

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Composition of Catalyst

The metal content was characterized by Atomic Absorbance Spectroscopy (AAS) and the results are shown in Table 4.1. There are three types of catalyst. The first type represented by 'A' means the monometallic Pt catalyst. Type 'B' and 'C' catalysts mean bimetallic Pt-Sn and Pt-Li catalysts respectively. The 'D' series stands for the trimetallic Pt-Sn-Li catalysts which have different Li/Pt ratios. The percentage of metals characterized by AAS are not equal to the desired amount. This may be due to the preparation techniques. However, the approximate Li to Pt ratios are 0.1, 0.89, 1.9, 2.55, 3.77 for D1, D2, D3, D4 and D5, respectively, and are nearly the same as the nominal ratios of 0.125, 1, 2, 2.5, 3.75. The latter ratios will be referred through this research.

4.2 Effect of Promoters on Activity and Selectivity of the Propane Dehydrogenation Reaction

The activity of catalysts is studied in a quartz tube reactor at 600 °C and 5 psig. In a previous work (Lieske and Volter, 1984), the dilution of catalytically active Pt with a catalytically inactive atom was found to improve the activity of the catalyst due to an ensemble effect and/or a ligand effect. Figures 4.1 and 4.2 present the conversion and selectivity of propane dehydrogenation as a function of time. The bimetallic Pt-Sn catalyst shows a

Table 4.1 Composition analysis of the catalysts

Catalyst type	Pt (%wt)	Sn (%wt)	Li (%wt)	Li/Pt ratio
A	0.4	-	-	-
B	0.42	0.77	-	-
C	0.43	-	0.41	0.95
D1	0.39	0.78	0.04	0.1
D2	0.44	0.81	0.39	0.89
D3	0.41	0.8	0.78	1.9
D4	0.4	0.79	1.02	2.55
D5	0.39	0.79	1.47	3.77

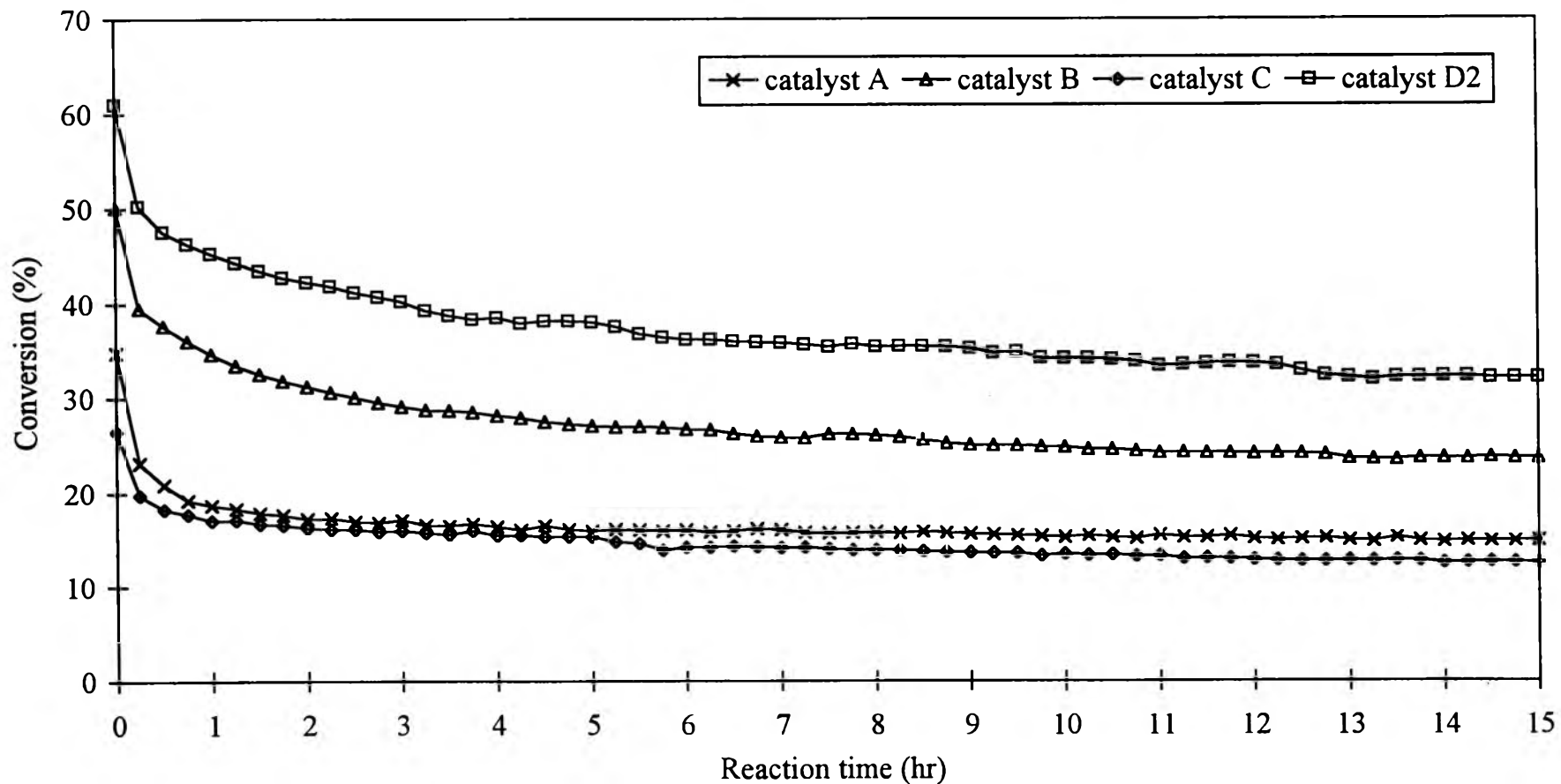


Figure 4.1 The conversion of propane at 600°C as a function of reaction time over the alumina-supported catalyst.

