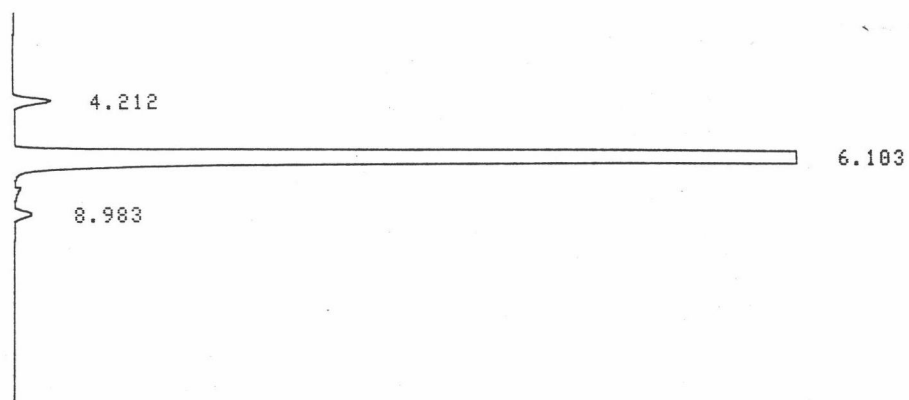# CHAPTER VI

DISCUSSION

In this research, propane dehydrogenation reaction was performed at temperature of 500°C and atmospheric pressure because of two reasons. First, the thermal cracking reaction does not occur at this temperature. This was identified by comparing the chromatograms of feed stream and product stream resulted from test run at the above conditions with no catalyst bed. Both streams have the same chromatogram pattern as shown in Figure 6.1. Therefore, the products of the reaction performed in this research should be the result of the catalyst activity alone.

Second, there is an evidence showing that the aging of metal-supported catalyst, indicated by the sintering effect as measured by the decrease of metal dispersion, becomes effective only beyond 540 °C [51]. Therefore, the catalyst deactivation at this reaction temperature of 500°C should be mainly the result of coke deposition on the catalyst.

The points that will be discussed for this research can be classified into 2 parts, one concerning the deactivation which, described above, is due to coke formation on catalyst surface. The other will deal with the characterization of coke deposits by determining the irreversible coke, responsible for long term deactivation, deposited on various catalysts. Because of the
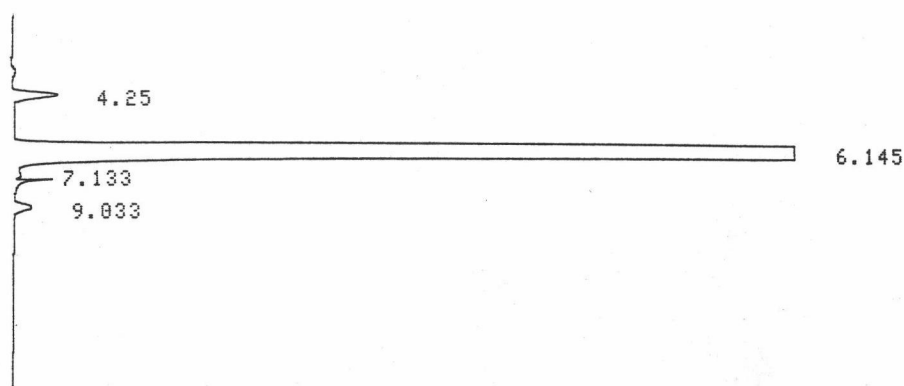
```
        4.212

                                                                    6.103

        8.983


CHROMATOPAC   C-R6A              FILE        7
SAMPLE NO   0                    METHOD      441
REPORT NO   47

PKNO      TIME       AREA   MK  IDNO      CONC      NAME

  1      4.212        712               0.0133   Ethane-ethylene
  2      6.103     5347180             99.9607   Propane
  3      8.983       1390   V            0.026   Butane
                  ---------          -------------
         TOTAL    5349281                 100
```

