

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Composition of Catalyst

The catalysts were prepared by the impregnation method. The metal content was characterized by AAS and EDX. The surface area, total pore volume and average pore diameter were characterized by BET. The results are shown in Table 4.1, 4.2 and 4.3 respectively. The percentage of metals measured by AAS and EDX are nearly the same but not equal to the desired amount. This may be due to the preparation techniques. However, the approximate Sn/Pt ratios are not much different from the nominal ratio of 0.5, 1.0, 1.5, 2.0 and 2.5.

Table 4.1 Characteristics of the catalysts investigated by AAS

| Catalyst | Pt (wt%) | Sn (wt%) | Li (wt%) | Sn/Pt ratio |
|----------|-------------|-------------|-------------|----------------|
| A | 0.39 | - | - | - |
| B | 0.40 | - | 0.48 | - |
| C | 0.41 | 0.79 | - | 1.93 |
| D1 | 0.42 | 0.25 | 0.42 | 0.59 |
| D2 | 0.40 | 0.45 | 0.42 | 1.12 |
| D3 | 0.40 | 0.66 | 0.48 | 1.65 |
| D4 | 0.42 | 0.79 | 0.45 | 1.88 |
| D5 | 0.42 | 0.96 | 0.48 | 2.28 |

Table 4.2 Characteristics of catalysts investigated by EDX

| Catalyst | Pt (wt%) | Sn (wt%) | Cl (wt%) | Sn/Pt ratio |
|----------|-------------|-------------|-------------|----------------|
| A | 0.59* | - | 0.14 | - |
| B | 0.36* | - | 0.14 | - |
| C | 0.40 | 0.84 | 0.22 | 2.10 |
| D1 | 0.43 | 0.29 | 0.12 | 0.67 |
| D2 | 0.42 | 0.41 | 0.10 | 0.98 |
| D3 | 0.42 | 0.68 | 0.13 | 1.62 |
| D4 | 0.41 | 0.88 | 0.12 | 2.15 |
| D5 | 0.42 | 1.09 | 0.16 | 2.60 |

* The values are much different from AAS result because of non-homogeneous of the prepared catalysts and the limitation of EDX equipment.

Table 4.3 Physical properties of catalysts investigated by BET

| Catalyst | Surface area (m ² /g) | Total pore volume (cc/g) | Average pore radius (°A) |
|----------|-------------------------------------|-----------------------------|------------------------------|
| A | 121.6 | 0.043 | 7.128 |
| B | 116.8 | 0.042 | 7.174 |
| C | 123.0 | 0.042 | 6.878 |
| D1 | 112.6 | 0.040 | 7.128 |
| D2 | 109.6 | 0.039 | 7.286 |
| D3 | 120.0 | 0.041 | 6.870 |
| D4 | 112.8 | 0.040 | 7.101 |
| D5 | 111.2 | 0.040 | 7.257 |

4.2 Effect of Promoters on Activity and Selectivity of Butane Dehydrogenation Reaction

Dilution of catalytically active Pt atom with a catalytically inactive Sn atom has been employed as a means of studying the intrinsic activity of ensembles of contiguous Pt atoms of different sizes. For this work the activity data were obtained in quartz tube reactor. The activity is compared in terms of the conversion of butane dehydrogenation and the selectivity to 1-butene, trans-2-butene, cis-2-butene and 1,3 butadiene on the different type of catalysts. Figure 4.1 presents conversion and Figure 4.2 presents the selectivity to 1-butene, as a function of reaction time. The selectivities of the other products are shown in the Appendix.

The effect of promoters, tin (Sn) and lithium (Li) on activity are observed at 600 °C. Figure 4.1 and 4.2 illustrates that both conversion and selectivity can be improved by adding Li. 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. For example, when the acidity of alumina is increased, there is a progressive increases in the cracking selectivity, even though the total activity only increase slightly (Burch and Garla, 1981). Consequently, the side reactions were suppressed when Li was used to neutralize those sites. Alkali doping can also be employed to prevent the deposition of coke on the nickel catalysts used in steam-reforming and it may be assumed that this effect is also partly due to the neutralization of acid center (W.D.Mross, 1983). 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 weaker than on the unpromoted catalyst (Wongkolkitsilp, 1996), resulting in a higher selectivity to C₄-olefins of Pt-Li/Al₂O₃ catalyst.