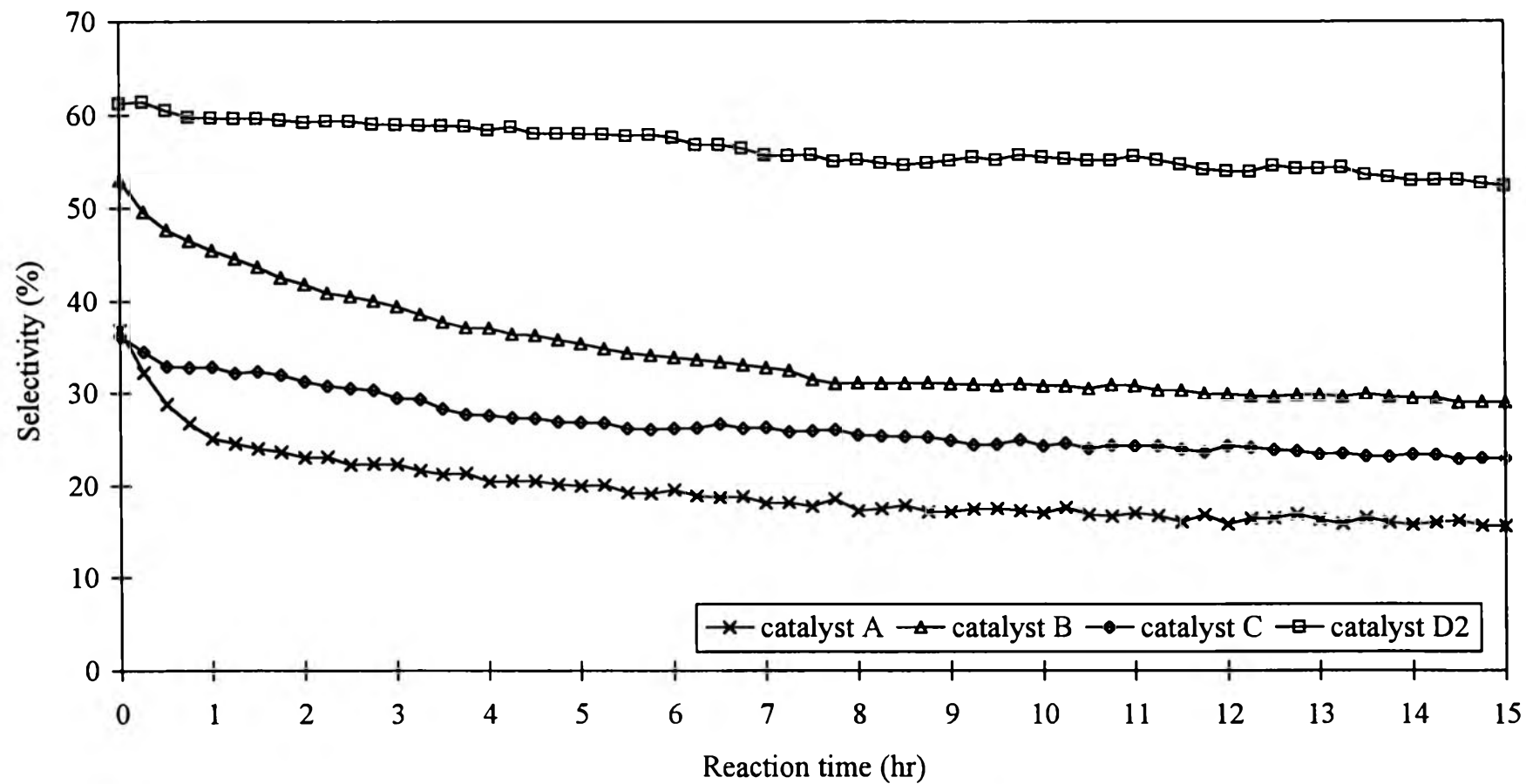


Figure 4.2 The selectivity to propylene at 600°C as a function of reaction time over the alumina-supported catalyst.

substantial increase in activity of propane dehydrogenation compared to the Pt/Al₂O₃ catalyst. Furthermore, the selectivity of the Pt/Al₂O₃ catalyst is also modified by addition of tin (Dautzenberg et al., 1980). This is because the size of surface Pt ensembles is decreased in the presence of tin, thereby inhibiting the formation on the surface of highly dehydrogenated hydrocarbon species required for hydrogenolysis, isomerization and coke formations. Accordingly, the attenuation of these reactions enhances the selectivity for the propane dehydrogenation reaction that can proceed over small ensembles of surface Pt atoms (Barias et al., 1996).

The effect of lithium is also observed on activity and selectivity. The conversion by the catalyst cannot be improved by added Li although the selectivity is increased. This effect can be explained by Li neutralizing the intrinsic acidity of the support (Afonso et al., 1994). From the literature, it was found that the acidity of support was responsible for the undesired reactions. Consequently, the side reactions were suppressed when Li was used to neutralize those sites. In addition, there is an evidence that Li may donate electrons to Pt. When hydrocarbons are adsorbed on this structure, the Pt-C bond is stronger but the C-H bond is weaker than those of the unpromoted catalyst resulting in a higher selectivity to propylene of the Pt-Li/Al₂O₃ catalyst. The addition of Li to the monometallic Pt/Al₂O₃ decreases the conversion of propane which is not similar to the addition of tin. The origin of this difference may be related to the nature and location of lithium on the catalyst surface. Sn is stabilized by formation of a Sn-aluminate surface complex which has an oxidation state more than zero (Adkins and David, 1984). While Pt supports on this surface resulting in an increase of Pt dispersion (Barias et al., 1996). *Dispersion* can be defined by the ratio of platinum exposed on the surface to the total platinum loading. Thus, only added lithium is not enough to promote the activity of catalyst.

When trimetallic catalyst of Pt-Sn-Li/Al₂O₃ is employed, it shows that not only is the conversion by the catalyst improved but also the selectivity to propylene. The higher selectivity over the Pt-Sn-Li/Al₂O₃ catalyst suggests that the addition of lithium further decreases the size of the surface Pt ensembles (Cortright and Dumesic, 1995). This effect of lithium helps to increase the Pt dispersion. The more Pt with surface exposure, the more the active sites. Therefore, a superior propane dehydrogenation rate is obtained.

Figure 4.3 shows the selectivity of by-product methane with the reaction time. The decrease in production rate of methane for the trimetallic catalyst corresponds to the increase in selectivity to propylene. This also confirms the effect of lithium as a neutralization species by decreasing cracking on acidic sites.

4.3 Effect of Promoters on Coke Formation

The amount of coke on the catalyst was characterized by the Elemental Analyzer and is shown in Figure 4.4. The carbon content is determined from an exposure of the catalyst to the reactants at 2, 4, 6, 8 and 15 hours, respectively. Initially, the amount of carbon deposited grows rapidly since all surface Pt sites are fresh and uncovered. After a period of time, most surface Pt sites are blocked and cannot be used further. The coking rate then becomes slower. This phenomenon is consistent with the observed activity of the catalyst because it exhibits a sharp decrease at first and then only a minor change is observed at longer times. The slight change is due to the essentially constant coverage of carbonaceous deposits on the active Pt (Barbier et al., 1985).

