# CHAPTER V

## RESULTS AND DISCUSSION

In this research, the gas-phase dehydrogenation of propane was carried out in a fixed bed reactor. The results and discussion were categorized into four parts as follows.

Catalyst characterization.

Effect of catalyst composition.

Effect of reaction parameters.

Catalyst deactivation.

## Catalyst characterization

### 1. Determination of metal contents.

The metal content of catalysts were analyzed by Atomic Absorption (AA) and Inductively Coupled Plasma Emission Spectrometry (ICPS) methods described in chapter IV. The results were shown in Table 5.2. The amount of metal content of prepared catalysts were closed to their designed loading value.

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

| Catalyst | Metal Loading (%wt) | | | | |
|---|---|---|---|---|---|
| | Pt | Sn | Li | Na | K |
| Pt-Sn/Al$_2$O$_3$ | 0.3 | 0.3 | – | – | – |
| Pt-Sn-Li/Al$_2$O$_3$ | 0.3 | 0.3 | 0.6 | – | – |
| Pt-Sn-K/Al$_2$O$_3$ | 0.3 | 0.3 | – | – | 0.6 |
| Pt-Sn-Na/Al$_2$O$_3$ | 0.3 | 0.3 | – | 0.1 | – |
| Pt-Sn-Na/Al$_2$O$_3$ | 0.3 | 0.3 | – | 0.3 | – |
| Pt-Sn-Na/Al$_2$O$_3$ | 0.3 | 0.3 | – | 0.6 | – |
| Pt-Sn-Na/Al$_2$O$_3$ | 0.3 | 0.3 | – | 0.75 | – |
| Pt-Sn-Na/Al$_2$O$_3$ | 0.3 | 0.3 | – | 1.0 | – |

**Table** 5.2 The metal content of catalysts prepared in this rearch.

| Catalyst | Metal Loading (%wt) | | | | |
|---|---|---|---|---|---|
| | Pt* | Sn* | Li** | Na** | K** |
| Pt–Sn/Al$_2$O$_3$ | 0.304 | 0.292 | – | – | – |
| Pt–Sn–Li/Al$_2$O$_3$ | 0.299 | 0.266 | 0.528 | – | – |
| Pt–Sn–K/Al$_2$O$_3$ | 0.283 | 0.311 | – | – | 0.577 |
| Pt–Sn–Na/Al$_2$O$_3$ | 0.304 | 0.300 | – | 0.130 | – |
| Pt–Sn–Na/Al$_2$O$_3$ | 0.304 | 0.280 | – | 0.280 | – |
| Pt–Sn–Na/Al$_2$O$_3$ | 0.288 | 0.269 | – | 0.590 | – |
| Pt–Sn–Na/Al$_2$O$_3$ | 0.278 | 0.319 | – | 0.690 | – |
| Pt–Sn–Na/Al$_2$O$_3$ | 0.280 | 0.303 | – | 0.920 | – |

* measured by Inductively Coupled Plasma Emission Spectrometry.

** measured by Atomic Absorption

2. Determination of metal sites.

The metal sites of catalysts were measured by the CO adsorption method described previously in chapter 4. The results were shown in Table 5.3.

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

| Catalyst | Metal Active Sites (molecule of CO/grm of catalyst) |
|---|---|
| (0.3 wt%)Pt–(0.3 wt%)Sn/Al$_2$O$_3$ | $3.1695 \times 10^{18}$ |
| (0.3 wt%)Pt–(0.3 wt%)Sn–(0.6 wt%)Li/Al$_2$O$_3$ | $3.2580 \times 10^{18}$ |
| (0.3 wt%)Pt–(0.3 wt%)Sn–(0.6 wt%)Na/Al$_2$O$_3$ | $4.2598 \times 10^{18}$ |
| (0.3 wt%)Pt–(0.3 wt%)Sn–(0.6 wt%)K/Al$_2$O$_3$ | $4.1717 \times 10^{18}$ |
| (0.3 wt%)Pt–(0.3 wt%)Sn–(0.1 wt%)Na/Al$_2$O$_3$ | $3.6532 \times 10^{18}$ |
| (0.3 wt%)Pt–(0.3 wt%)Sn–(0.3 wt%)Na/Al$_2$O$_3$ | $3.6735 \times 10^{18}$ |
| (0.3 wt%)Pt–(0.3 wt%)Sn–(0.6 wt%)Na/Al$_2$O$_3$ | $4.2598 \times 10^{18}$ |
| (0.3 wt%)Pt–(0.3 wt%)Sn–(0.75 wt%)Na/Al$_2$O$_3$ | $4.0220 \times 10^{18}$ |
| (0.3 wt%)Pt–(0.3 wt%)Sn–(1.0 wt%)Na/Al$_2$O$_3$ | $3.9947 \times 10^{18}$ |

3. Determination of BET suface area.

The BET surface area of catalysts were measured by the method described in chapter 4 section 3. The results are shown in Table 5.4 compared to the alumina support . The modified catalysts had the surface area of about 300 $m^2$/g.

