

CHAPTER V

RESULTS

In this research, the gas-phase dehydrogenation of propane was performed in a fixed bed reactor described in Chapter IV. The results were categorized into three parts as the follows.

- 5.1 Catalyst characterization.
- 5.2 Catalyst deactivation.
- 5.3 Coked catalyst characterization.

5.1 Catalyst characterization.

The catalysts prepared in this research with their designed metals loading are shown in Table 5.1. All of them were characterized to measure the metal contents, metal active sites, and the BET surface area.

5.1.1 Determination of metal contents.

The metal content of catalysts were analyzed by Atomic Absorption (AA) and Inductively Coupled Plasma Emission Spectrometry (ICPS) method described in section 4.2.1. The results are shown in Table 5.2. The amounts of metal contents of prepared catalysts are close to their designed loading value.

Table 5.1 Designed metal loading of catalysts prepared in this research.

Catalyst	Metal Loading (% wt.)			
	Pt	Sn	Re	Li
Pt/Al ₂ O ₃	0.3			
Pt-Sn/Al ₂ O ₃	0.3	0.3		
Pt-Re/Al ₂ O ₃	0.3		0.3	
Pt-Sn-Li/Al ₂ O ₃	0.3	0.3		0.6
Pt-Re-Li/Al ₂ O ₃	0.3		0.3	0.6

Table 5.2 The metal content of catalysts prepared in this research.

Catalyst	Metal Content (% wt.)			
	Pt(*)	Sn(*)	Re(*)	Li(**)
Pt/Al ₂ O ₃	0.285			
Pt-Sn/Al ₂ O ₃	0.281	0.298		
Pt-Re/Al ₂ O ₃	0.282		0.270	
Pt-Sn-Li/Al ₂ O ₃	0.279	0.266		0.585
Pt-Re-Li/Al ₂ O ₃	0.286		0.296	0.507

(*) measured by Inductively Coupled Plasma Emission Spectrometry.

(**) measured by Atomic Absorption.

5.1.2 Determination of metal active sites.

The metal active sites of catalysts were measured by the CO adsorption method described in section 4.2.2. The results are shown in Table 5.3. The Pt/Al₂O₃ catalyst has the highest metal active sites. The Pt-Sn/Al₂O₃ and Pt-Sn-Li/Al₂O₃ catalysts have the amounts of metal sites lower than Pt-Re/Al₂O₃ and Pt-Re-Li/Al₂O₃.

Table 5.3 The metal site of catalysts measured by CO adsorption.

Catalyst	Metal active sites (molecule of CO/gram of catalyst)
Pt/Al ₂ O ₃	2.7641 × 10 ¹⁸
Pt-Sn/Al ₂ O ₃	1.0140 × 10 ¹⁸
Pt-Re/Al ₂ O ₃	1.4458 × 10 ¹⁸
Pt-Sn-Li/Al ₂ O ₃	1.0645 × 10 ¹⁸
Pt-Re-Li/Al ₂ O ₃	1.8688 × 10 ¹⁸

5.1.3 Determination of BET surface area.

The BET surface area of catalysts were measured by the method described in section 4.2.3. The results are shown in Table 5.4. Compared to the alumina support, the Pt/Al₂O₃ and Pt-Sn/Al₂O₃ has the surface area higher. On the contrary, the Pt-Sn-Li/Al₂O₃ catalyst which has amount of metal loading higher than both Pt/Al₂O₃ and Pt-Sn/Al₂O₃ has lower surface area.

Table 5.4 The BET surface area of catalysts.

Catalyst	Surface area (m ² /gm.)
Alumina support	315.90
Pt/Al ₂ O ₃	365.73
Pt-Sn/Al ₂ O ₃	351.15
Pt-Re/Al ₂ O ₃	285.01
Pt-Sn-Li/Al ₂ O ₃	282.07
Pt-Re-Li/Al ₂ O ₃	298.47

5.2 Catalyst deactivation by propane dehydrogenation.

The catalysts prepared in this research were rapidly deactivated by propane dehydrogenation reaction which was performed at temperature of 500 C and atmospheric pressure for 20 hours.

Typical time on stream curves of propane conversion are given in Figure 5.1. In this figure, the extent of decay of different catalysts will be compared. Both Pt-Sn-Li/Al₂O₃ and Pt-Sn/Al₂O₃ have very high initial activity followed by high deactivation rate. On the contrary, the initial activity of Pt-Re/Al₂O₃ and Pt-Re-Li/Al₂O₃ is rather stable with low deactivation rate.

The catalytic properties of the catalysts studied are given in Figure 5.2-5.5, where propylene selectivities, methane selectivities, ethane-ethylene selectivities, and propylene space time yields are compared.