Figure 4.4 clearly shows the influence of tin on the bimetallic Pt-Sn catalyst. The addition of Sn can maintain the activity and selectivity

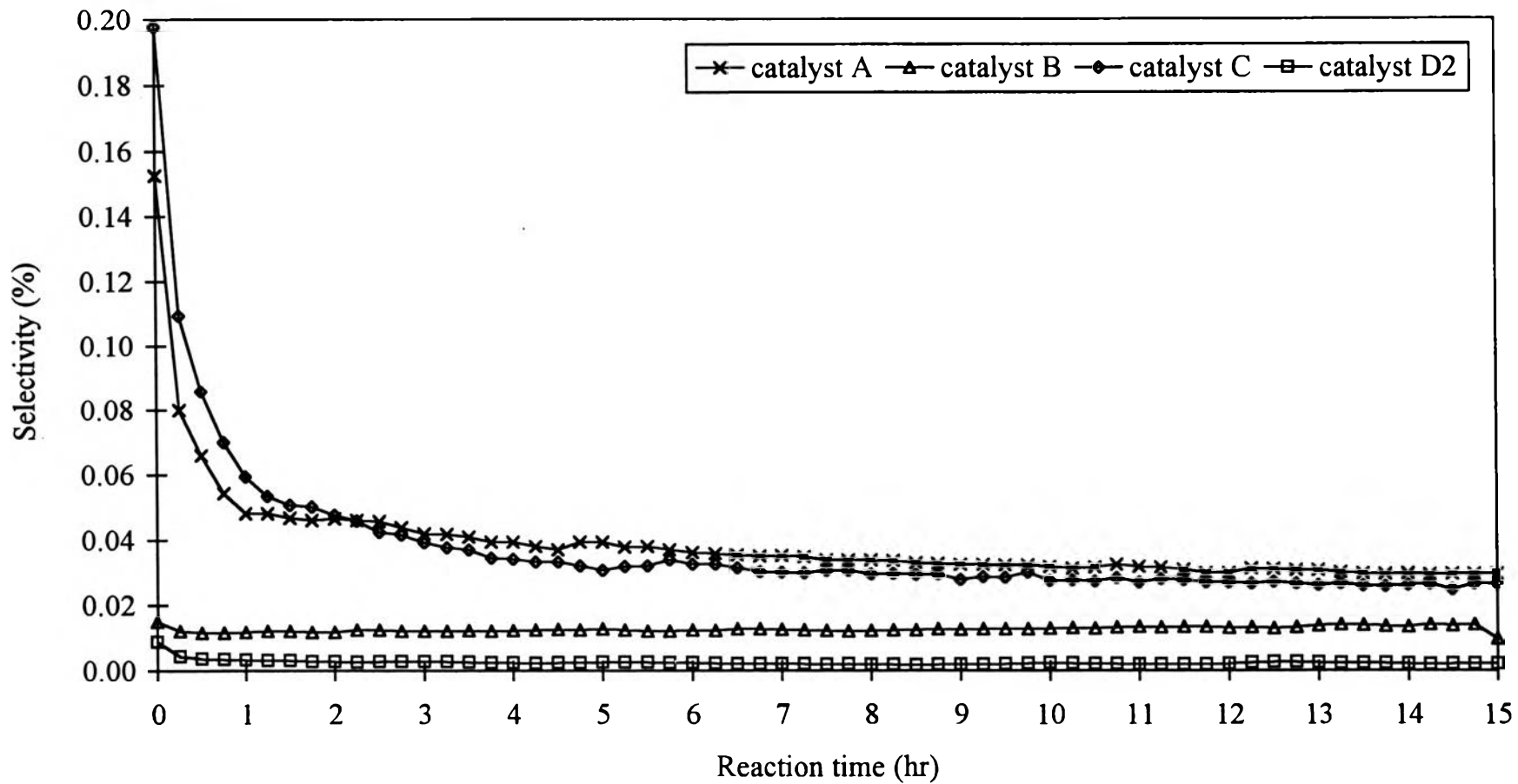


Figure 4.3 The selectivity of methane as a by-product at 600°C over the alumina-supported catalyst.