(A) Feed stream


```
        4.25

                                                                    6.145

      7.133
        9.033


CHROMATOPAC   C-R6A              FILE      - 7
SAMPLE NO   0                    METHOD      441
REPORT NO   48

PKNO      TIME       AREA   MK  IDNO      CONC      NAME

  1      4.25         889               0.0165   Ethane-ethylene
  2      6.145     5371572   S          99.8898   Propane
  3      7.133       3781    T           0.0703   Propylene
  4      9.033       1258    T           0.0234   Butane
                  ---------          -------------
         TOTAL    5377500                 100
```

(B) Product stream

Figure 6.1 The chromatograms of feed and products stream after

flowing throught the reactor with no catalyst bed at

500 C and atmospheric pressure.

experiments were done under the above fixed conditions, the variations were made on the main catalyst itself (Pt/Al₂O₃). The results can then be explained more clearly according to the variations as follows :

(1) Incorporation of the second metals (Sn or Re) onto the main precursor (Pt/Al₂O₃).

(2) Incorporation of the third metal (Li) onto both bimetallic catalysts (Pt-Re/Al₂O₃ and Pt-Sn/Al₂O₃).

6.1 Catalyst deactivation.

The propane conversion curves of all catalysts studied in the research, Figure 5.1, drop sharply within the first half of an hour and then slightly decrease with longer time on stream because of the self-poisoning phenomena of cokes. This self-poisoning reaction is the structure sensitive side reaction, and always accompanies with the hydrocarbon reactions on transition metals [29]. The rate of which is not proportional to metallic area but depends on the dispersion of the metal and more generally, on the method of preparation of the catalyst.

In order to characterize the extent of deactivation, the equation given by Voorhies [52] was modified to the following form :

$$\log (X_t/X_f) = \log A - n \log t \qquad (6.1)$$

where X_t is the conversion of a given product at moment t, X_f is the conversion measured in the first 5 minutes, the ratio X_t/X_f is

defined as a measure of deactivation and will be referred to as relative activity values. The rate of deactivation ,n, can be evaluated by equation 6.1. The higher the absolute value of n is the higher the rate of deactivation of the reaction studied. The deactivation patterns of the studied catalysts are given in Figure 6.2. The corresponding values of ,n, for different catalysts can be obtained from the slope of the straight line part the curves (2 hours of time on stream). The results are shown in Table 6.1. From this table, the rate of deactivation of Pt-Sn/Al_2O_3 is the highest and for Pt-Re-Li/Al_2O_3 the rate is the lowest.

Table 6.1 The initial rate of deactivation, n.

Catalyst	Initial rate of deactivation, n(*).
Pt/Al_2O_3	0.5425
Pt-Sn/Al_2O_3	0.7793
Pt-Re/Al_2O_3	0.4361
Pt-Sn-Li/Al_2O_3	0.5608
Pt-Re-Li/Al_2O_3	0.2911

(*) : This value was calculated from only a straight line part.