**Table 5.4** The BET surface area of catalysts.

| Catalyst | Surface Area ($m^2$/gm) |
|---|---|
| Alumina Support | 315.90 |
| (0.3 wt%)Pt-(0.3 wt%)Sn/$Al_2O_3$ | 320.19 |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6 wt%)Li/$Al_2O_3$ | 248.17 |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6 wt%)Na/$Al_2O_3$ | 288.78 |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6 wt%)K/$Al_2O_3$ | 303.72 |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.1 wt%)Na/$Al_2O_3$ | 319.87 |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.3 wt%)Na/$Al_2O_3$ | 291.58 |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6 wt%)Na/$Al_2O_3$ | 288.78 |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.75 wt%)Na/$Al_2O_3$ | 273.39 |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(1.0 wt%)Na/$Al_2O_3$ | 265.76 |

4. Electrical Conductivity Measurement .

The global conductivity of catalysts were measured by the method described in chapter 4. The results are shown in Table 5.5

**Table 5.5** The Electrical Conductivity of catalysts

| Catalyst | Conductivity ( $ohm^{-1}$ $cm^{-1}$) |
|---|---|
| $Al_2O_3$ | $2.15 \times 10^{-6}$ |
| (0.6 wt%)Li/$Al_2O_3$ | $5.58 \times 10^{-6}$ |
| (0.6 wt%)Na/$Al_2O_3$ | $5.23 \times 10^{-6}$ |
| (0.6 wt%)K/$Al_2O_3$ | $4.04 \times 10^{-6}$ |
| (0.3 wt%)Pt-(0.3 wt%)Sn/$Al_2O_3$ | $12.40 \times 10^{-6}$ |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6 wt%)Li/$Al_2O_3$ | $21.80 \times 10^{-6}$ |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6 wt%)Na/$Al_2O_3$ | $74.70 \times 10^{-6}$ |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6 wt%)K/$Al_2O_3$ | $26.60 \times 10^{-6}$ |

**Table 5.5** (Continued)

| Catalyst | Conductivity ( $ohm^{-1}$ $cm^{-1}$) |
|---|---|
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.1 wt%)Na/Al$_2$O$_3$ | 46.70 x 10$^{-6}$ |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.3 wt%)Na/Al$_2$O$_3$ | 49.70 x 10$^{-6}$ |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.75 wt%)Na/Al$_2$O$_3$ | 50.90 x 10$^{-6}$ |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(1.0 wt%)Na/Al$_2$O$_3$ | 49.90 x 10$^{-6}$ |

In this research, propane dehydrogenation reaction was performed at the temperature of 600 °C which was used in the commercial process. And H$_2$ /HC ratio = 1.0 was used for supressed coke deposition without compromising its performance.

Effect of catalyst composition.

1. Effect of alkali metal addition as promoter.

Dehydrogenation species were produced by a metal in bi- or multimetallic catalysts. Because the thermodynamics of the dehydrogenation reaction was desirable to work at high temperature and low pressure, these are the conditions that also favor coke formation. So there is an attemp to use bi-or multimetallic catalysts supported on alumina to suppress coke formation which promoted conversion and propylene selectivity. Supported platinum was well-known catalyst. The addition of a a second metal such as tin improved the activity and selectivity of catalysts and of the alkali not only reduced the catalysts acidity or suppressed carbonaceous deposits but also increased the activity of the catalysts. The results shown in Figure 5.1 indicate that the Pt-Sn base catalyst exhibited the lowest Yield Per Pass (YPP) whereas addition of Li, K or Na would increase YPP of catalysts, respectively. This could be explained in terms of metal active sites as shown in Table 5.3 , i.e. the number of active sites expressing the catalyst activity falled in the following order: Na>K>Li>Pt-Sn based catalyst. These results back up to the improved YPP of catalyst.

