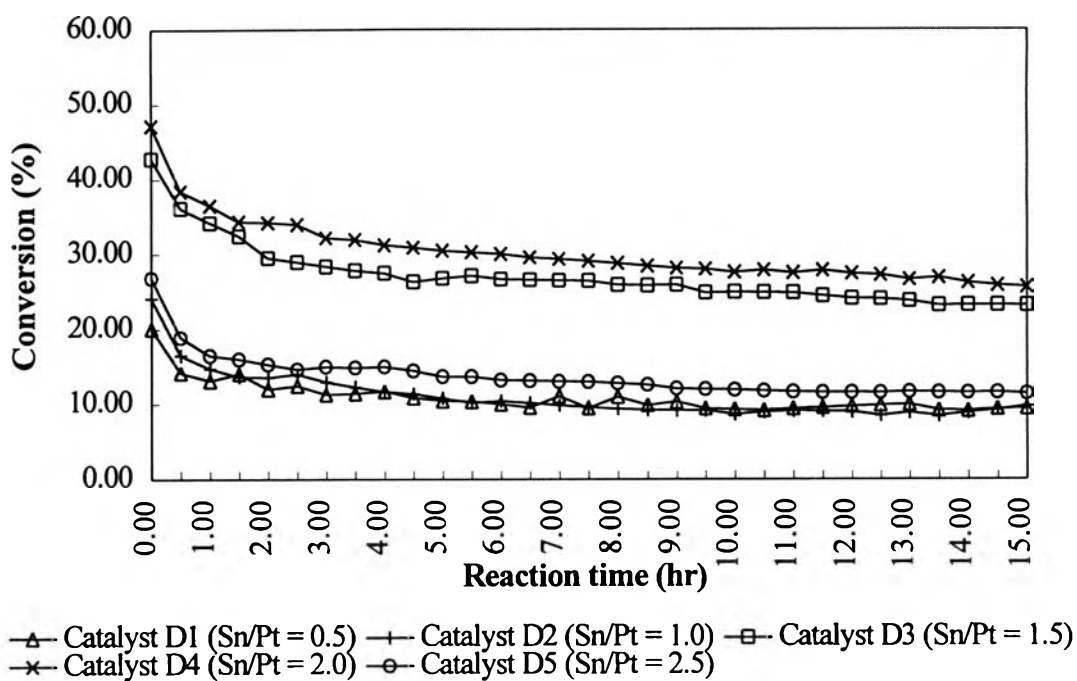


Figure 4.6 The conversion of propane dehydrogenation at 600 °C as a function of reaction time at different Sn/Pt ratio.