Deactivation of the catalysts could be explained by the mechanism of propane dehydrogenation reaction. Based on Pt/Al_2O_3 catalyst, the addition of Sn to Pt/Al_2O_3 catalyst enhanced the activity of catalysts because of changes in electronic properties of Pt crystallites caused by the incorporation of metallic Sn to from solid solution with Pt resulting in electron-rich Pt site [53]. When
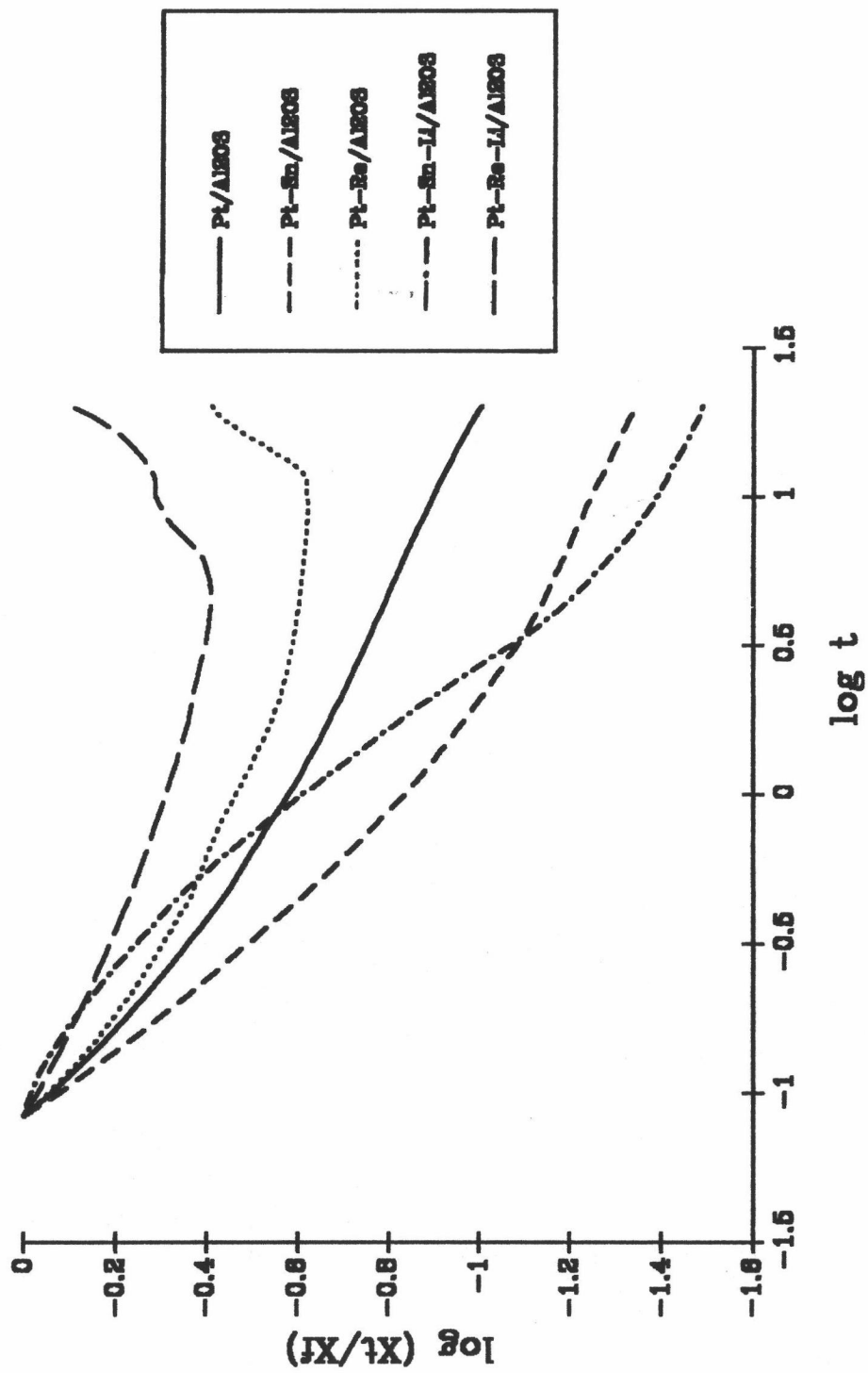
Figure 6.2 Deactivation pattern of studied catalysts.

log t

log (Xt/Xf)

Pt/Al2O3
Pt–Sn/Al2O3
Pt–Re/Al2O3
Pt–Sn–Li/Al2O3
Pt–Re–Li/Al2O3

propane was adsorbed on these electron-rich Pt site the stronger Pt-H interaction induced the C-H bond to be weaker and more easily broken to from propylene products compared to the unpromoted Pt catalyst. The dehydrogenation activity of this catalyst was then higher than the base Pt/Al_2O_3 catalyst. This resulted in high rate of coke precursor production. Thus, the deactivation rate was also high.