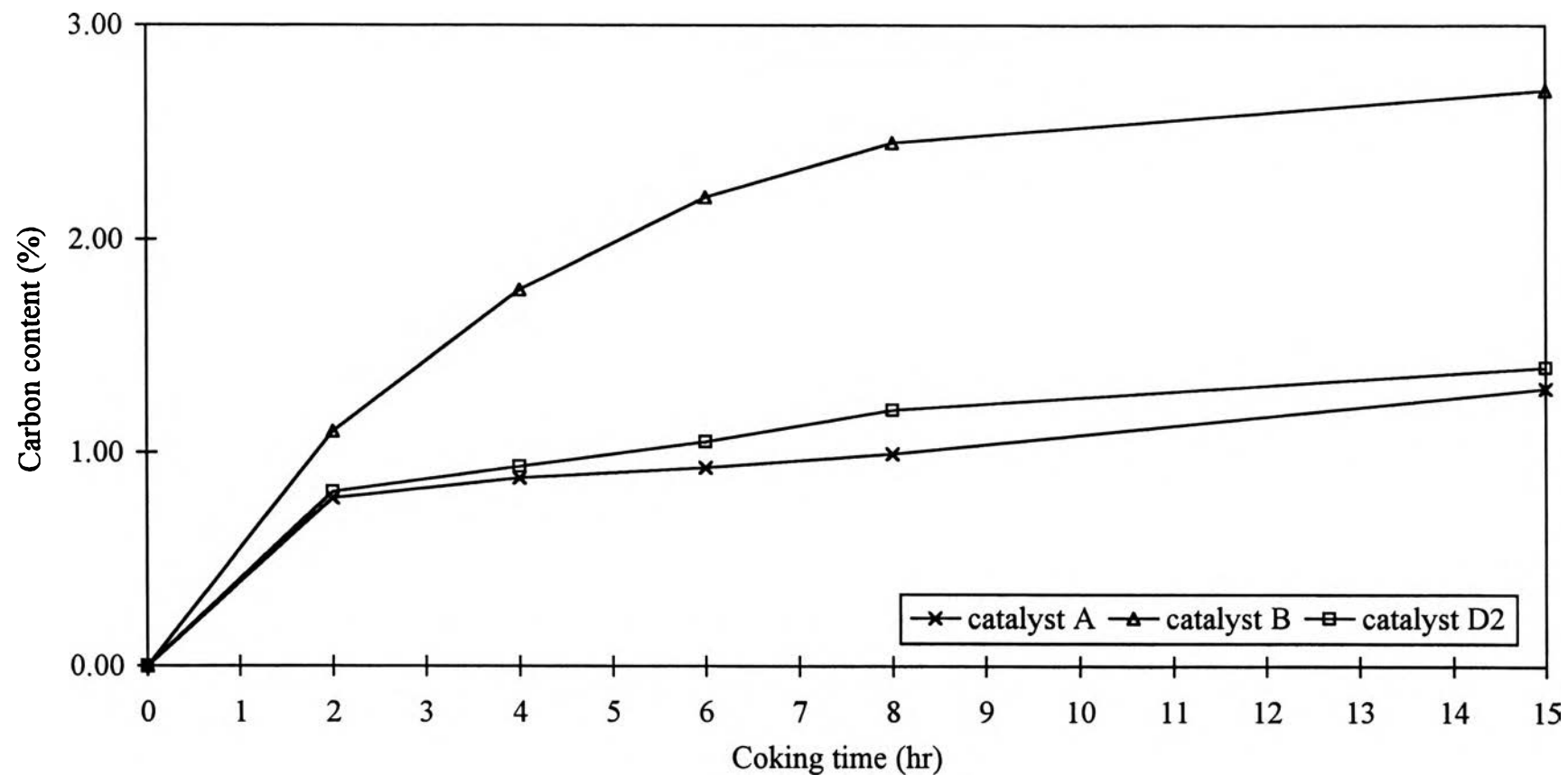


Figure 4.4 The variation of the amount of carbon deposited on the alumina-supported catalyst as a function of coking time.

while the coking is quite high. This phenomenon can be explained by the *drain-off mechanism*. Generally, the coke initially forms on the Pt surface and subsequently migrates to the support. It seems that in the presence of tin, the mobility of the carbonaceous deposits can be increased and then the coke deposits can be drained off from the active surface of Pt and then relocated on the support. The drain-off mechanism allows the active Pt sites to remain uncovered upon the addition of tin while the coking reaction proceeds. The reason that the Pt-Sn/Al₂O₃ has the highest amount of carbon is due to the quite high surface area of the carrier. The more surface area of the alumina, the more available surface for coke deposition.

The coke content of the Pt/Al₂O₃ has the lowest value compared with the other two samples. Why does the unpromoted catalyst show this result? It should have the highest amount of carbon deposits. It can be assumed that the substantially lower activity is responsible for this occurrence. The lower conversion of propane also produces less coke.

The addition of lithium to the Pt-Sn/Al₂O₃ catalyst can further suppress the coke deposited on the catalyst. This effect comes from the neutralization effect of lithium. Moreover, the higher activity of the trimetallic Pt-Sn-Li catalyst produces approximately the same amount of coke as on the Pt/Al₂O₃ catalyst. This also suggests that the activity and selectivity over the lifetime of the catalyst can be improved with the addition of lithium. In order to confirm the results, fresh and spent catalysts were also characterized in terms of the physical properties of the catalysts. The BET surface area, total pore volume and average pore diameter are tabulated in Table 4.2. The data given correspond to the conditions used in Figure 4.4. The decrease in surface area and pore volume of the catalyst is due to coke formation on the catalyst. It has been found that most of the coke formed tends to block the smaller pores of the catalyst leading to an increase in the average pore diameter of the

Table 4.2 Physical properties of the fresh and spent catalysts

Catalyst type	S(m ² /g)			V _p (ml/g)			D _p (Å)		
	fresh	spent	%change	fresh	spent	%change	fresh	spent	%change
A	204.8	201.2	-1.76%	0.5637	0.5626	-0.20%	55.05	55.92	1.58%
B	206.5	188.1	-8.91%	0.5831	0.5022	-13.87%	51.45	56.47	9.76%
D2	208.4	196.5	-5.71%	0.5637	0.5508	-2.29%	54.11	56.08	3.64%

Notes: S = surface area

V_p = total pore volume

D_p = average pore diameter

catalyst (Kirsensztejn et al., 1991).

The monometallic Pt/Al₂O₃ catalyst exhibits the lowest changes in surface area, pore volume and pore diameter of catalyst. On the other hand, the Pt-Sn supported on alumina reveals the highest changes in surface area, pore volume and pore diameter of catalyst because of the high surface area of the support as previously described. Although the decrease in surface area and pore volume is very high for the Pt-Sn catalyst, it still performs with high activity and selectivity for propane dehydrogenation. Table 4.2 also shows that the cracking reactions can be lowered with the addition of tin.

4.4 Role of Lithium on Activity and Selectivity of the Propane Dehydrogenation Reaction

The effect of lithium on activity and selectivity of propane was also investigated by varying the lithium content from 0.05% to 1.5% by weight. Figure 4.5 and 4.6 show that the addition of lithium in excess may not improve the activity and selectivity of the dehydrogenation catalyst. There is a limit of the amount of added Li that provides a better yield. A Li/Pt ratio of unity (D2 catalyst) clearly yields the highest activity and selectivity. A very high lithium concentration appears to deteriorate the intrinsic activity of catalyst. The reason that higher lithium contents give lower activities is due to the reduction of Pt dispersion. This result is linked to the presence of residual nitrate ions which are originally introduced during the impregnation of lithium with LiNO₃. The drop in the platinum dispersion is due to the simultaneous reduction of residual nitrate ions with the platinum precursor (Passos et al., 1992). Hence, some platinum active sites may not be reduced to the metallic state resulting in a lower Pt dispersion. Nevertheless, alkali ions also have