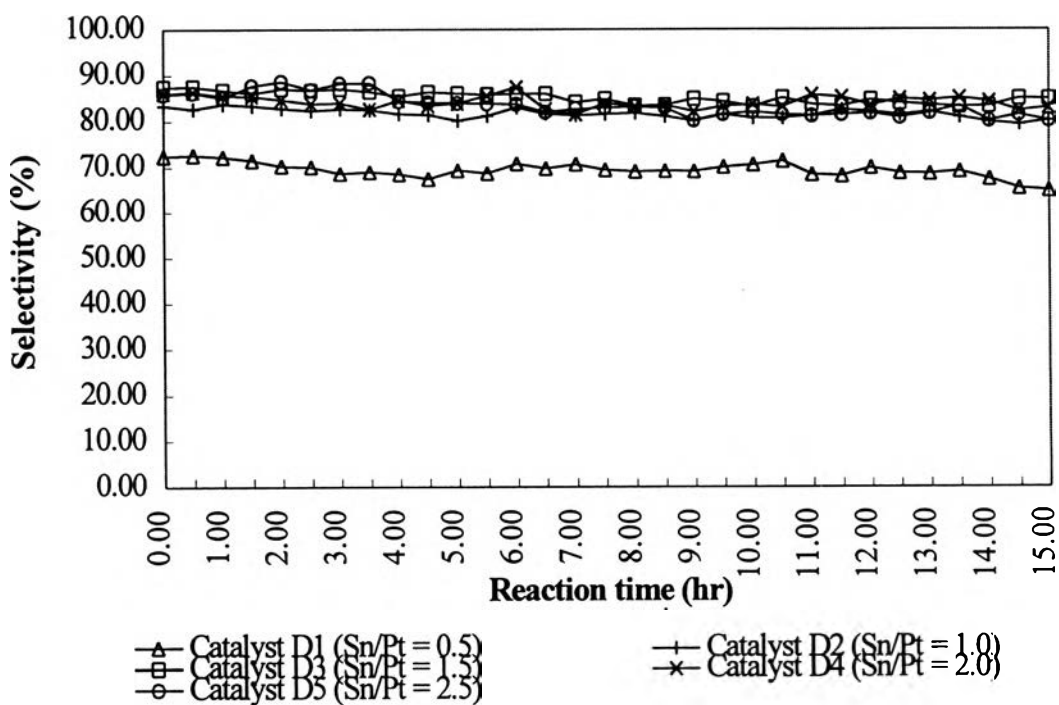


Figure 4.7 The selectivity of propane dehydrogenation at 600 °C as a function of reaction time at different Sn/Pt ratio.

From Figure 4.6 and 4.7, It can be seen that the influence of Sn can enhance initial activity of propane dehydrogenation and its selectivity when compared to the unpromoted catalyst. This implies that one role of Sn seems to be to improve the dispersion of the Pt. Barias et al., 1996 and Burch R., 1981, suggest that the dispersion of Pt is increased when Sn is present and possibly the more Sn addition the more dispersion of Pt which causes higher activity. The further addition of Sn into Pt-Li/Al<sub>2</sub>O<sub>3</sub> catalyst (at Sn/Pt ratio of 2.5) leads to a lower initial dehydrogenation activity which may suggest that Sn may remove some active sites of Pt atoms by forming an alloy with Pt. Lieske and Volter, 1984, reported that the Sn content of the alloy increases with increasing total Sn content. During the first period of reaction, the activity drops very rapidly because coke formation on the catalyst occurs very rapidly as can be seen in Figure 4.8.

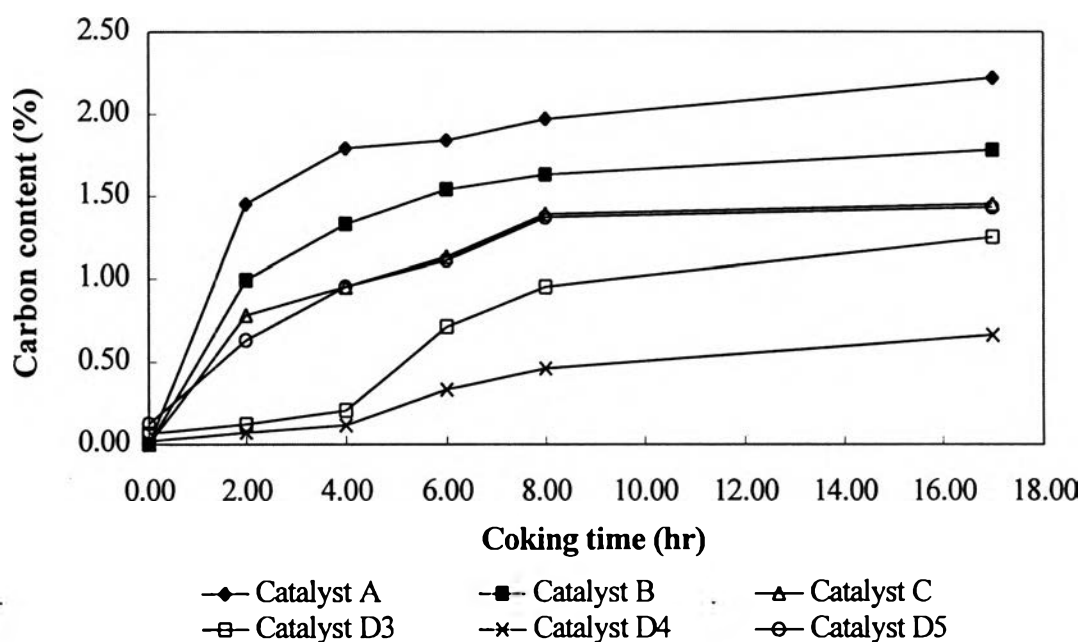


Figure 4.8 The variation of the amount of carbon deposited on the whole catalyst as a function of coking time.