For the $Pt-Re/Al_2O_3$ catalyst, the addition of Re to Pt/Al_2O_3 catalyst did not improve the catalytic activity because alloying between Re and Pt caused the geometric dilution [54] (some of Pt surface sites were blocked by Re). Thus, the activity of this catalyst and also the deactivation rate were lower than Pt/Al_2O_3 catalyst due to the lost active sites.

Lithium addition to $Pt-Sn/Al_2O_3$ increased the activity of the catalyst because the alkaline lithium would act as an electron donor to Pt [55], thus inducing the hydrogen spill-over. Therefore, the rate of coke formation was lowered because of the continuous coke precursor hydrogenation caused by spill-over hydrogen. Moreover, the initial rate of deactivation of $Pt-Sn-Li/Al_2O_3$ was lower than $Pt-Sn/Al_2O_3$ catalyst.

Incorporation of Li to $Pt-Re/Al_2O_3$ did not change the activity of the catalyst but could induce hydrogen spillover phenomena. In addition to the fact that Re in $Pt-Re/Al_2O_3$ functioned as a coke precursors interceptor and hydrogenolytic agent [14], the deactivation rate of this catalyst is also lowerd because of the hydrogen spill-over effect in increasing hydrogenolytic activity of Re component for coke precursor removal.

6.2 <u>Coked catalyst characterization</u>.

6.2.1 <u>Comparison of the amounts of coke deposits among</u> <u>various studied catalysts</u>.

In comparison to the Pt/Al_2O_3 catalyst, the $Pt-Sn/Al_2O_3$ catalyst has the higher total amount of coke deposits. This can be explained that the higher dehydrogenating activity of $Pt-Sn/Al_2O_3$ caused the higher coke precursors, thus the increased coke deposits on catalyst surface. From TPO results, it was shown by H/C ratio that coke deposits on $Pt-Sn/Al_2O_3$ was more irreversible than coke on Pt/Al_2O_3 because this catalyst had a high dehydrogenation activity in converting coke to be more irriversible.

For $Pt-Re/Al_2O_3$ catalyst, the total amounts of coke higher than the Pt/Al_2O_3 catalyst. This could be explained that Re, presented in Re^o or Re^{n+} were able to intercept coke precursors and protect Pt atoms by a preferential coke deposition on themselves [14]. This explanation is in agreement with the results presented by Bertolacini [56] who found that the amount of coke deposited on platinum was lowered by a simple mixture of the Pt/Al_2O_3 and Re/Al_2O_3 monometallic catalysts.

The coke deposits on $Pt-Re/Al_2O_3$ catalyst had the H/C ratio higher than Pt/Al_2O_3. This meant that coke on $Pt-Re/Al_2O_3$ would be less irreversible (lower degree of graphitization). This was also because of the high hydrogenolytic activity of rhenium [57].