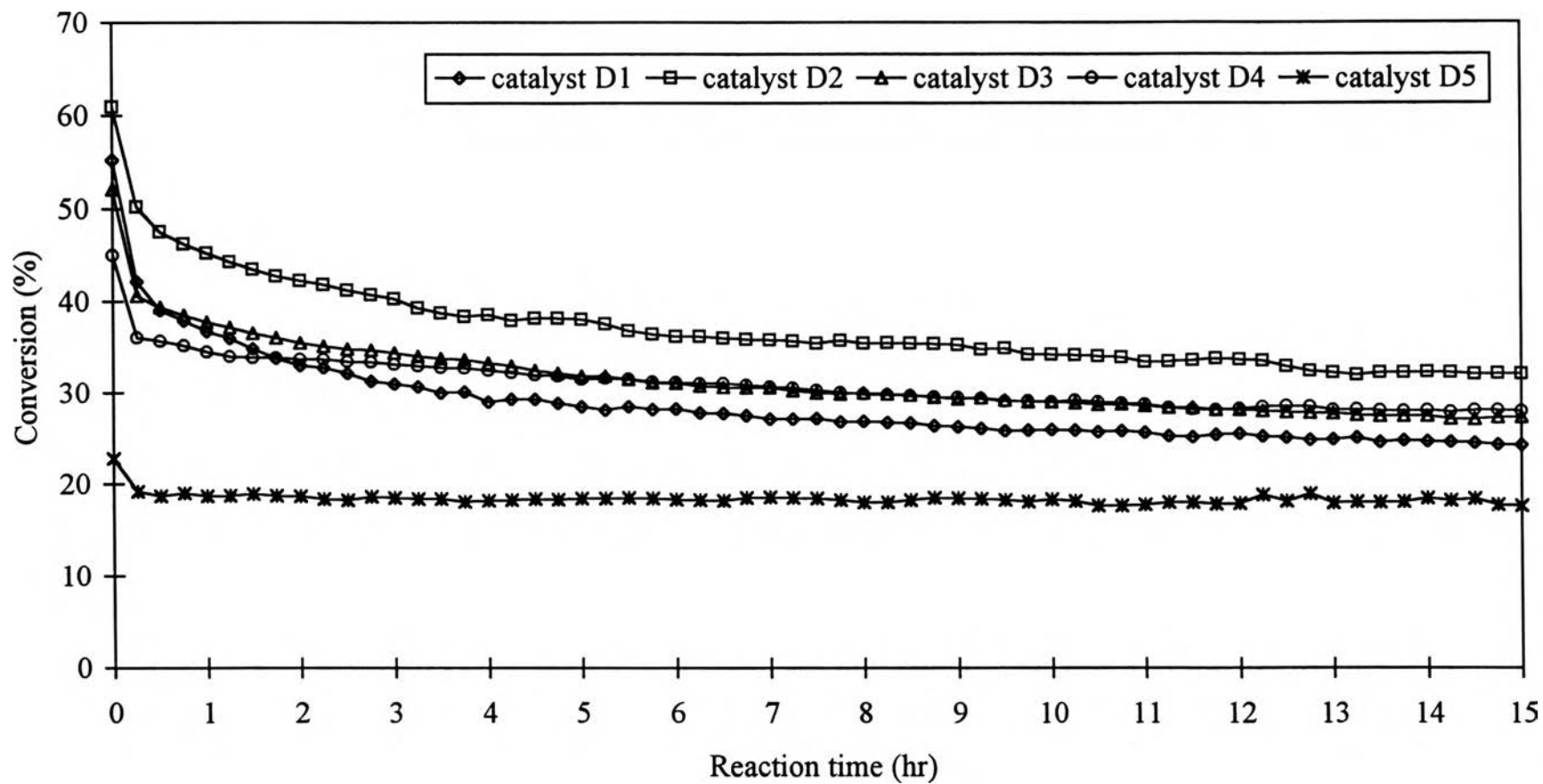


Figure 4.5 The conversion of propane as a function of reaction time with various Li/Pt ratios for the Pt-Sn-Li/Al₂O₃ catalyst.

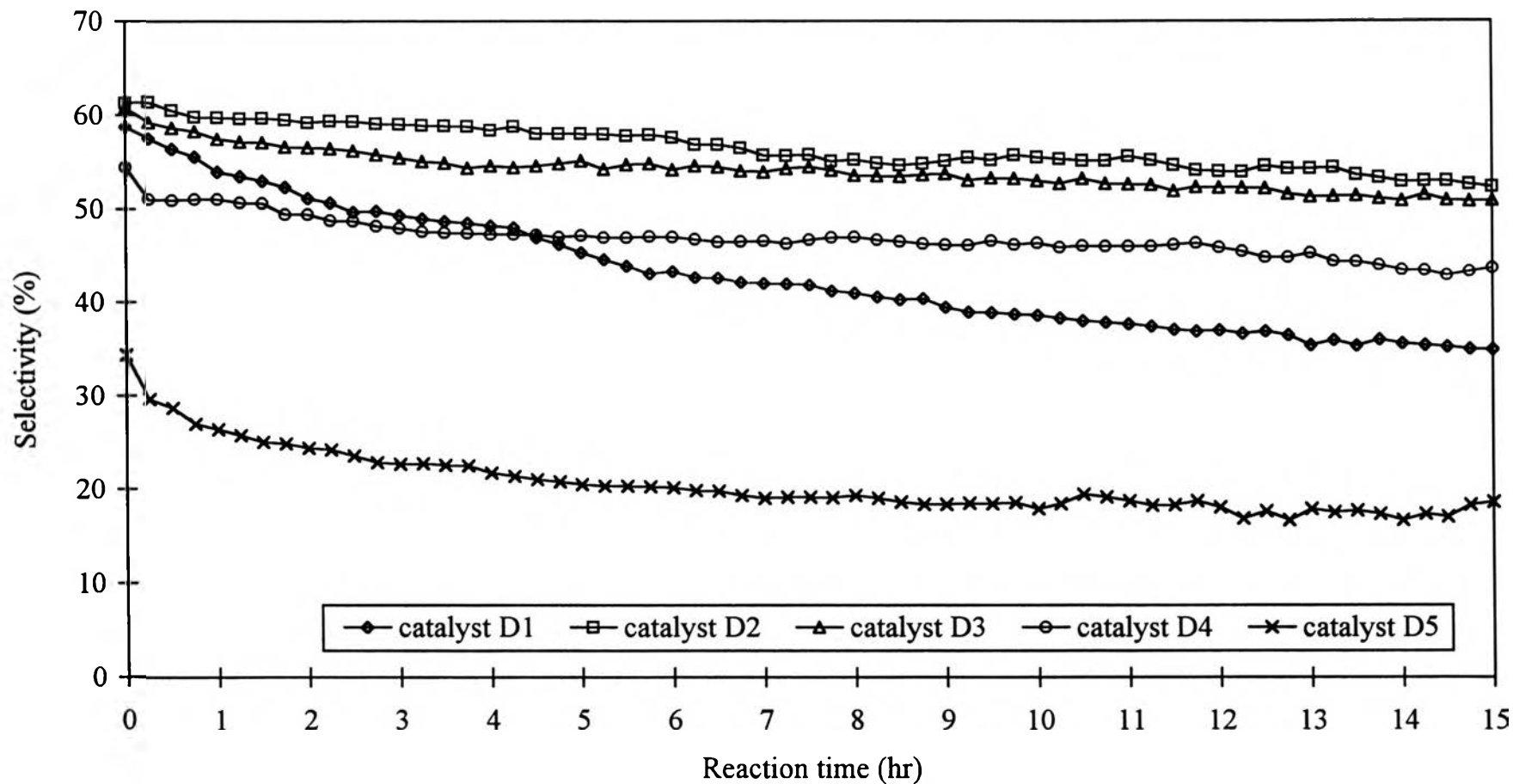


Figure 4.6 The selectivity to propylene as a function of reaction time with various Li/Pt ratios for the Pt-Sn-Li/Al₂O₃ catalyst.

an effect on the structure of alumina. Since higher concentrations of alkali accelerate the recrystallization of the alumina support and thereby reduce the effective lifetime of catalyst causing a decrease in the active surface area (Mross, 1983).