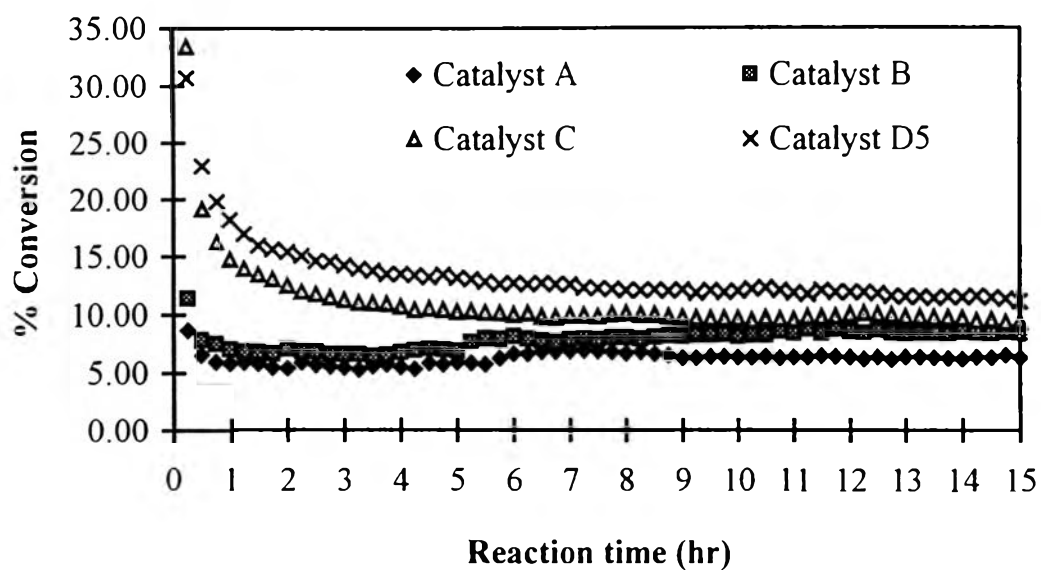


Figure 4.1 The conversion of butane dehydrogenation at 600 °C as a function of reaction time on alumina-supported catalyst.

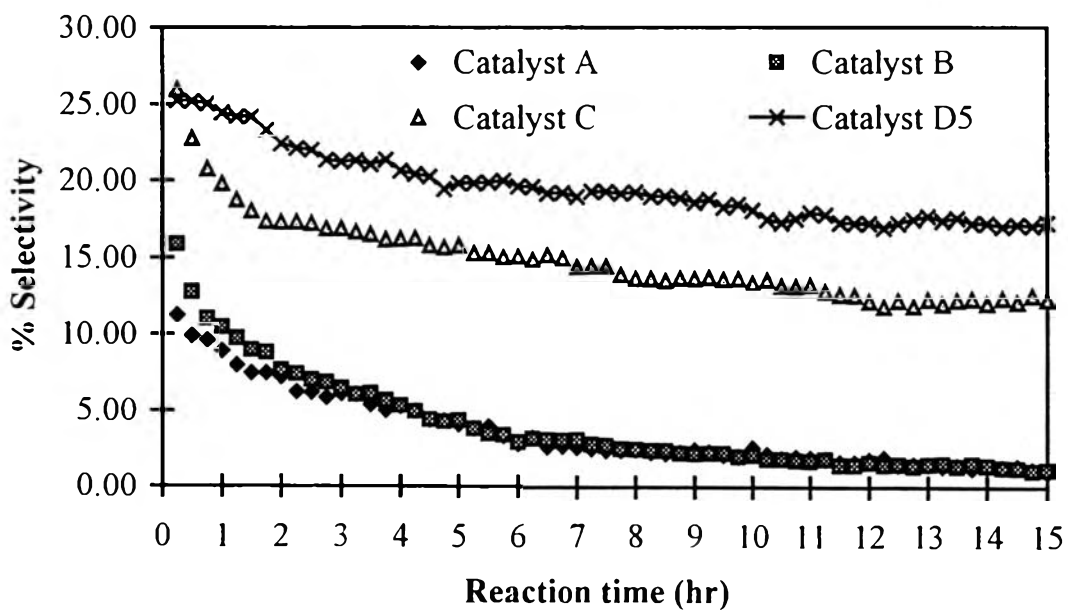


Figure 4.2 The selectivity of butane dehydrogenation to 1-butene at 600°C on alumina-supported catalyst.

The influence of tin on the performance of supported Pt catalyst also can be seen in the figures. Addition of Sn to Pt/Al₂O₃ catalyst markedly increases dehydrogenation activity for butane. Since Pt is more highly dispersed on the Sn containing support than on alumina alone (Davis, 1993). It furthermore, followed that not only the activity but also the selectivity of the Pt function is modified by addition of tin (Dautzenberg et al., 1980 and Balakrishnan and Schank, 1991). 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 formation (Cortright and Dumesic, 1995 and Resasco et al., 1994). Accordingly, the attenuation of these reactions enhances the selectivity for dehydrogenation reaction that can proceed over smaller ensembles of surface Pt atoms (Barias et al., 1996). In Ni-Cu alloys, for example, the rate of hydrogenolysis of ethane decreases by several orders of magnitude when Cu is added, and this is explained on the basis of a reduction in the number of Ni ensembles large enough to catalyze this reaction (Burch and Garla, 1981). A similar explanation has been proposed to account for the greater stability of bimetallic Pt catalysts.