In previous works, the addition of alkali metal reduced the catalyst acidity, thus inhibiting coke formation [19,54,55]. Furthermore the addition of alkali metal actually increased the activity (YPP of catalyst) of catalyst by increasing conductivity
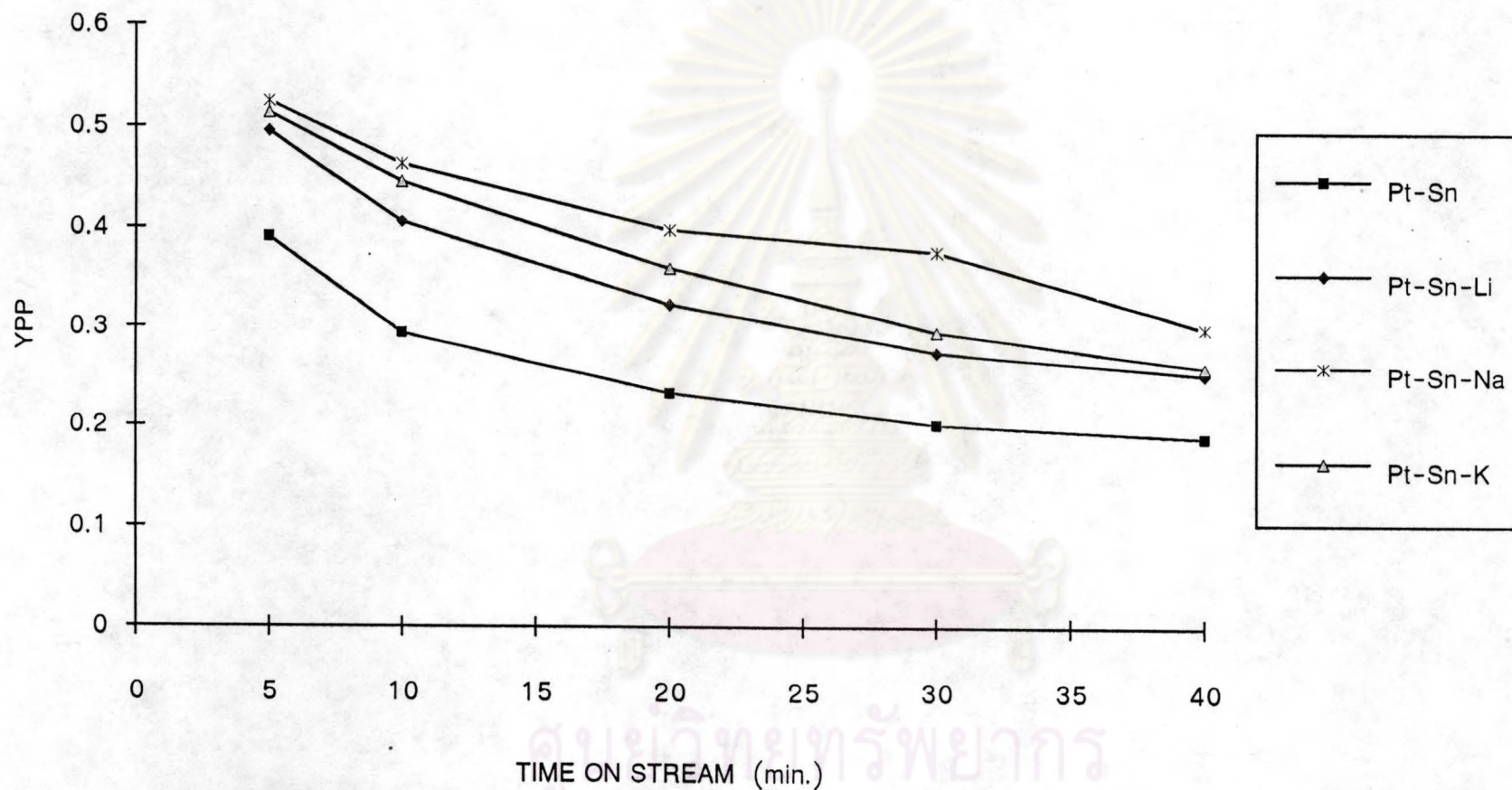
**Figure 5.1** YPP of catalyst VS. Time on stream (min.)

Catalyst : (0.3 wt%) Pt-(0.3 wt %)Sn/Al$_2$O$_3$ Third Metal : Li, Na, and K, Temperature : 600 $^\circ$C,

GHSV = 22,525 hr$^{-1}$, weight of catalyst : 0.1 gram, Feed = H$_2$ +20% propane in N$_2$ , H$_2$:HC ratio = 1.0

from $12.40 \times 10^{-6}$ to $21.80\text{-}74.70 \times 10^{-6}$ which could convert to free electron as shown in Table 5.6 resulting in eletron-rich Pt sites. Alkali metal addition increased activity thus resulting in higher YPP. For % increased YPP was much more than % increased active site since the free electron value improved strength of active sites as shown in Table 5.7. When propane was adsorbed on these electron-rich Pt sites, the stronger Pt-H interaction the weaker and more easily broken the C-H bond to form propylene products compared to the unpromoted base catalyst. The dehydrogenation activity of these catalysts was then higher than activity of Pt-Sn/$Al_2O_3$ catalyst containing alkali metal which served as an electron donor to Pt [56], thus inducing the hydrogen spill-over. Therefore, the continuous coke precursor hydrogenation caused by spill-over hydrogen. Moreover, the amount of coke deposit was lower than that of Pt-Sn/$Al_2O_3$ catalyst. These are illustrated in Figure 5.2 which shows the amount of coke and decreasing graphitic coke because the H/C ratio increased from 0.36, 0.48, 0.53 and 0.59 of Pt-Sn based catalyst, Li, K and Na, respectively.