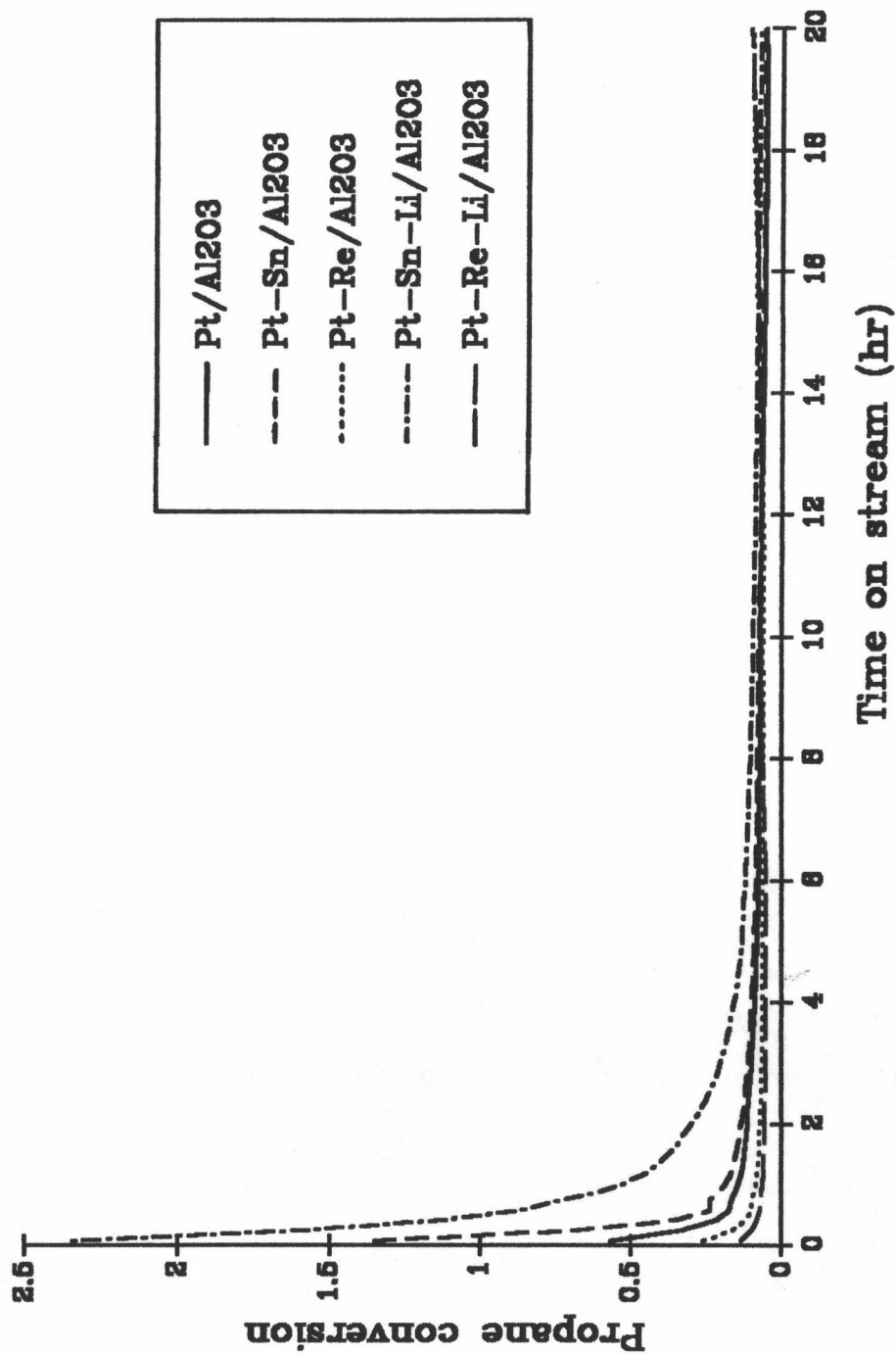


Figure 5.1 Propane conversion curve of studied catalysts.

Condition : Temperature = 500 °C, GHSV. = 22,525 hr⁻¹,

Weight of catalyst = 0.1 gram, Feed = 20 % propane in N₂.