In order to prove this result, the conversions of propane after reaction time of 5 hours and 15 hours are plotted as a function of reaction time shown in Figure 4.7. The Li/Pt ratio of 0.1 which corresponds to a small amount of lithium added gives nearly the same result as the lithium unpromoted bimetallic Pt-Sn catalyst. The catalyst that the ratio of Li/Pt is around 1 produces a great amount of propylene either after 5 hours or 15 hours of reaction time.

4.5 Role of Lithium on Coking Reaction

The coking rate of the Pt-Sn-Li on Al_2O_3 , as shown in Figure 4.8, acts in the same manner as the other catalysts. In the first period of reaction, the activity for propane dehydrogenation decreases rapidly while the carbonaceous deposits are quickly produced over the surface area of active Pt. As the reaction time continues, the activity and coke concentration become constant.

It seems that the coke content of the Pt-Sn-Li/ Al_2O_3 depends on the activity of catalyst. More coke is produced with the higher conversions of propane. Although the catalyst with the Li/Pt ratio of unity (D2 catalyst) exhibits the best dehydrogenation activity and selectivity, it also produces the highest amount of coke. One may think that this is not the best ratio of Li to Pt, but the results should be investigated further by other characterization methods before choosing the best Li/Pt ratio. Lithium may, like tin, help the mobility of coke precursors to move from metal sites to the support. Temperature Programmed Oxidation or TPO is one of methods which might

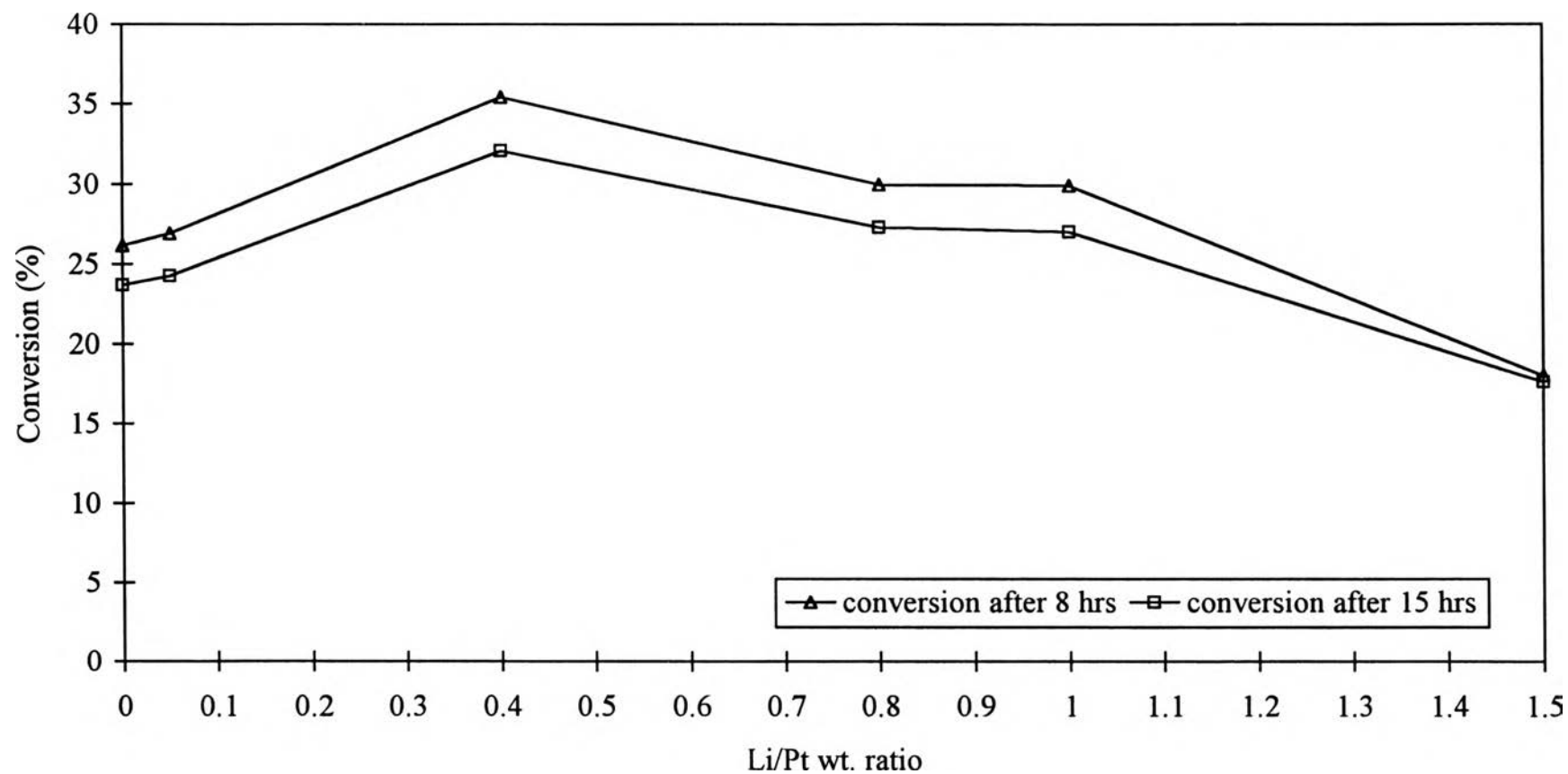


Figure 4.7 The conversion of propane at 600°C as a function of Li/Pt ratio over the Pt-Sn-Li/Al₂O₃ catalyst.