**Table 5.6** Free electron of catalysts.

| Sample | Free electron ( $ohm^{-1}$ $cm^{-1}$) |
|---|---|
| (0.3 wt%)Pt-(0.3 wt%)Sn/$Al_2O_3$ | - |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6 wt%)Li/$Al_2O_3$ | $1.64 \times 10^{-6}$ |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6 wt%)Na/$Al_2O_3$ | $54.90 \times 10^{-6}$ |
| (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6 wt%)K/$Al_2O_3$ | $8.02 \times 10^{-6}$ |

**Table 5.7** % Improved YPP of catalysts by increasing active sites and increasing free electron. (alkali metal group)

| Sample | % improved YPP | % improved active site | % the rest | free e⁻ ( $ohm^{-1}cm^{-1}$) |
|---|---|---|---|---|
| Pt-Sn-Li | 21.52 | 7.48 | 14.04 | $1.64 \times 10^{-6}$ |
| Pt-Sn-Na | 34.71 | 16.20 | 18.51 | $54.90 \times 10^{-6}$ |
| Pt-Sn-K | 31.04 | 14.44 | 16.60 | $8.02 \times 10^{-6}$ |
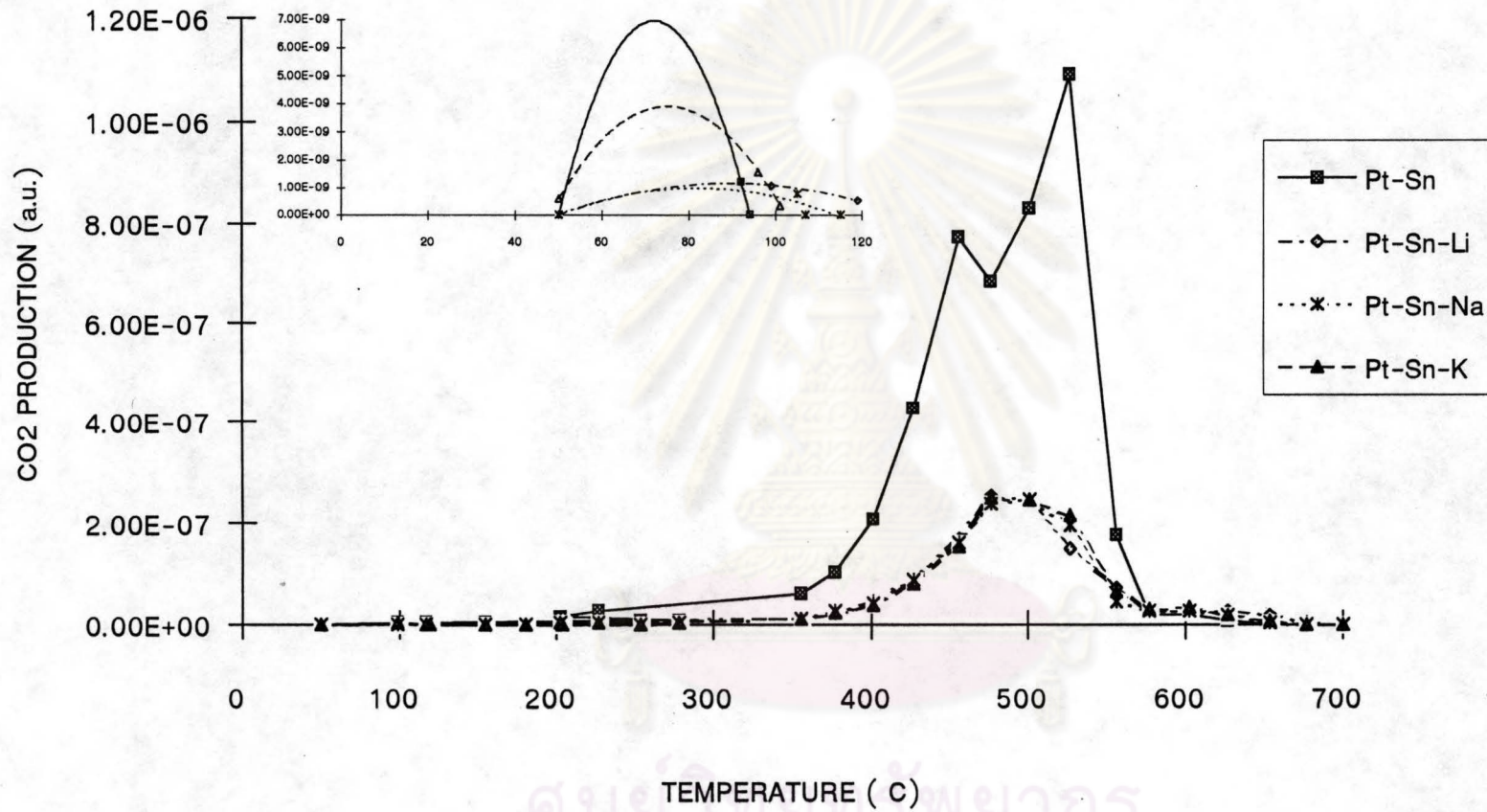
**Figure 5.2** Temperature Programmed Oxidation of various coke catalysts