We can say that Sn has more positive effect in promoting the activity and selectivity of Pt/Al₂O₃ catalyst than Li at these conditions by decreasing the size of Pt surface ensembles. Sn has a significant effect on metal sites whereas Li has little effect on the metal sites.

When trimetallic catalyst of Pt-Li-Sn/Al₂O₃ is employed, it shows that not only is the conversion by trimetallics higher than bimetallics but also the selectivity to C₄-olefins because of the influence of both decreasing the ensemble size by Sn and neutralizing the acidity of support site by Li.

When comparing the catalyst activity of the catalysts prepared by the “complex” method, impregnating alumina with a complex solution of H₂PtCl₆

with SnCl_2 and LiNO_3 (Wongkolkitilp, 1996) and the “non-complex” method used in this thesis, it is found that the activity of the catalysts prepared by the complex method was better than for the non-complex one. Lei Yuan Jin, 1990 believes that the platinum ion and the tin ion on the support are in a random, disordered distribution in the catalyst prepared by the non-complex method. When using the platinum-tin complexing method, the platinum ion and tin ion are in a ratio of $\text{Sn/Pt} = 2:1$ in the complex, that is, one platinum ion combines with two tin ions, closely. Through drying, calcining and reducing, one platinum atom has two tin atoms close in its surrounding, and an atomic cluster is easily formed, thus the formation of an ordered distribution would strengthen the interaction between platinum and tin. Consequently, the catalytic performance of the catalyst prepared by the complex method was remarkably improved.

4.3 The Role of Sn on the Butane Dehydrogenation Reaction

To investigate the role of Sn in more detail, the butane dehydrogenation data were observed at 600°C with five catalysts that employ Pt-Li-Sn/ Al_2O_3 catalyst. These catalysts consisted of Sn/Pt wt. ratio from 0.5 to 2.5 at the fixed concentration of Pt and Li of 0.40 wt%. The conversion and selectivity to 1-butene by these catalysts are compared in Figure 4.3 and 4.4 respectively. The selectivity to other products is shown in the Appendix.

It is evident that no single mechanism can account for the different ways in which a second metal may influence the stability of a Pt catalyst. Figure 4.5 summarises some possible models for Pt-Sn catalysts, all of which, in principle, could contribute to the overall increase in stability. In the particular case of our catalysts, we believe that an electronic modification is

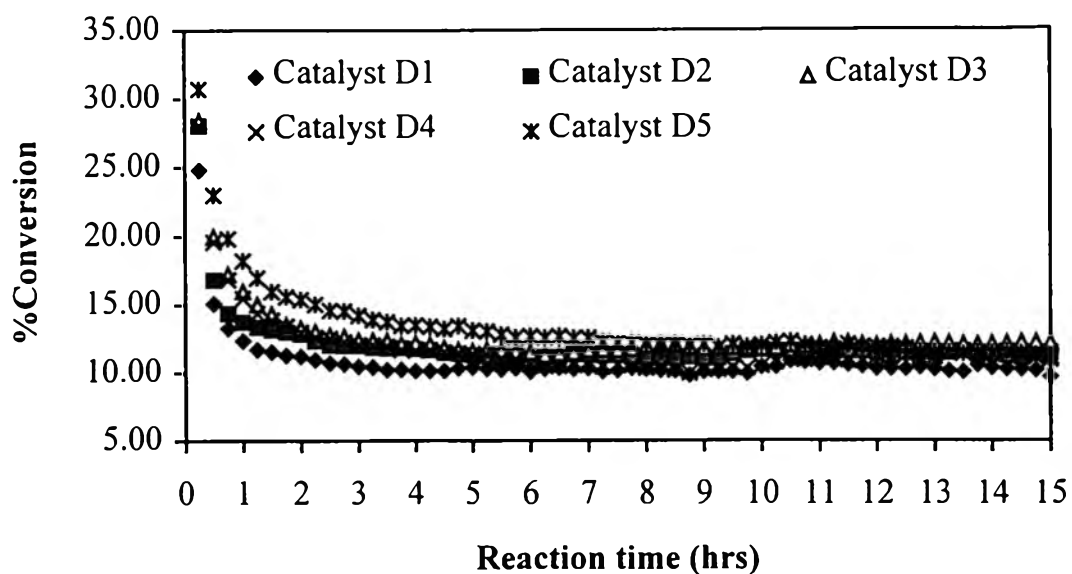


Figure 4.3 The conversion of butane dehydrogenation at 600 °C as a function of reaction time on alumina-supported catalyst at different Sn/Pt ratios.