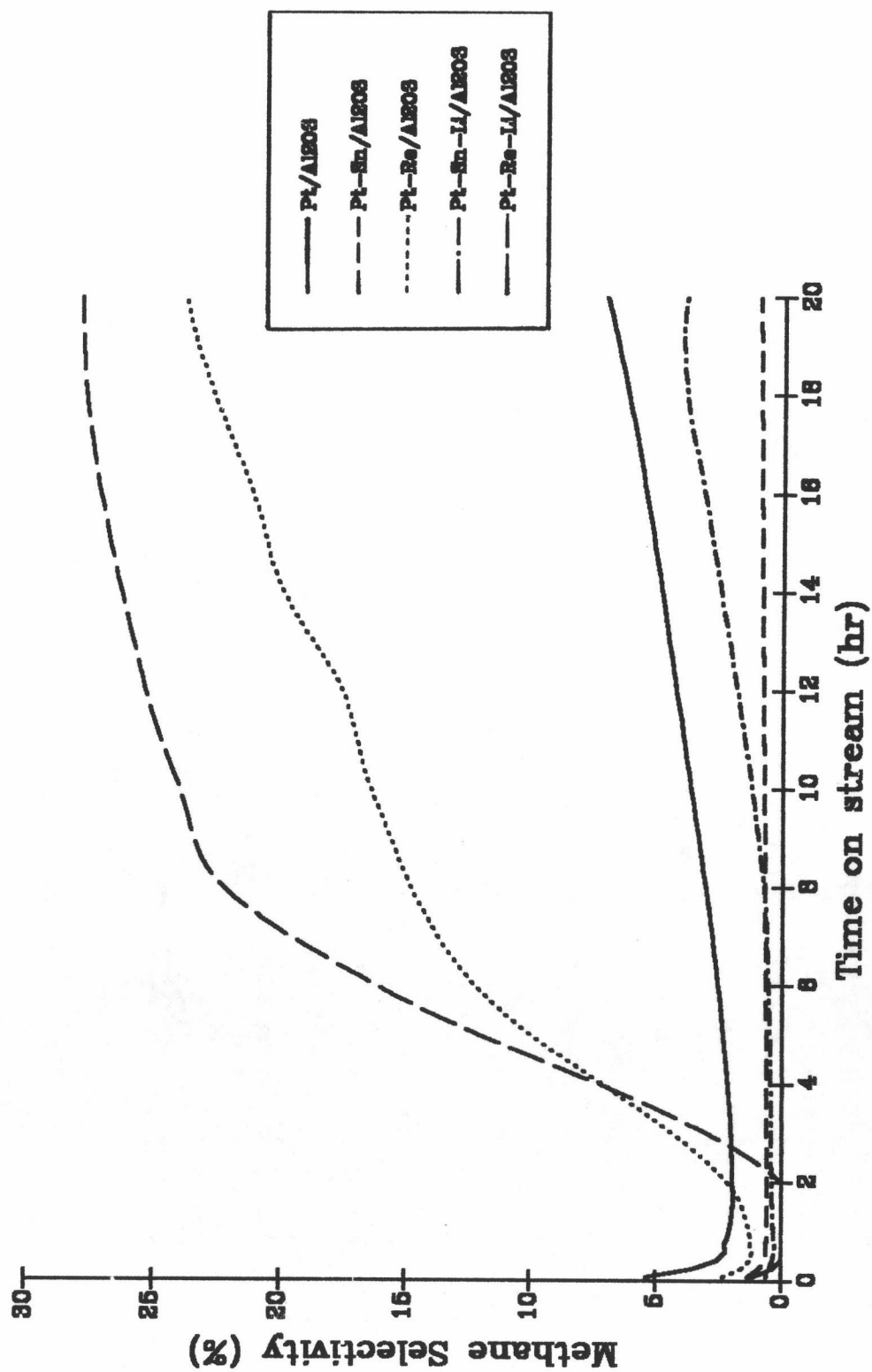


Figure 5.2 Methane selectivity curve of studied catalysts.

Condition : Temperature = 500 °C, GHSV. = 22,525 hr⁻¹,

Weight of catalyst = 0.1 gram, Feed = 20 % propane in N₂.

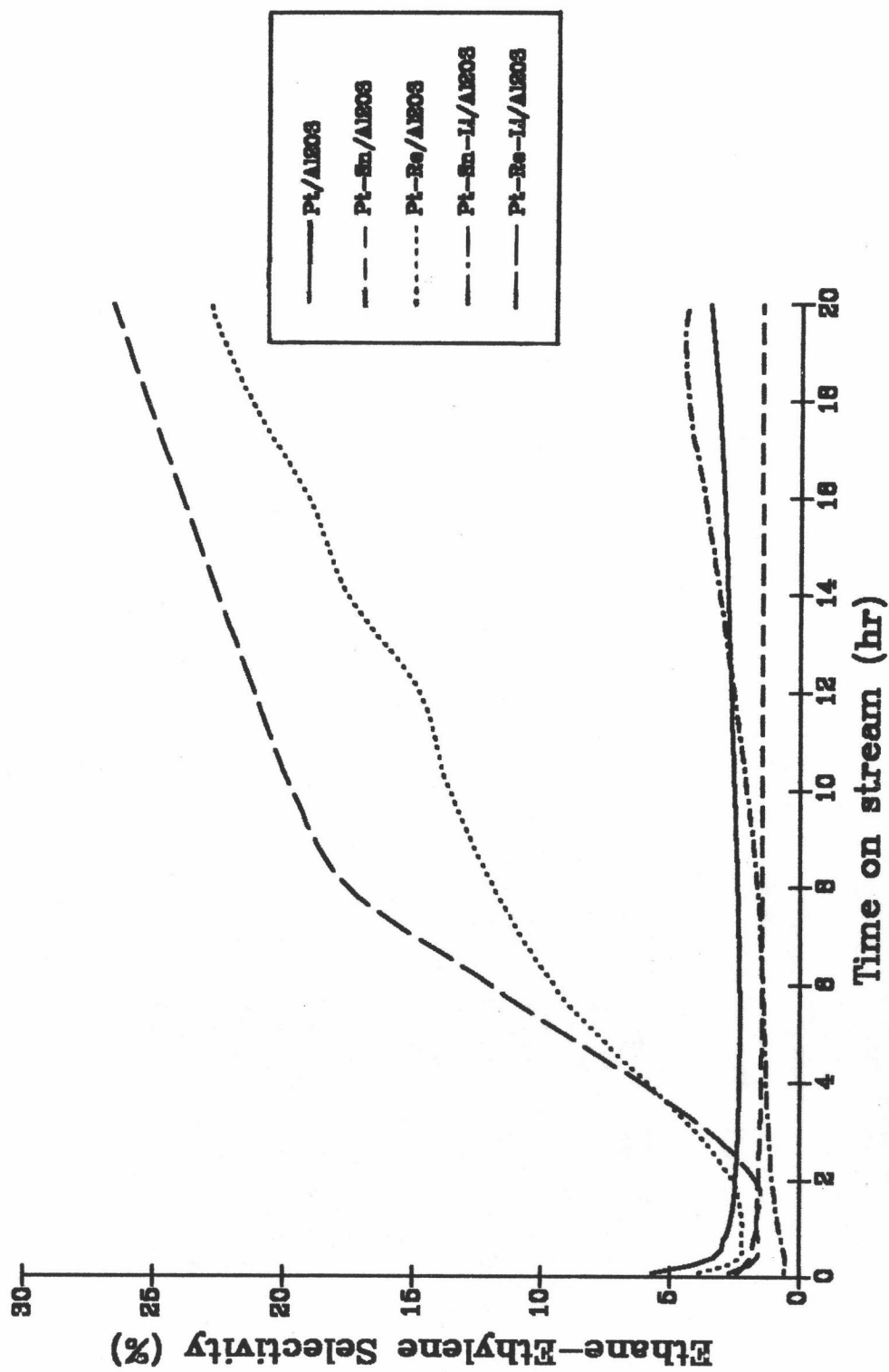


Figure 5.3 Ethane-ethylene selectivity curve of studied catalysts.