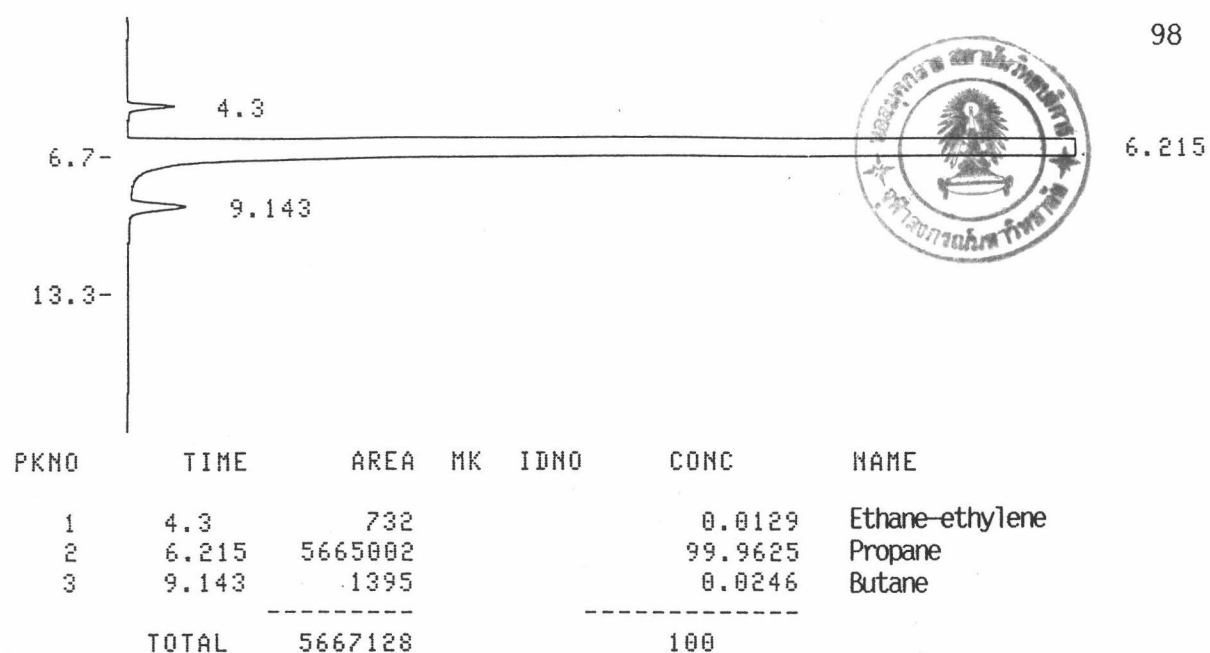In comparison to their base catalyst, the $Pt-Sn-Li/Al_2O_3$

and Pt-Re-Li/Al$_2$O$_3$ catalysts both have the lower total amounts of coke deposits. The H/C ratio of these coke was higher than their base catalysts. This might be resulted from the increased hydrogen spill-over effect caused by lithium component that removed coke precursor and altered the nature of coke to be more reversible.

6.2.2 Comparison of irreversible coke deposits on metal sites among Pt/Al$_2$O$_3$, Pt-Sn/Al$_2$O$_3$, Pt-Sn-Li/Al$_2$O$_3$.
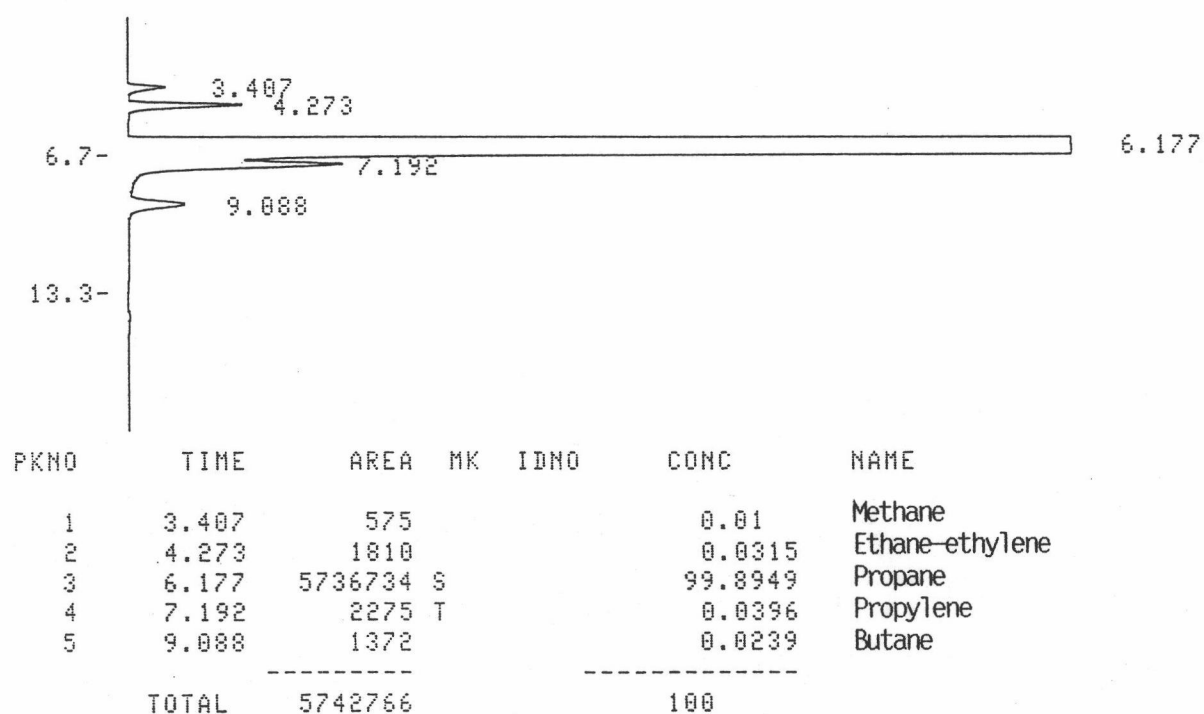
From literature, the dehydrogenation reaction and the hydrogenolysis reaction took place on the metal active sites. On the other hand, the hydrocracking reaction occured on acidic sites [58]. To investigate from what source hydrogenolytic products (methane, ethane, and ethylene) came, the alumina support which treated by the same conditions as catalyst was subjected to the reaction and the chromatograms of the feed and product stream are compared in Figure 6.3. From this figure, it was concluded that the hydrogenolytic products occurred very low at the acidic sites of the support (lower than that occurred at metal active sites of catalyst ten-fold). Therefore, the propane conversion in this study only happened on metal sites of the catalyst. The deactivation of the catalyst will be resulted from the coverage of metal sites by irreversible coke.