#### 4.4 The Role of Sn on the Coke Formation

The influence of Sn in reducing coke formation can be seen in Figure 4.8 which shows the variation of the amount of carbon deposited on the whole catalyst as a function of coking time measured on the different samples which were operated at 600 °C. It can be noted that initially the amount of carbon deposited grows rapidly after which the formation of these deposits becomes slower. This phenomenon is consistent with the activity of propane dehydrogenation which decreases rapidly in the first period and then only a minor changes in the activity (Figure 4.6) which can be explained by the constant coverage by coke of the active Pt with the time of reaction (Barbier et al., 1985). The more coke deposition the less selectivity to propylene as can be seen in Figure 4.4.

The effect of Li and Sn in promoting the reduction carbon deposits on the alumina-supported catalyst when compared to the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst can also be observed. However Sn has a more positive effect than Li. Since Li has an effect in neutralizing of the acidity of the support, therefore coke deposition on Pt-Li/Al<sub>2</sub>O<sub>3</sub> depends on migration of coke precursors from the metal to the support. However Pt-Sn/Al<sub>2</sub>O<sub>3</sub> has an effect in reducing the Pt ensembles that are required for coke formation. The Pt-Sn-Li/Al<sub>2</sub>O<sub>3</sub> catalyst performance in resistance to coke deposition can be explained by the fact that when Pt-Li/Al<sub>2</sub>O<sub>3</sub> catalyst is enriched with Sn the degree of isolation of Pt atoms can be expected to be appreciable. Due to the coke reaction requiring at least 3 contiguous sites (Margifalvi et al., 1985) coke deposition is then reduced. The dehydrogenation reaction, however, can proceed on small ensembles of surface of Pt atoms (Cortright and Dumesic, 1995 and Resasco et al., 1994). Consequently, the decreased size of the surface Pt ensembles caused

by addition of both Sn and Li leads to high selectivity for propane dehydrogenation to propylene.

It is also possible that another role of Sn is to remove the initial intermediate (e.g., a dehydrogenated specie) created by the metal function. Via diffusion, these intermediates migrate to the acidic function site of alumina where they are converted to coke precursors. This coke precursor may migrate to the metal function or stay on the acidic function. This drain-off mechanism which has been proposed by (Lieske et al., 1987 and Lin et al., 1990) suggests that on the Sn containing catalyst, the coke precursor is adsorbed less strongly consequently they are more mobile and more easily migrate to the alumina where they are finally deposited as coke. This drain-off effect provides for a larger portion of active Pt sites remaining free for hydrocarbon adsorption. The more Sn addition, the more reduction in the rate of coke formation until further addition of Sn (at Sn/Pt ratio of 2.5) leads to increasing the rate of coke formation which may be due to formation of a PtSn alloy (Lieske and Volter, 1984). This changes the behavior of catalyst from high to low resistance to coke deposition. It can be said that the more alloy formation the more coke formation on the whole catalyst, and most of the coke deposited is on the support because the catalyst has decreased metal active sites. More experiments are needed to validate this proposal.

Table 4.1 confirms the result in Figure 4.8 that for Pt-Sn-Li/Al<sub>2</sub>O<sub>3</sub> catalyst, which has the lowest rate of coke formation, when compared to unpromoted catalyst or catalyst that is promoted with only Li or Sn. There is a slight decrease in surface area and pore volume due to the coke formation on the catalyst. The coke may plug the smaller pores of the catalyst so it makes the average pore diameter of spent catalyst higher than fresh catalyst. The

more resistance to coke deposition, the less change in the pore diameter, surface area and pore volume.

Table 4.1 Physical properties of fresh and spent catalyst.