Condition : Temperature = 500 °C, GHSV. = 22,525 hr⁻¹,

Weight of catalyst = 0.1 gram, Feed = 20 % propane in N₂.

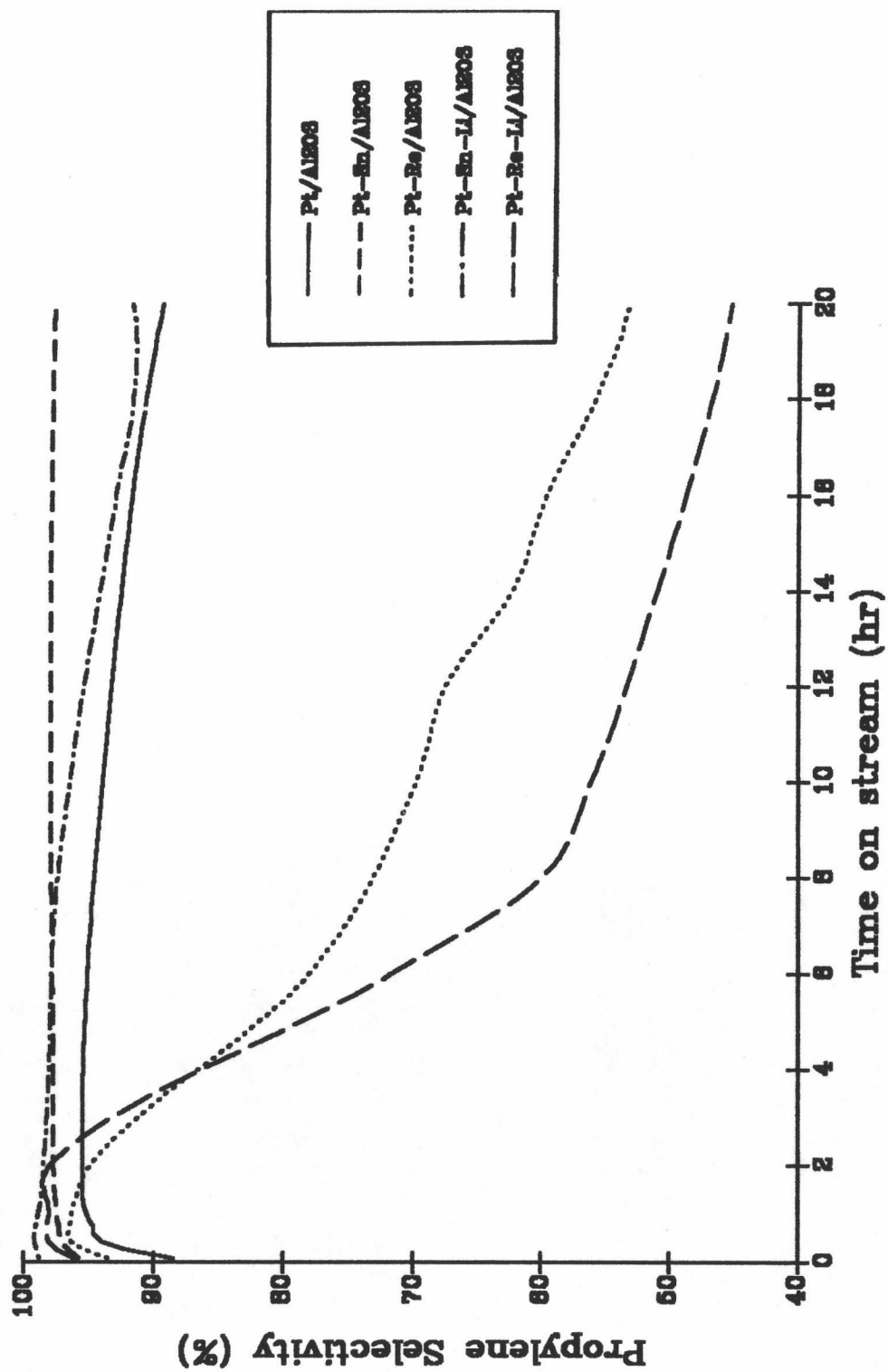


Figure 5.4 Propylene selectivity curve of studied catalysts.

Condition : Temperature = 500 °C, GHSV. = 22,525 hr⁻¹,

Weight of catalyst = 0.1 gram, Feed = 20 % propane in N₂.