In commercial process, the long term deactivation of catalysts caused by irreversible coke has the effect on productivity and also profit. Thus, the improvement of catalyst performance and the change of coke formation characteristics will certainly make a page of catalyst technology history. In this research, when the total irreversible coke obtained from TPO data was higher, the irreversible coke deposited on the metal site was also higher, as

98


```
PKNO      TIME       AREA   MK  IDNO      CONC     NAME

  1       4.3         732                0.0129    Ethane-ethylene
  2       6.215    5665002               99.9625   Propane
  3       9.143      1395                0.0246    Butane
                  ---------            -------------
         TOTAL    5667128                 100
```

(A) Feed stream


```
PKNO      TIME       AREA   MK  IDNO      CONC     NAME

  1       3.407       575                0.01      Methane
  2       4.273      1810                0.0315    Ethane-ethylene
  3       6.177    5736734  S            99.8949   Propane
  4       7.192      2275   T            0.0396    Propylene
  5       9.088      1372                0.0239    Butane
                  ---------            -------------
         TOTAL    5742766                 100
```

(B) Product stream

Figure 6.3   The   chromatograms of feed   and   products   stream   after
             flowing   through   the reactor   with   contained   alumina
             support   (which   treated   by   the   same   conditions   as
             catalyst) at 500°C and atmospheric pressure.

shown in Table 5.8 - 5.10. The results also summarized and shown in Table 6.2.

Table 6.2 The amounts of metal sites covered by irreversible coke deposition and the percentage coverage at the 5 min. of time on stream of Pt/Al_2O_3, $Pt-Sn/Al_2O_3$, and $Pt-Sn-Li/Al_2O_3$ catalysts.

Catalyst	Amounts of metal site covered by irreversible coke deposition (sites)	Percentage coverage
Pt/Al_2O_3	6.08×10^{17}	22.01
$Pt-Sn/Al_2O_3$	5.07×10^{17}	50.00
$Pt-Sn-Li/Al_2O_3$	1.52×10^{17}	14.29

From Table 6.2, the percentage coverage could be ordered as follows :

$$Pt-Sn/Al_2O_3 > Pt/Al_2O_3 > Pt-Sn-Li/Al_2O_3.$$

The existing of Sn alone caused the percentage coverage to be higher than Pt/Al_2O_3 though both its propane conversion and propylene selectivity were high. Incorporation of both Sn and Li gave the best result in that the percentage coverage was the lowest and both propane conversion and propylene selectivity were the hightest resulted from the H_2 spillover phenomena promoted by Li.