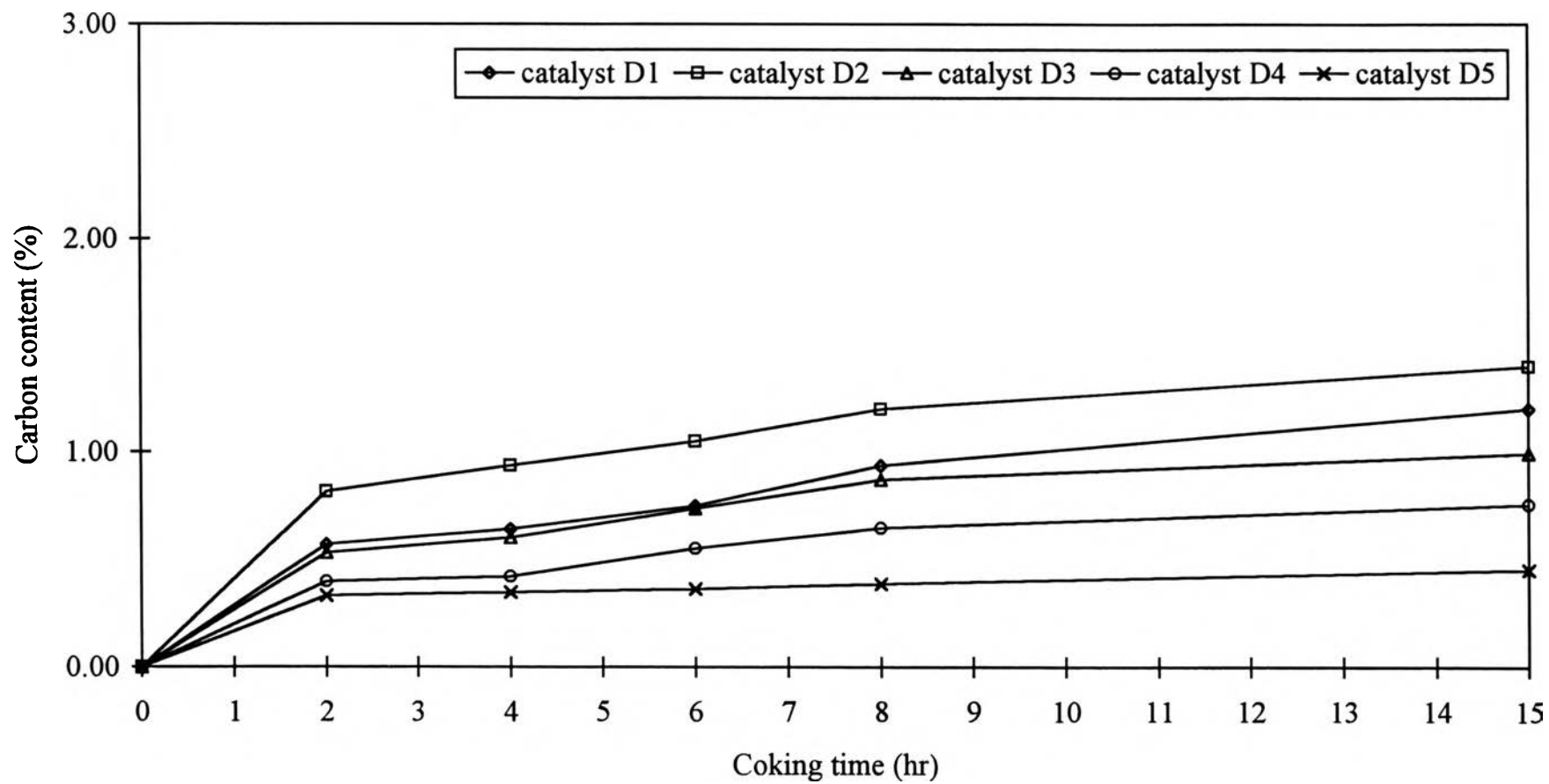


Figure 4.8 The variation of the amount of carbon deposited on the 0.40%Pt-0.80%Sn-x%Li/Al₂O₃ catalyst as a function of coking time.

validate this hypothesis. Presently, it can only be said that in order to choose the best ratio of Li/Pt, the coke content, activity and selectivity of the catalyst should be collectively considered.

4.6 Repetitive Reaction-Regeneration Cycle Experiments

These experiments were done in order to study the catalysts' behavior in an industrial application. Industrially, a commercial catalyst is utilized until it shows a loss of productivity and is then regenerated to save the expense on purchasing a new catalyst. Figures 4.9 and 4.10 compare the conversion and selectivity among three catalysts which were the best three catalysts obtained from this study based on their activity and selectivity. In experiments the catalyst was left in the reactor for 8 hours during the reaction phase. Then, it was regenerated for 1 hour by flowing 1 %vol O₂ to burn off the coke deposits. After that, the catalyst was reused to study its performance after regeneration. This cycle was repeated for eight times.

These three catalysts behave in the same manner. They all have the highest activity in the first cycle, and show a significant drop in the second cycle and a few changes over the next six cycles. However, the selectivity of these catalysts shows an interesting behavior as it rises in the second cycle and then gradually decreases over the following cycles. The sharp decrease in conversion for the catalysts may be due to the evaporation of lithium as a promoter during the high temperature treatment. It is also found that the agglomeration of adjacent Pt particles may occur under the high temperature circumstances in the presence of hydrogen. The agglomeration of Pt particles causes the reduction of dispersion and activity of catalyst. However, the catalysts still have a higher selectivity in the second cycle which may come from the lower conversion in this cycle. For the successive cycles, most of Pt