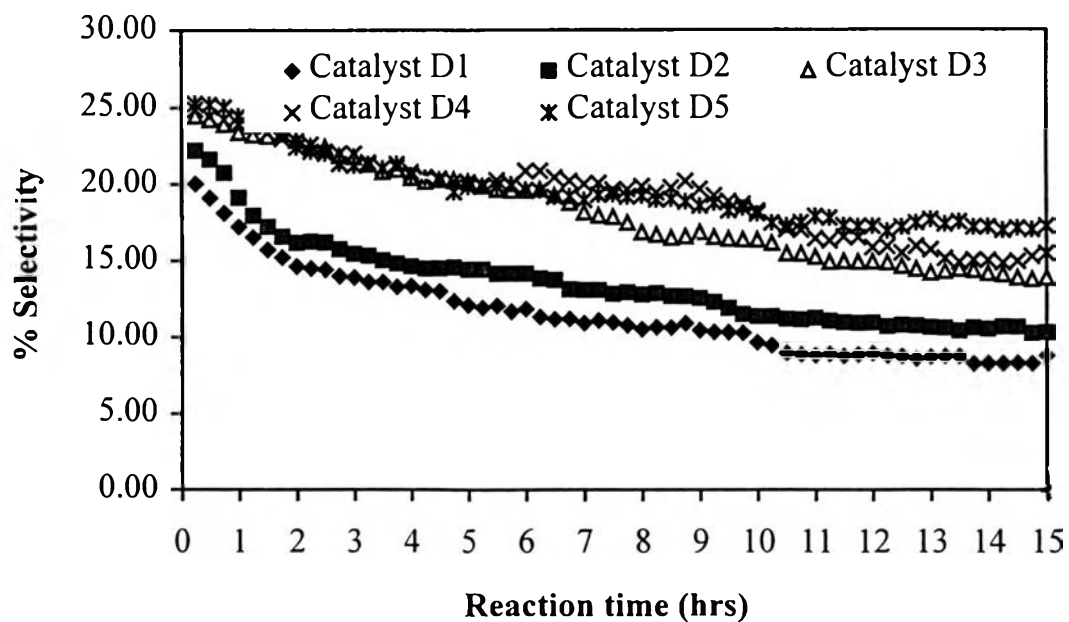


Figure 4.4 The selectivity of butane dehydrogenation to 1-butene at 600 °C on alumina-supported catalyst at different Sn/Pt ratios.

significant. An geometric/ensemble effect is more likely. The reason for this is that in case of the alumina supported sample an interaction between Sn(II) and alumina (conceivably forming a tin-aluminate complex) can lead to a spreading out of tin on the alumina support. In the case of the silica supported sample, this tin-support interaction effect either does not exist or is comparatively much weaker and hence, tin tends to form larger particles with a smaller fraction of metal exposed on the surface where XPS can probe it. So significant amounts of Sn can be reduced to the zero-valent state and this Sn could be alloyed with Pt samples after reduction (Balakrishnan and Schwank, 1991).

- (1) alloy formation
 - (a) ensemble effect
 - (b) electronic modification
- (2) direct intervention
 - (a) electronic

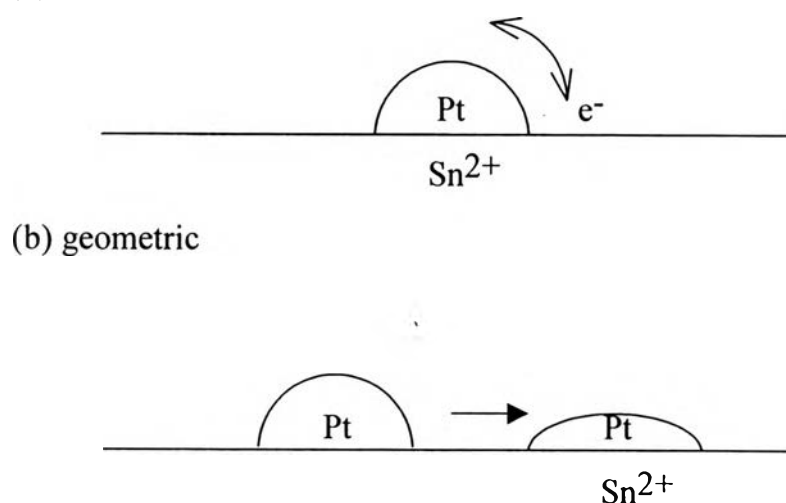


Figure 4.5 Possible models for the Pt-Sn catalysts.

It can be seen that the influence of Sn can enhance initial activity of butane dehydrogenation and its selectivity . This implies that one role of Sn seems to be to improve the dispersion of Pt. Adkins and Davis, 1984, represent the model for the alumina catalyst as schematically shown in Figure 4.6 . The added tin is present as an eggshell of “tin aluminate” surrounding the alumina support with the Pt(0) or Rh(0) supported on the “tin aluminate”.