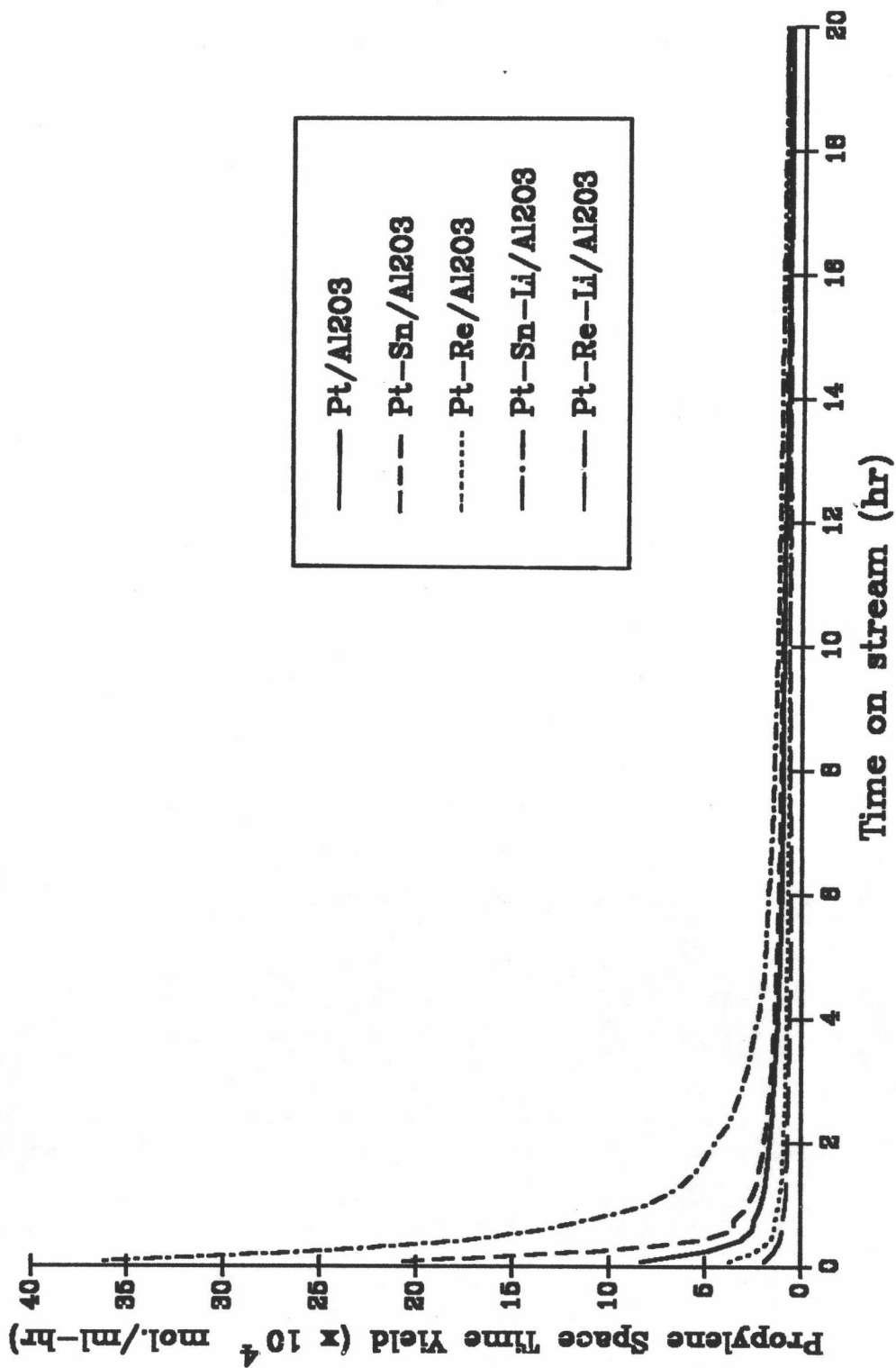


Figure 5.5 Propylene space time yield curve of studied catalysts.

Condition : Temperature = 500 °C, GHSV. = 22,525 hr⁻¹,

Weight of catalyst = 0.1 gram, Feed = 20 % propane in N₂.

In comparison to the base Pt/Al₂O₃ catalyst, the selectivity of Pt-Re/Al₂O₃ and Pt-Re-Li/Al₂O₃ have been significantly altered. The selectivity for hydrogenolysis of these catalysts (i.e. formation of methane and ethane-ethylene) were higher than Pt/Al₂O₃. On the other hand, Pt-Sn/Al₂O₃ and Pt-Sn-Li/Al₂O₃ catalysts showed higher selectivities of propylene than Pt/Al₂O₃.

5.3 Coked catalyst characterization.

5.3.1 Weight of coke.

The weight of coke deposited on the surface of catalyst, which had been used for the dehydrogenation of propane for 20 hours of time on stream, were measured by the method described in section 4.4.1. The results are given in Table 5.5.

Table 5.5 Weight of coke deposits on surface of catalyst measured by DTG.

Catalyst	Weight of coke (% wt.)
Pt/Al ₂ O ₃	13.02
Pt-Sn/Al ₂ O ₃	13.82
Pt-Re/Al ₂ O ₃	13.20
Pt-Sn-Li/Al ₂ O ₃	12.05
Pt-Re-Li/Al ₂ O ₃	11.01

In comparison to the base Pt/Al₂O₃ catalyst, the Pt-Sn/Al₂O₃ catalyst had the highest amounts of coke deposit. The lithium promoted catalysts, Pt-Sn-Li/Al₂O₃ and Pt-Re-Li/Al₂O₃, had coke deposit lower than their base catalysts, Pt-Sn/Al₂O₃ and Pt-Re/Al₂O₃, respectively.

5.3.2 Temperature programmed oxidation of coked catalyst.

The location and composition of coke deposited on the catalyst, which had been used for the dehydrogenation of propane for 20 hours of time on stream, were characterized by Temperature Programmed Oxidation (TPO) method.

The TPO method yields the information of the total amounts of coke by the amounts of CO₂ production. The amounts of reversible coke and irreversible coke are categorized by the peak area of low and high oxidation temperature, respectively. The degree of graphitization is measured by the hydrogen/carbon atomic ratio.

The TPO pattern of the studied catalysts are shown in Figure 5.6. The oxidation of all of the catalyst occurs in the range of temperature between 50–700 C. The shape of TPO patterns are different from one sample to another. However, all of the patterns showed two oxidation temperature zones, one at about 110 C and the other at about 450 C. The area under the curves of the low and the high oxidation temperature zones shows the amounts of reversible coke and the amounts of irreversible coke on the catalysts, respectively.