Catalyst type	$S^a$ (m <sup>2</sup> /g)			$V_p^b$ (cc/g)			$D_p^c$ (Å)		
	fresh	coke	% change	fresh	coke	% change	fresh	coke	% change
Pt	106.3	101.0	4.99	0.2183	0.1977	9.44	41.2	44.9	8.98
Pt-Li	98.5	92.5	6.09	0.2252	0.1938	13.94	41.1	45.4	10.46
Pt-Sn	105.8	102.3	3.31	0.2284	0.2149	5.91	40.5	42.5	4.94
Pt-Sn-Li	98.3	96.2	2.14	0.2094	0.2036	2.77	42.6	43.2	1.41

<sup>a</sup> S = Surface are      <sup>b</sup> V<sub>p</sub> = Pore volume      <sup>c</sup> D<sub>p</sub> = Average pore diameter

#### 4.5 Repeated Reaction-Regeneration Cycles

Figure 4.9 and 4.10 compare the conversion and the selectivity of propane dehydrogenation in 8 cycles and 8 hr of reaction in each cycle. Then followed by the regeneration step in each cycle with 1 vol% O<sub>2</sub> in N<sub>2</sub> to burn the coke deposited on the catalyst. After that, the catalyst is reduced and reused in another reaction cycle. It can be seen that the conversion in the second cycle of each samples is higher than the first and the other cycles. These results suggest that the redispersion of Pt in oxygen is possible in the presence of chloride ion which remain on the catalyst during the preparation step (Lieske et al., 1983). As a result, Pt is removed from the Pt crystallite and disperses on the alumina support. So it will enhance the activity and selectivity for propylene in the second cycle. For the next cycle the activity and selectivity gradually drops because of the decomposition of chloride ion at the severe conditions over a long time. Also the repeated coking-regeneration

cycles may lead to increased alloying of the catalyst. Consequently, the activity of dehydrogenation reaction is reduced (Barias et al., 1996). This illustrates that the treatment with  $O_2$  is not only a means of burning off the coke but also a means to restore or to control the dispersion of Pt. When the ratio of Sn/Pt is varied, it still gives the same enhanced performance in promoting the activity and selectivity in the second cycle and at the Sn/Pt wt ratio of 2 give the highest conversion which is consistent to the results as mentioned above. In the later cycles, because of alloy formation or sintering, the metal active sites of catalyst may be reduced. These can be confirmed by doing the more experiments in chemisorption.