## 2. Effect of Alkali Metal Loading

Performance of noble metallic catalysts can be increased by using metal additives commonly called "promoter" ,which leading to an increase in the alkali metal loading. Figure 5.3 shows various Na to Pt ratio versus YPP at 5 minutes of time on stream. The optimum loading obtained was found to be 2.0. This might possibly be implied that the active sites were increased until the optimum Na/Pt ratio was reached then the curve declined. It was suggested that Pt was hindered by Na additives which could be affirmed by the reduction the active sites of Pt-Na/Al$_2$O$_3$ ($1.8 \times 10^{18}$ molecule of CO/grm of catalyst).

## Effect of Reaction Parameters.

In this part of experiment, the effect of temperature was studied with the temperature ranging from 500 °C to 650 °C at space velocity of 22,525 hr$^{-1}$. The results are shown in Figure 5.4. The catalysts used including 0.3, 0.3 and 0.6 weight percent of platinum, tin and sodium on alumina support ,respectively.

The temperature dependence on propane conversion is depicted in Figure 5.5. An Increase in the temperature resulted in higher conversion according to the thermodynamics point of view, dehydrogenation reaction is an reversible endothermic reaction. Then increasing the temperature leaded to an increase in the reaction but propylene selectivity as shown in Figure 5.6 was decreased, light gases (composing one or two carbon atoms) were increase that is due to the increasing effect of hydrogenolysis and thermal cracking reaction as shown in Figure 5.7 and Figure 5.8.

However, the propane dehydrogenation reaction displayed the highest ypp of reaction temperature at 600 °C as illustrated in Figure 5.4.
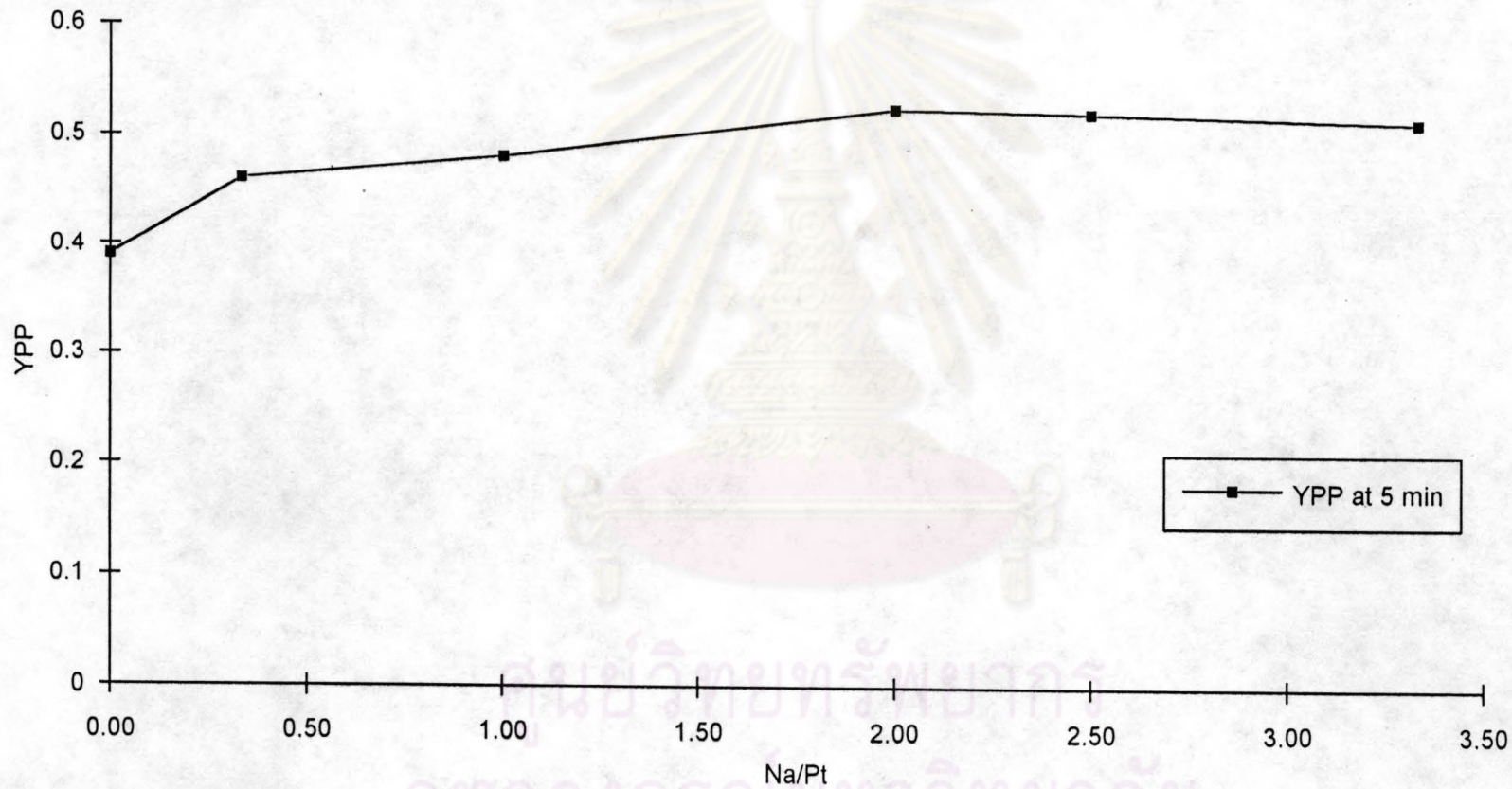
**Figure 5.3** YPP of catalyst VS. Na/Pt ratio