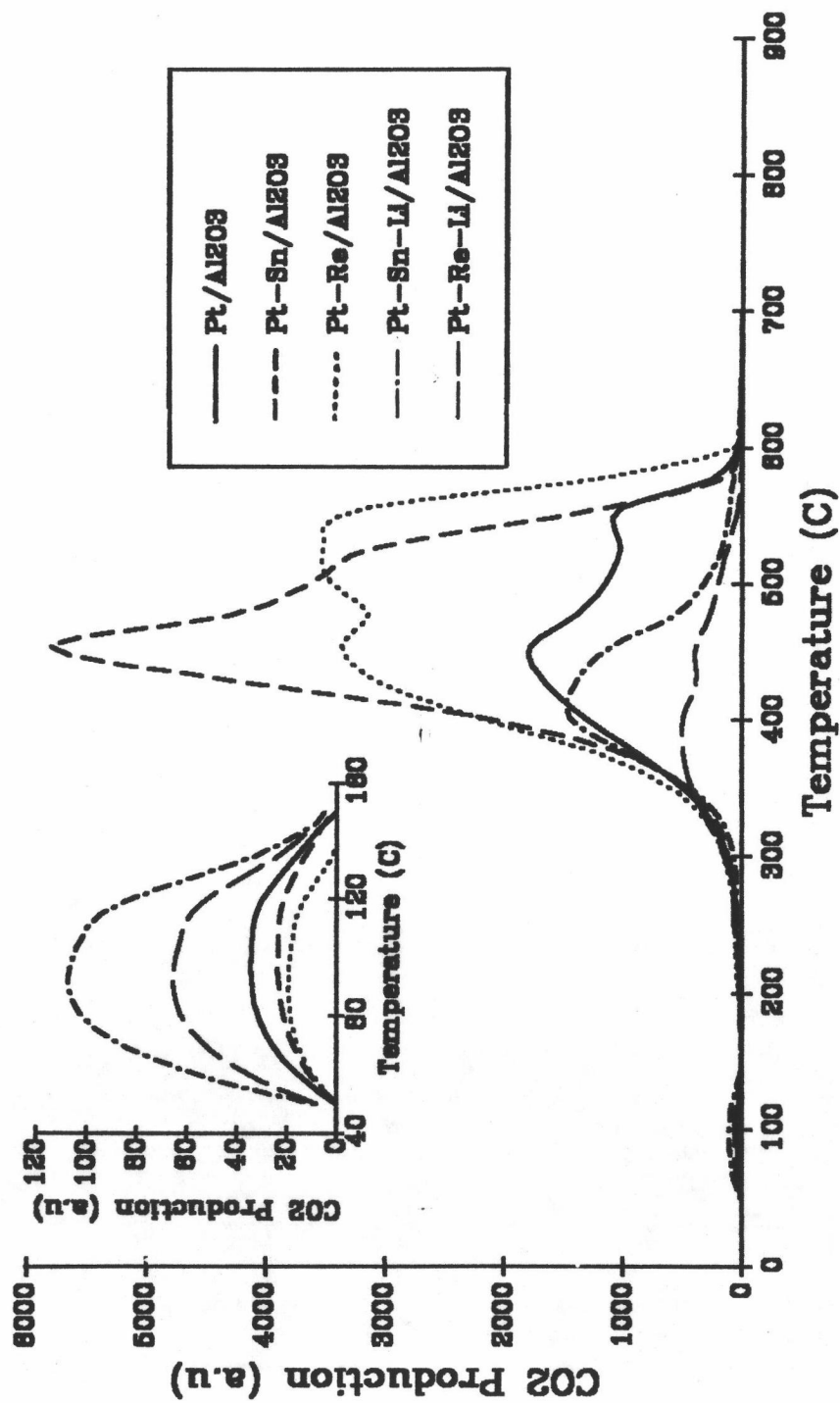


Figure 5.6 Temperature Programmed Oxidation of various coked catalysts.

From the TPO pattern, the total amounts of coke deposits on studied catalysts could be arranged in the following order :
 $\text{Pt-Sn/Al}_2\text{O}_3 > \text{Pt-Re/Al}_2\text{O}_3 > \text{Pt/Al}_2\text{O}_3 > \text{Pt-Sn-Li/Al}_2\text{O}_3 > \text{Pt-Re-Li/Al}_2\text{O}_3$ (corresponding with the measurement by thermogravimetric method in Table 5.5).

The amounts of reversible coke of all catalysts is very low and appears at the same temperature (110 C). The amounts of irreversible coke are different from one catalyst to the other and appear at around 400–450 °C.

In comparison to the base $\text{Pt/Al}_2\text{O}_3$ catalyst, the amounts of irreversible coke on $\text{Pt-Sn/Al}_2\text{O}_3$ and $\text{Pt-Re/Al}_2\text{O}_3$ are higher. The lithium promoted catalysts have the irreversible coke lower than their base catalyst. The high oxidation temperature zone of $\text{Pt/Al}_2\text{O}_3$, $\text{Pt-Sn/Al}_2\text{O}_3$, and $\text{Pt-Re/Al}_2\text{O}_3$ appear at about the same temperature around 450°C. The lithium promoted catalysts have the high oxidation temperature peak at around 400 C which are lower than their base catalysts.

The hydrogen to carbon atomic ratio of coked catalysts, which calculated by the moles of oxygen consumed and the moles of carbon dioxide produced (derived in Appendix A.4), are shown in Table 5.6.