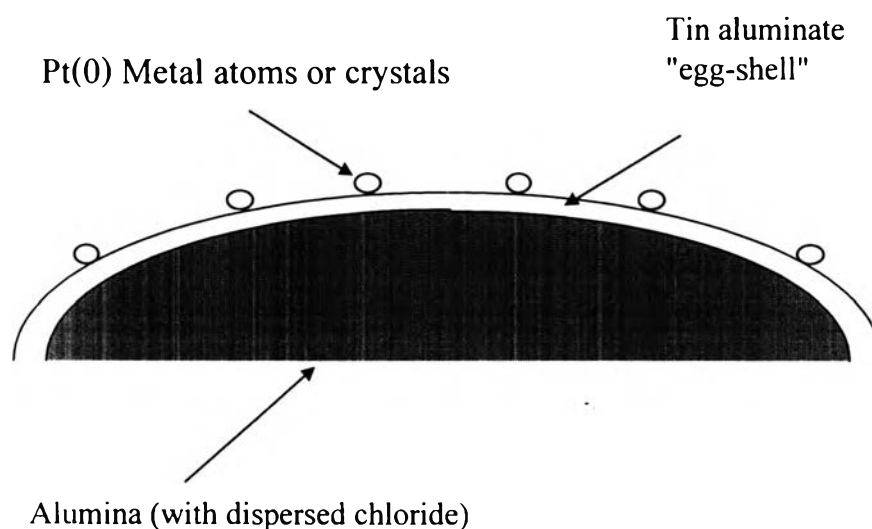


Figure 4.6 Schematic representation of a reduced Pt-Sn/Al₂O₃.

One could envision a scenario where the distance between Pt atoms tends to increase as more tin is added (Balakrishnan and Schwank, 1991). Barias et al., 1996 and Burch and Garla ,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 caused higher activity.

The TEM results (see Appendix) do not show the surface clearly. They showed little black spots dispersed in the Pt catalyst picture and bigger black

area dispersed when more tin added. It seems to be that addition of more tin creates larger new tin-aluminate surface spread on the alumina support.

4.4 Product Distribution of Butane Dehydrogenation Reaction

All types of catalysts give the same trend of product distribution as shown in Figure 4.7. It presents that the selectivity to 1-butene and trans-2-butene are the highest and nearly the same values followed by 1,3 butadiene and cis-2-butene, respectively. This depends on its thermodynamics and adsorption ability. However, more experiments are needed to explain this result. This figure also shows that addition of tin gives the same trend for the product distribution, higher selectivity when higher tin content in the catalysts.

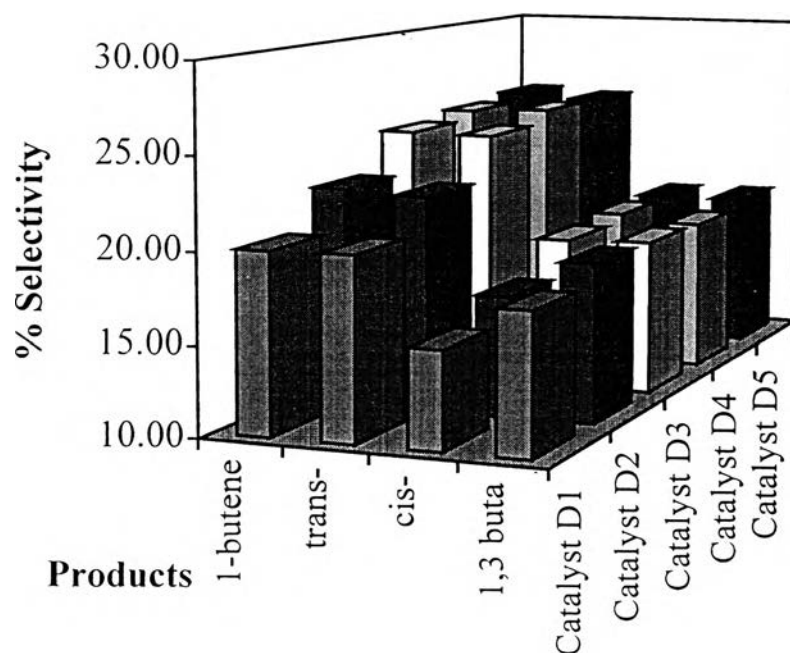


Figure 4.7 The comparison of distribution and selectivity of C₄-olefin products at various Sn/Pt ratios of Pt-Sn-Li catalysts.

4.5 The Role of Sn on the Coking Formation

The influence of Sn in coking formation can be seen in Figure 4.8 which shows the variation of the amount of carbon deposited on the whole catalysts as a function of reaction time as analyzed by the Elemental Analyzer. Initially, the amount of carbon deposited grows rapidly since all surface Pt sites are fresh and uncovered. After a period of time, most of 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 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).