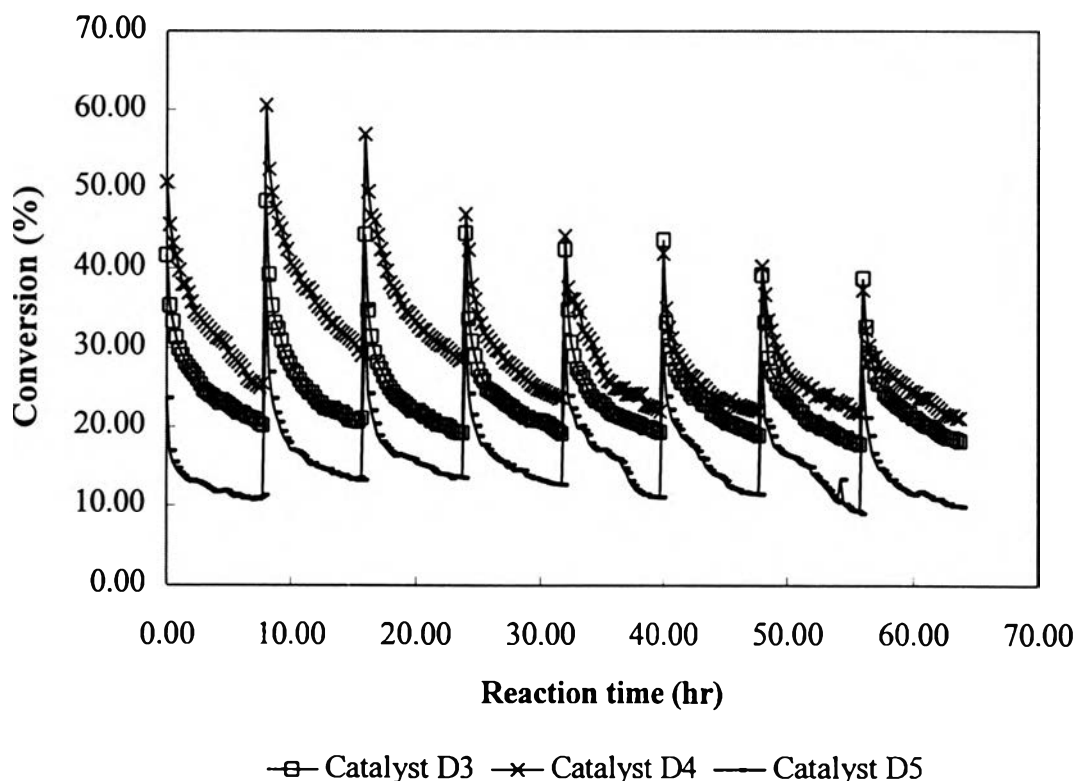


Figure 4.9 The conversion of propane dehydrogenation in 8 cycles at 600 °C over the 0.40%Pt-x%Sn-0.45%Li/Al<sub>2</sub>O<sub>3</sub> catalyst.

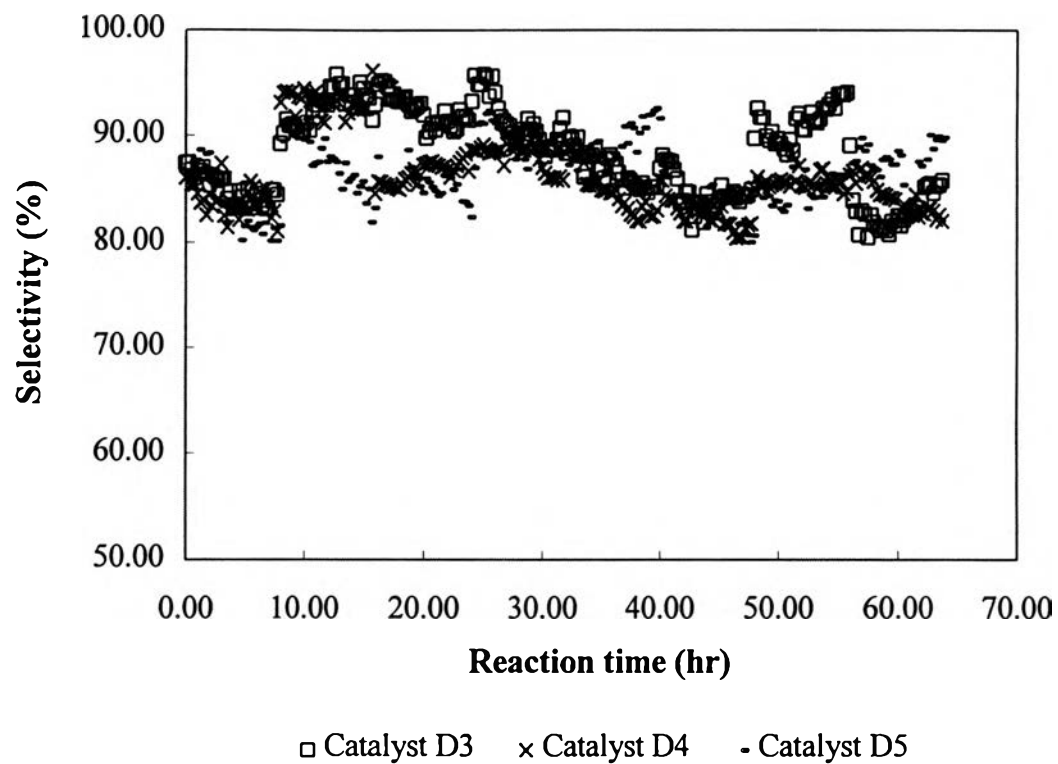


Figure 4.10 The selectivity of propane dehydrogenation in 8 cycles at 600 °C over the 0.40%Pt-x%Sn-0.45%Li/Al<sub>2</sub>O<sub>3</sub> catalyst.