From the H/C atomic ratio , the degree of graphitization of coked catalysts could be arranged in the following order :
 $\text{Pt-Sn/Al}_2\text{O}_3 > \text{Pt/Al}_2\text{O}_3 > \text{Pt-Re/Al}_2\text{O}_3 > \text{Pt-Sn-Li/Al}_2\text{O}_3 > \text{Pt-Re-Li/Al}_2\text{O}_3$.

In comparison to Pt/Al₂O₃, more irreversible coke is deposited on Pt-Sn/Al₂O₃ (lower H/C ratio), and more reversible coke is deposited on Pt-Re/Al₂O₃ (higher H/C ratio). The coke deposited on lithium promoted catalysts is more reversible than on their base catalysts.

Table 5.6 The hydrogen/carbon ratio of coke deposits on catalysts calculated by using results from TPO.

Catalyst	H/C Ratio of Coke
Pt/Al ₂ O ₃	0.12
Pt-Sn/Al ₂ O ₃	0.01
Pt-Re/Al ₂ O ₃	1.38
Pt-Sn-Li/Al ₂ O ₃	1.47
Pt-Re-Li/Al ₂ O ₃	2.41

Comparison of the H/C atomic ratio of coked catalysts to the H/C atomic ratio of various hydrocarbons (shown in Table 5.7), coke on Pt/Al₂O₃ and Pt-Sn/Al₂O₃ catalysts has the H/C ratio in the range of graphite to naphthalene. The coke on Pt-Re/Al₂O₃ and Pt-Sn-Li/Al₂O₃ has the H/C ratio in the range of the crude oil. The coke on Pt-Re-Li/Al₂O₃ has the H/C ratio in the range of paraffin to reformer combined feed.

Table 5.7 The hydrogen/carbon ratio of various hydrocarbons, petroleum cuts, coal liquids, and coals [50].

Compound	H/C atomic ratio
CH ₄	4.0
Paraffins	2.0
Naphthalene	0.8
Straight-run naphtha	1.9
Coal liquid naphtha	1.56
Crude oil	1.08 - 1.56
Syncrude	0.84 - 1.20
Coal	0.60 - 0.84
Reformer combined feed ^a	2.64 - 4.32

^aNaphtha + hydrogen with $3 < H_2/HC < 10$.

5.3.3 Determination of location of irreversible coke deposits on catalysts by regeneration method.

In this part, the Pt/Al₂O₃, Pt-Sn/Al₂O₃, and Pt-Sn-Li/Al₂O₃ catalysts were used for the propane dehydrogenation reaction for time on stream of 20 hours. The coked catalysts were regenerated by 1% O₂ in He gas mixture at 250 °C to oxidize the reversible coke. Then the regenerated catalyst was subjected to the reaction again to measure the effect of remained irreversible coke on propane conversion. Another catalyst was coked at the same condition but the coked catalyst was now regenerated at 500 °C to remove both of reversible and irreversible cokes, and put back on reaction stream. The difference of propane conversion between the

samples regenerated at 500°C and 250°C indicated the irreversible coke on metal site. The loss of metal active sites caused by platinum oxide formation were very small when compared to that caused by irreversible coke coverage on them and could be neglected (as shown in Appendix B).

The amounts of metal sites covered by irreversible coke deposition and the percentage coverage of the studied catalysts were calculated [APPENDIX A.5] and shown in Table 5.8-5.10.

Table 5.8 The amounts of metal sites covered by irreversible coke deposition and the percentage coverage of Pt/Al₂O₃ catalyst.

At 5 minutes of time on stream :

Initial conversion = 0.5675

Turn over number = 29.83 molecules/site-min.

Amounts of active site = 2.7641×10^{18} sites/g. cat.

Time on stream (min)	Δ conversion (500°C-250°C)	Amount of metal sites covered by coke deposition (sites)	Percentage coverage
5	0.1249	6.08×10^{17}	22.01
25	0.0462	2.25×10^{17}	8.14
45	0.0302	1.47×10^{17}	5.32
60	0.0261	1.27×10^{17}	4.60
120	0.0164	0.80×10^{17}	2.89

Table 5.9 The amounts of metal sites covered by irreversible coke deposition and the percentage coverage of Pt-Sn/Al₂O₃ catalyst.

At 5 minutes of time on stream :

Initial conversion = 1.35

Turn over number = 193.42 molecule/site-min.

Amounts of active site = 1.0140×10^{18} sites/g. cat.

Time on stream (min)	Δ conversion (500°C-250°C)	Amounts of metal sites covered by coke deposition (sites)	Percentage coverage
5	0.6750	5.07×10^{17}	50.00
25	0.1776	1.33×10^{17}	13.16
45	0.1144	8.59×10^{16}	8.47
60	0.0882	6.62×10^{16}	6.53
120	0.0616	4.63×10^{16}	4.56

Table 5.10 The amounts of metal sites covered by irreversible coke deposition and the percentage coverage of Pt-Sn-Li/Al₂O₃ catalyst.

At 5 minutes of time on stream :

Initial conversion = 2.32

Turn over number = 332.40 molecules/site-min.

Amounts of active site = 1.0645×10^{18} sites/g. cat.