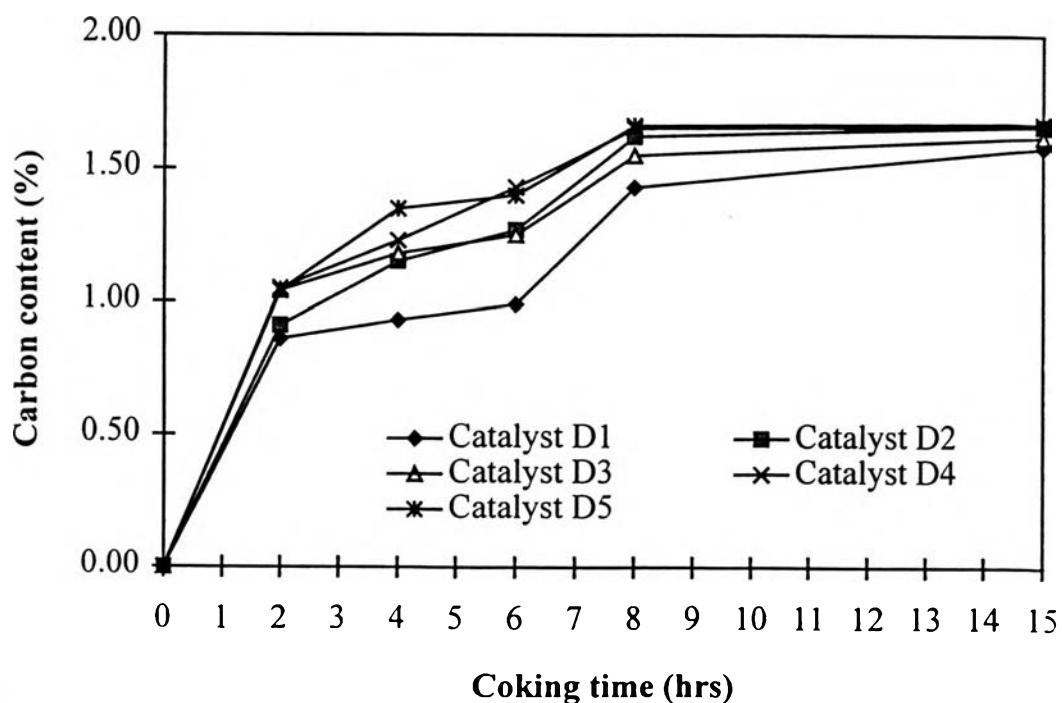


Figure 4.8 The variation of the amount of carbon deposited on the whole catalyst as a function of coking time.

Figure 4.8 shows the influence of tin on the trimetallic Pt-Li-Sn catalyst. It seems that the coke content depends on the activity of catalyst. The addition of Sn can maintain the activity and selectivity while the coking is quite high. A difference in interpretation of the role of tin exists. Burch and Garla, 1981 suggested that Sn modified the oxide support by eliminating very acidic sites required for coking reaction and replacing them with selective sites for dehydrogenation. They may either be low acidity sites already present on the alumina, or may be new sites of Sn(II) ions in the surface. They also explained that it maybe due to alter the local density of states at surface Pt atoms and this modifies the catalytic properties of these surface atoms, the main effect being to reduce the activity in coking reaction. Another role of Sn has been proposed by Lieke et al., 1987 called drain-off mechanism. Addition of Sn removes 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 and may then migrate to the metal function or stay on the acidic function. 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 large portion of active Pt sites remaining free for hydrocarbon adsorption. Therefore, addition of more Sn enhances selectivity to C4-olefins products and decreases selectivity to coke. The drain-off effect can be confirmed by TPO characterization (Teerasupaporn, 1998).

In order to confirm this results, fresh and spent catalysts at reaction time 15 hours were also characterized in terms of the physical properties of catalysts. The change of BET surface area, total pore volume and average pore diameter are tabulated in Table 4.4. The data given correspond to the condition used in Figure 4.3.

Table 4.4 Physical properties of fresh and spent catalyst investigated by BET

| Catalyst | Surface area (m ² /g) | | | Pore volume (cc/g) | | | Average pore radius (°A) | | |
|----------|----------------------------------|-------|---------|--------------------|-------|---------|---------------------------|-------|---------|
| | fresh | coked | %change | fresh | coked | %change | fresh | coked | %change |
| D1 | 112.6 | 110.1 | 2.22 | 0.040 | 0.039 | 1.67 | 7.128 | 7.169 | 0.58 |
| D2 | 109.6 | 101.2 | 7.66 | 0.040 | 0.037 | 7.76 | 7.286 | 7.227 | 4.23 |
| D3 | 120 | 106.2 | 11.51 | 0.041 | 0.038 | 8.49 | 6.870 | 7.161 | 0.81 |
| D4 | 112.8 | 104.5 | 7.36 | 0.040 | 0.037 | 7.02 | 7.101 | 7.127 | 0.37 |
| D5 | 111.2 | 106.6 | 4.14 | 0.040 | 0.038 | 4.88 | 7.257 | 7.197 | 0.83 |

The results show that when adding small amount of Sn (Sn/Pt ratio 0.5, 1.0 and 1.5), a significant decrease in surface area and pore volume due to the long reaction time. This result confirms the drain-off mechanism effect as described before.