Catalyst : $(0.3\ wt\%)Pt-(0.3\ wt\%)Sn-(0.6\ wt\%)Na/Al_2O_3$  Alkali metal loading : 0.1-1.0 wt%, Temperature : 600 $^{\circ}$C, GHSV = 22,525 $hr^{-1}$, weight of catalyst : 0.1 gram, Feed = $H_2$ +20% propane in $N_2$ , $H_2$:HC ratio = 1.0
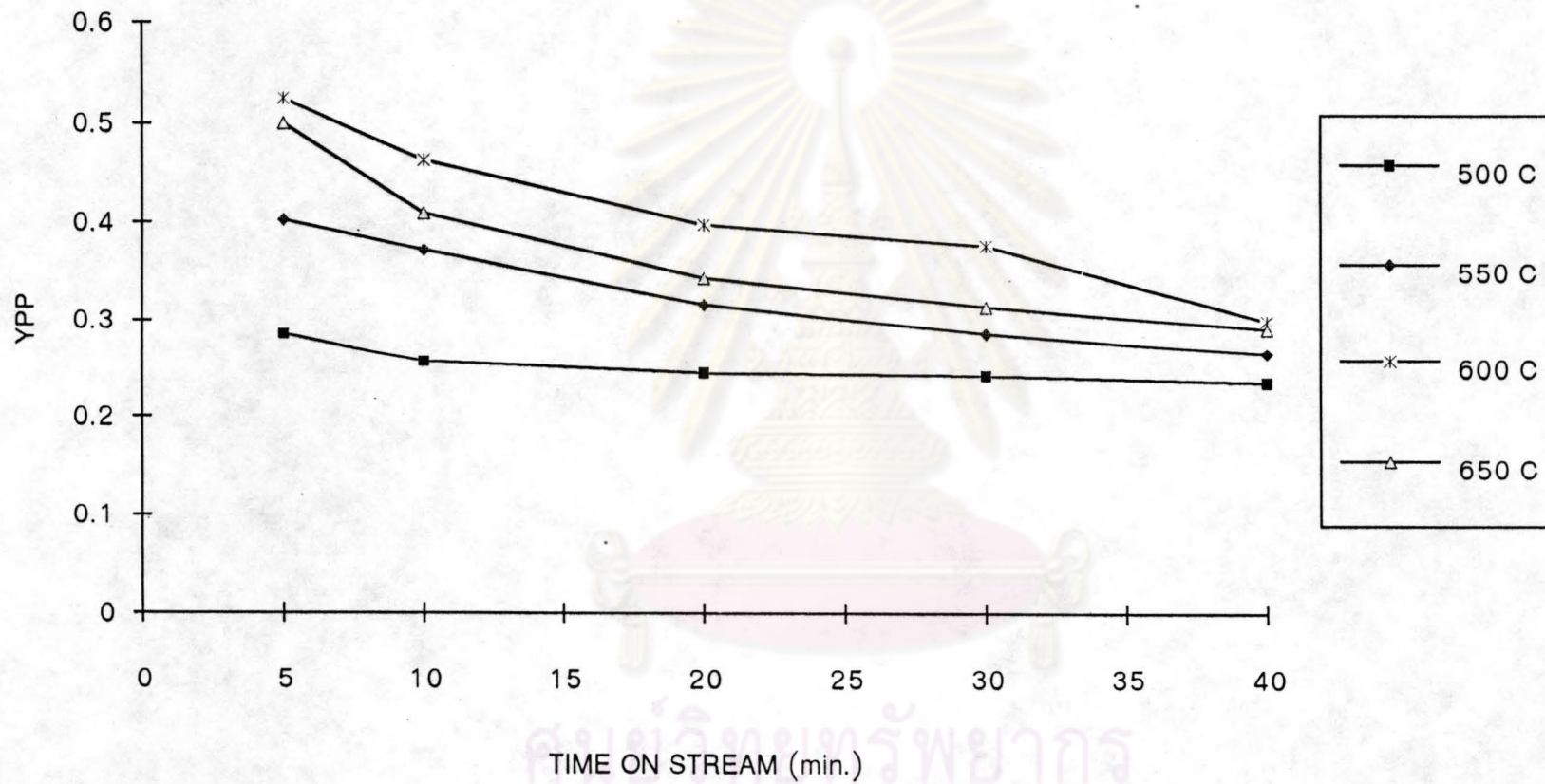
**Figure 5.4** YPP of catalyst VS. Time on stream (min.)