Time on stream (min)	Δ conversion (500 °C-250 °C)	Amounts of metal sites covered by coke deposition (sites)	Percentage coverage
5	0.3480	1.52×10^{17}	14.29
25	0.0880	3.85×10^{16}	3.61
45	0.0639	2.79×10^{16}	2.62
60	0.0300	1.31×10^{16}	1.23
120	0.0348	1.52×10^{16}	1.43

The amounts of catalyst metal sites covered by coke deposition could be arranged in the following order :



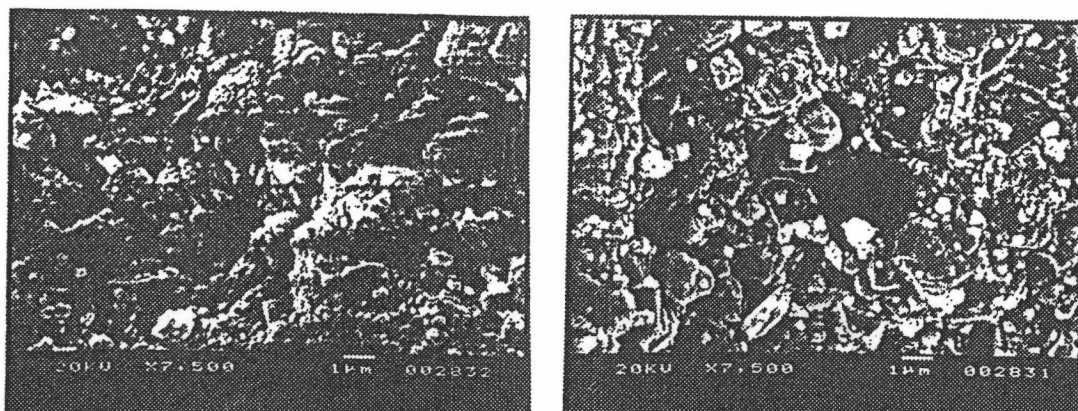
The percentage coverage could be arranged in the following order :



5.3.4 Scanning Electron Microscopy of Catalysts.

Scanning Electron Micrograph (SEM) of fresh catalysts and coked catalysts, after deactivation by propane dehydrogenation for 20 hours, are compared in Figure 5.7-5.12.

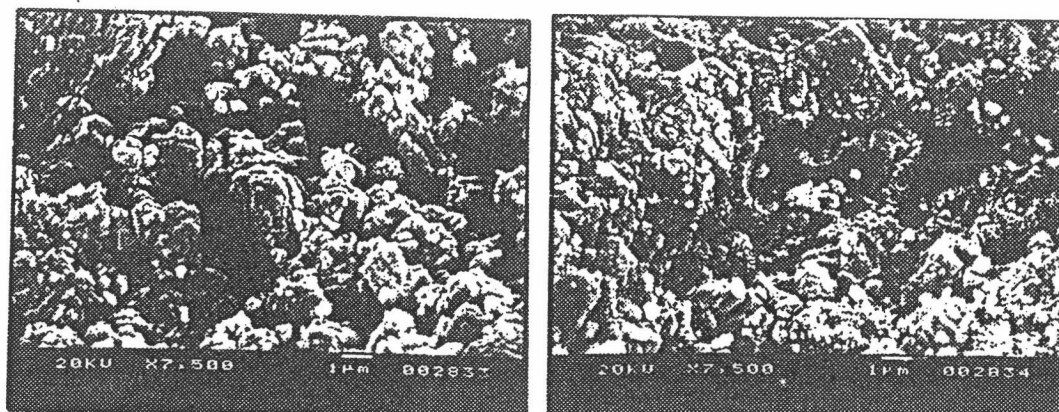
The fresh catalyst has clean crystalline structure. After 20 hours of time on stream, there are many small particles deposited on the surface of the catalysts.



(A)

(B)

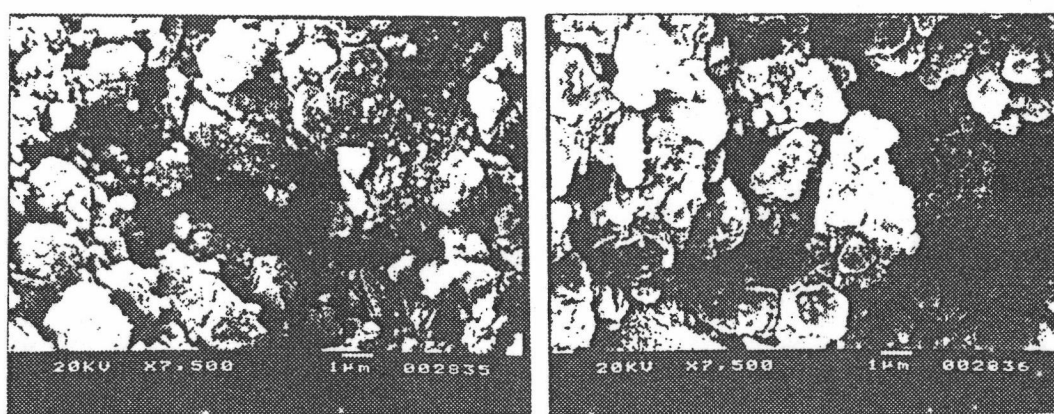
Figure 5.7 Scanning Electron Micrograph (SEM) of fresh Pt/Al₂O₃ catalyst (A) and coked Pt/Al₂O₃ catalyst (B).



(A)

(B)

Figure 5.8 Scanning Electron Micrograph (SEM) of fresh Pt-Sn/Al₂O₃ catalyst (A) and coked Pt-Sn/Al₂O₃ catalyst (B).



(A)

(B)

Figure 5.9 Scanning Electron Micrograph (SEM) of fresh Pt-Sn-Li/Al₂O₃ (A) catalyst and coked Pt-Sn-Li/Al₂O₃ (B) catalyst.