On the other hand, when adding more Sn (Sn/Pt ratio 1.5, 2.0 and 2.5), there is a slight decrease in surface area and pore volume and improves the selectivity. This evidence indicated that adding more Sn decreased catalyst activity so that coke formation is reduced. It may be caused by more alloy formation that decreased the active Pt sites when more tin was added. However this disagrees with the results from the Elemental Analyzer. So it need more experiments are needed to confirm this result.

In addition, the results indicate that it is not only the amount but the location of coke that is important in determining catalyst performance. The greater efficiency of the catalysts was due to both the amount of coke formed and its location (Davis, 1993).

4.6 Repeated Reaction-Regeneration Cycles

Figure 4.9, 4.10 and 4.11 compare the conversion, yield and selectivity of butane dehydrogenation in 8 cycles and 8 hours of reaction in each cycle. Then followed by the regeneration step in each cycle with 1 Vol% O₂ in N₂ to burn off the coke deposited on the catalyst. After that, the catalyst is reduced and reused in another reaction cycle. 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.

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 and especially in third cycles and a smaller changes over the next five cycles.

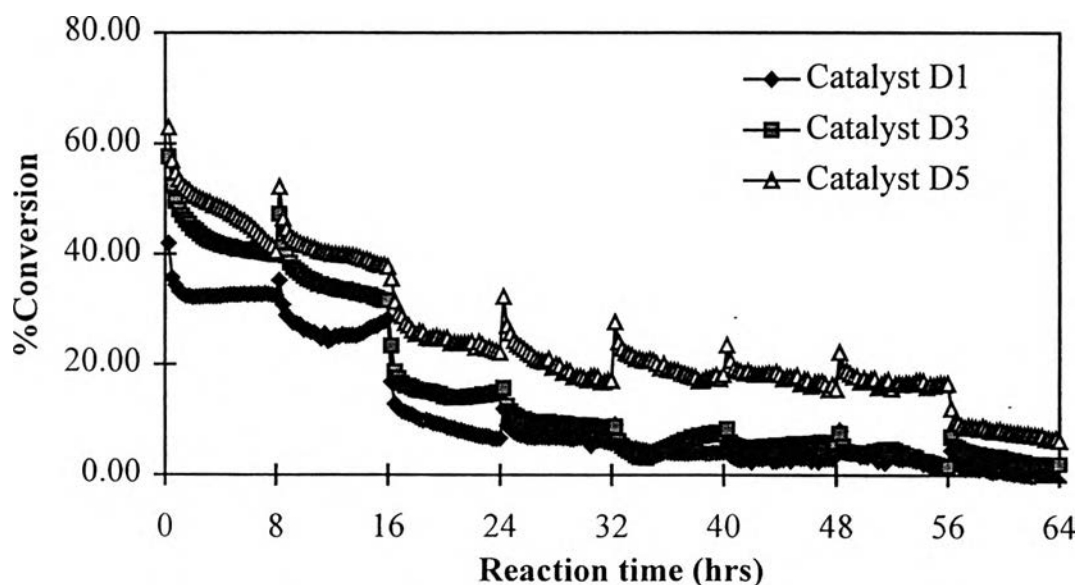


Figure 4.9 The conversion of butane dehydrogenation in 8 cycles at 600 °C over the 0.40%Pt-x%Sn-0.40%Li catalyst.