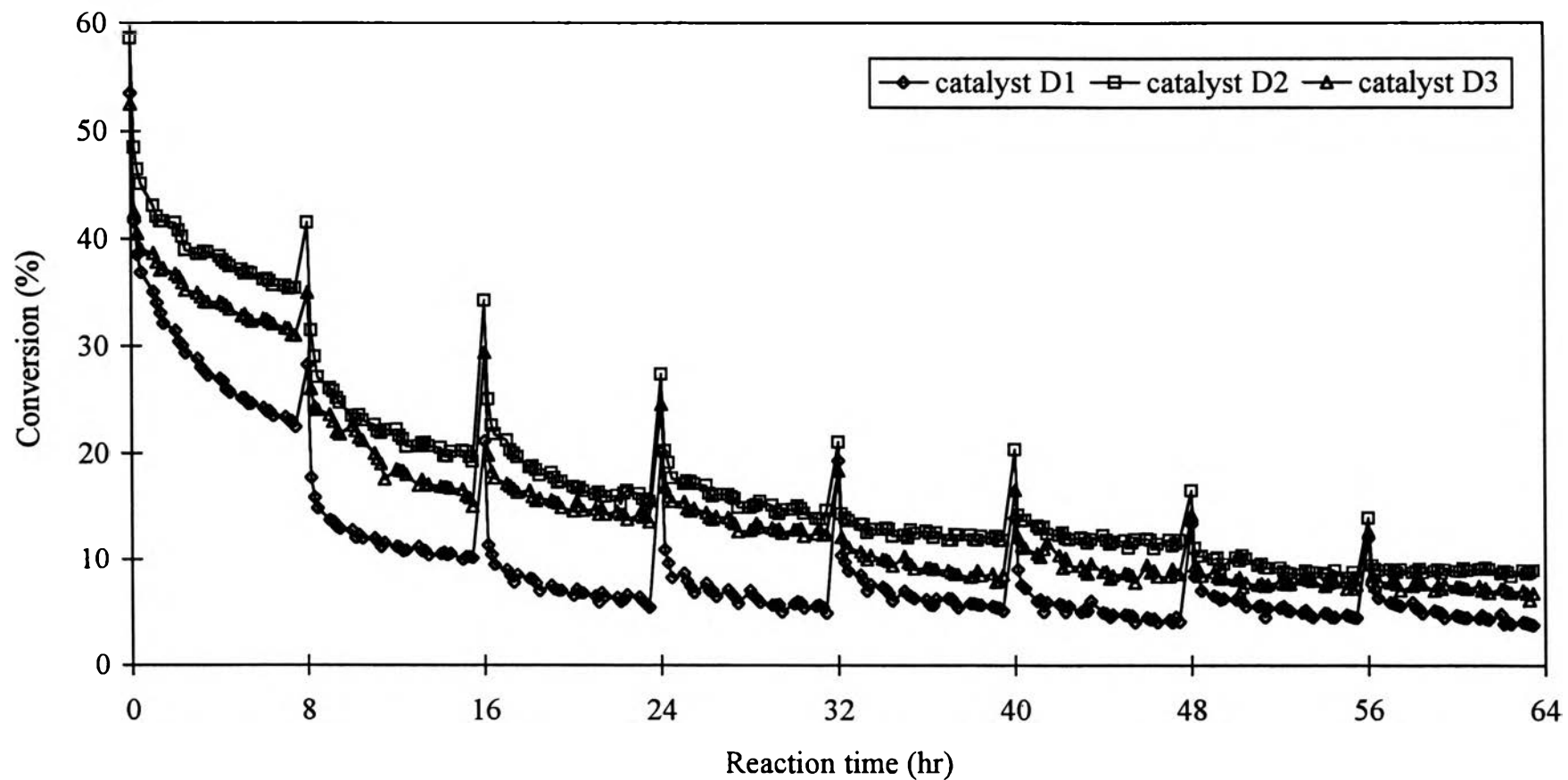


Figure 4.9 The conversion of propane for cycle run at 600°C over the 0.40%Pt-0.80%Sn-x%Li/Al₂O₃ catalyst.

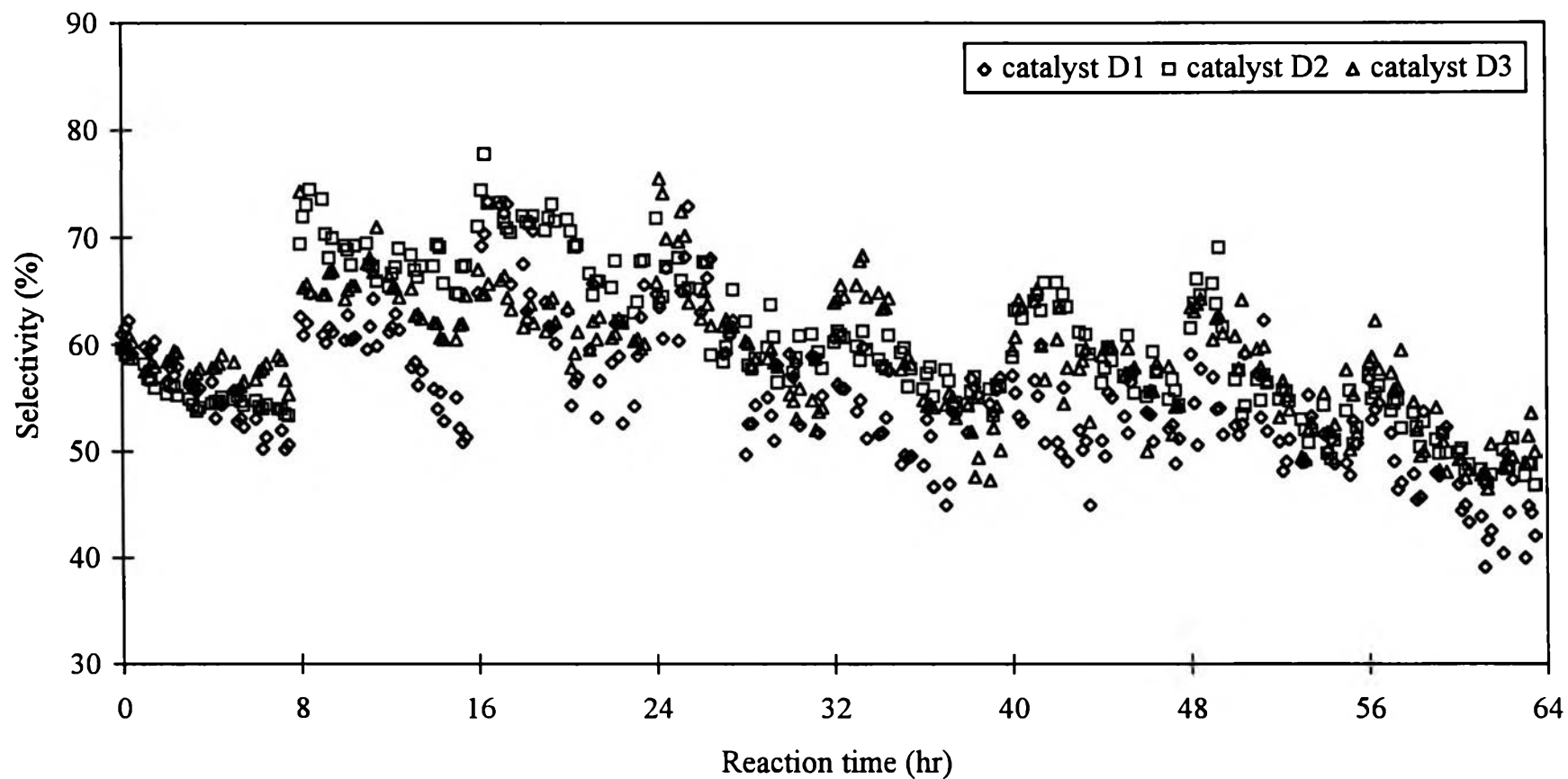


Figure 4.10 The selectivity to propylene for cycle run at 600°C over the 0.40%Pt-0.80%Sn-x%Li/Al₂O₃ catalyst.

particles may tend to become larger. Consequently, the number of surface Pt atoms which is exposed to the reactants goes down and results in the observed decrease conversion and selectivity. Since Pt dispersion was not carried out in this study, it would be desirable so as to validate this mechanism on this case.

The addition of chloride might help the redispersion of Pt particles but the catalyst should be doped with an optimum amount. Because doping with a very low concentration of chloride leads to sintering of the catalyst, while side reactions may be promoted with a high chloride content. The initial chloride concentration for this work was obtained from the support and also the hydrochloric acid which was used for the preparation of the catalyst. This chloride concentration was kept to be less than 1% by weight. This may not be high enough for the redispersion of platinum atoms. In a commercial process, chlorides will be added continuously in the form of chlorine gas for a better-long-term performance of catalyst.