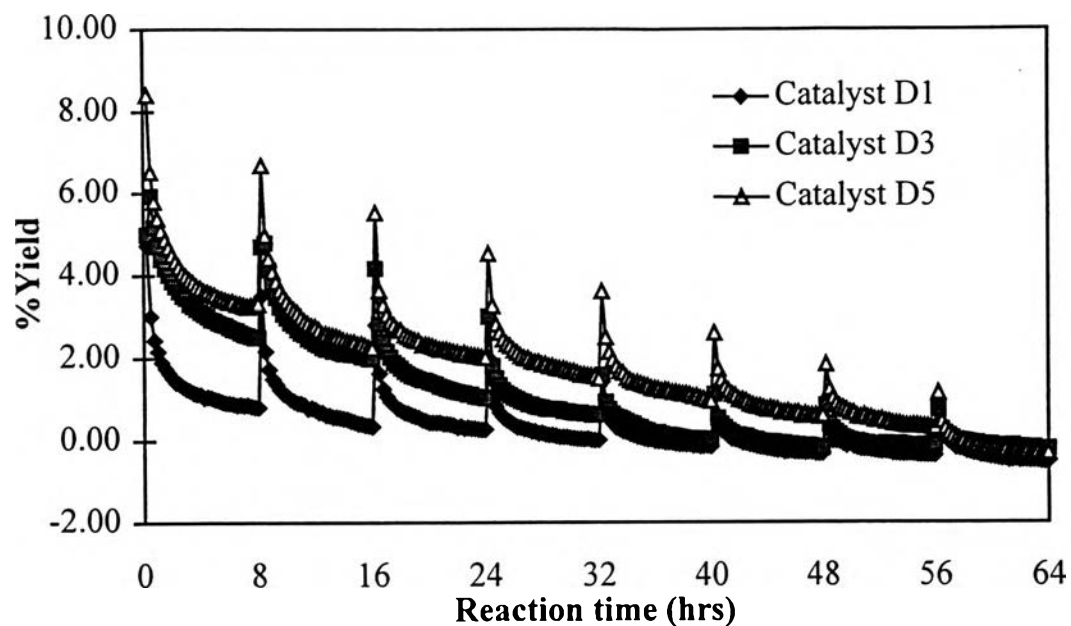


Figure 4.10 The yield of butane dehydrogenation in 8 cycles at 600 °C over the 0.40%Pt-x%Sn-0.40%Li catalyst.

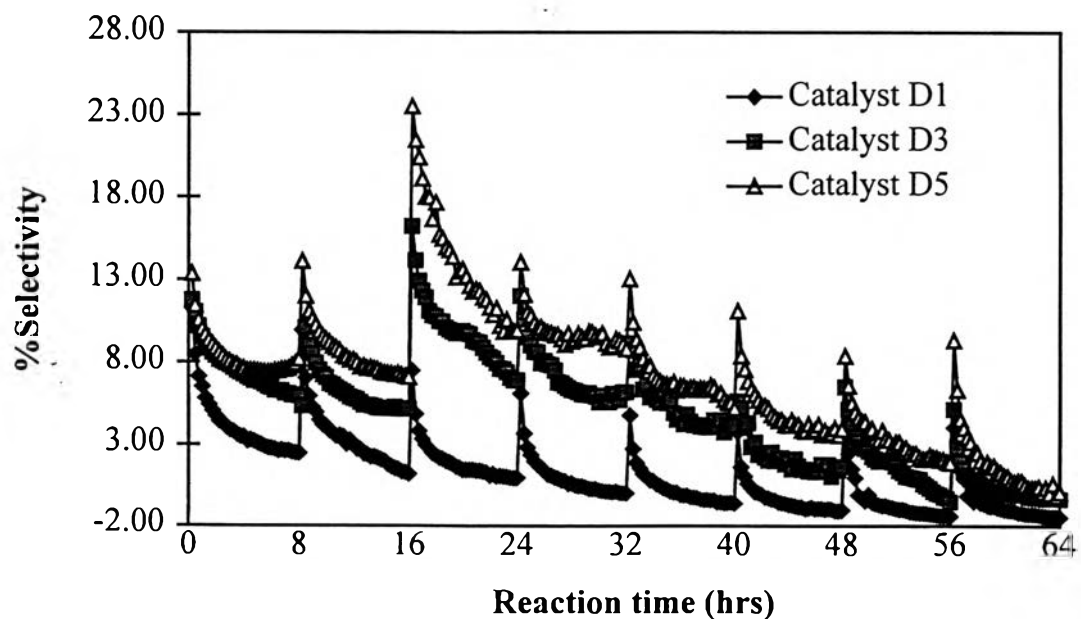


Figure 4.11 The selectivity to 1-butene of butane dehydrogenation in 8 cycles at 600°C over the 0.40%Pt-x%Sn-0.40%Li catalyst.

However, the selectivity of these catalysts shows an interesting behavior as it rises in the third cycle which may come from the effect of lower conversion in this cycle and the better rearrangement of Sn with the geometric sites of Pt. The selectivity gradually decreases over the following cycles.

Also the repeated coking-regeneration cycles may lead to increased alloying of the catalyst. Consequently, the number of surface Pt atoms which are exposed to the reactants goes down and results in the observed decrease of the activity of dehydrogenation reaction (Barias et al.,1996). This illustrates that the treatment with O₂ is not only a means of burning off the coke but also a means to restore or to control the dispersion of Pt.

An addition of chloride might help the redispersion of Pt particles but the catalyst should be doped with an optimum amount. Because doping with very low concentrations 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 less than 0.5% by weight. This may not be high enough for the redispersion of Pt atoms. In the commercial process, chlorides will be added continuously in the form of chlorine gas for a better-long-term performance of catalyst.