Catalyst : (0.3 wt%) Pt-(0.3 wt %)Sn-(0.6 wt%)Na/Al$_2$O$_3$ Temperature : 500-650 $^\circ$C, GHSV = 22,525 hr$^{-1}$, weight of catalyst : 0.1 gram, Feed = H$_2$ +20% propane in N$_2$ , H$_2$:HC ratio = 1.0
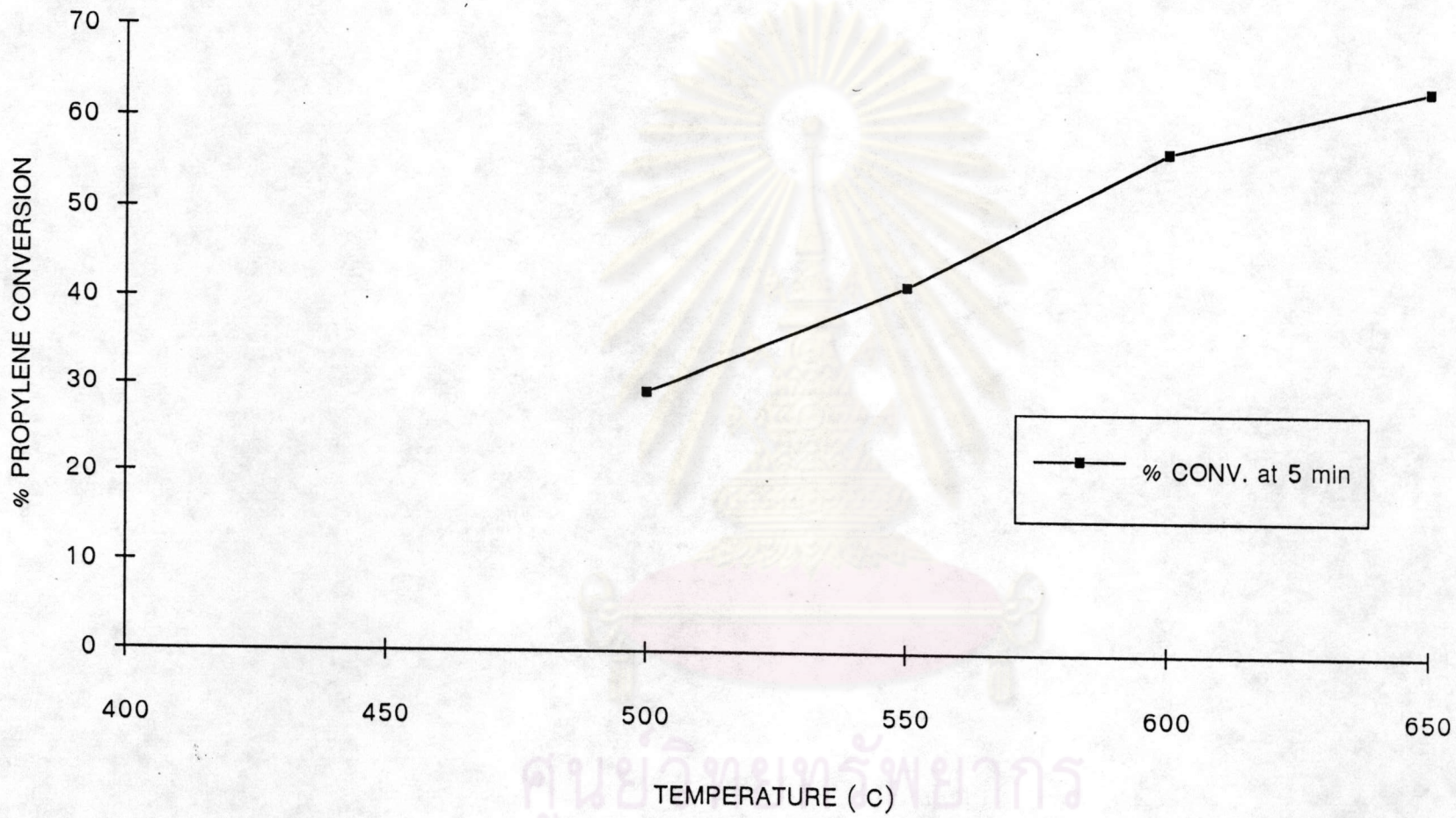
**Figure 5.5** % propane conversion VS. Temperature
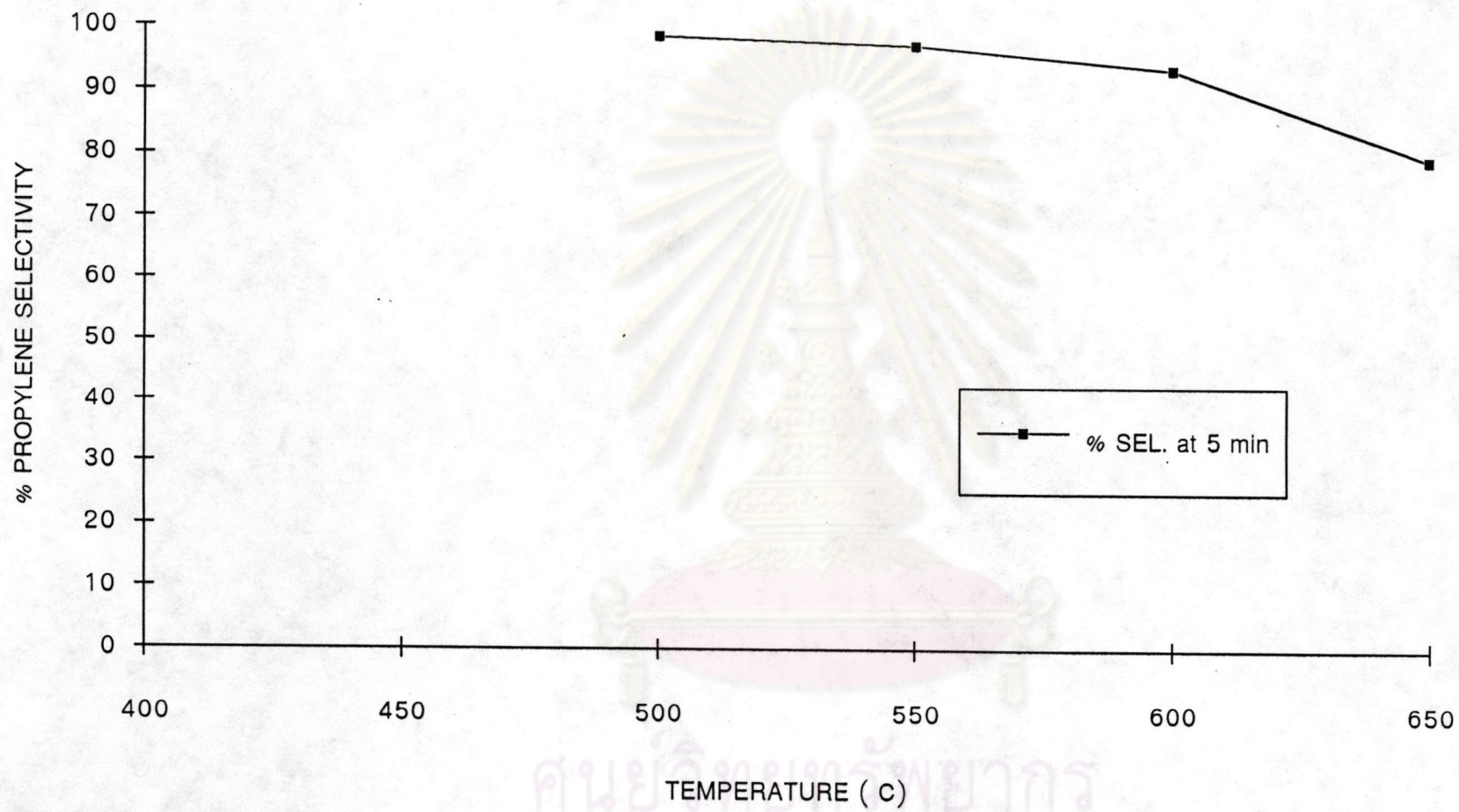
**Figure 5.6** % Propylene selectivity VS. Temperature
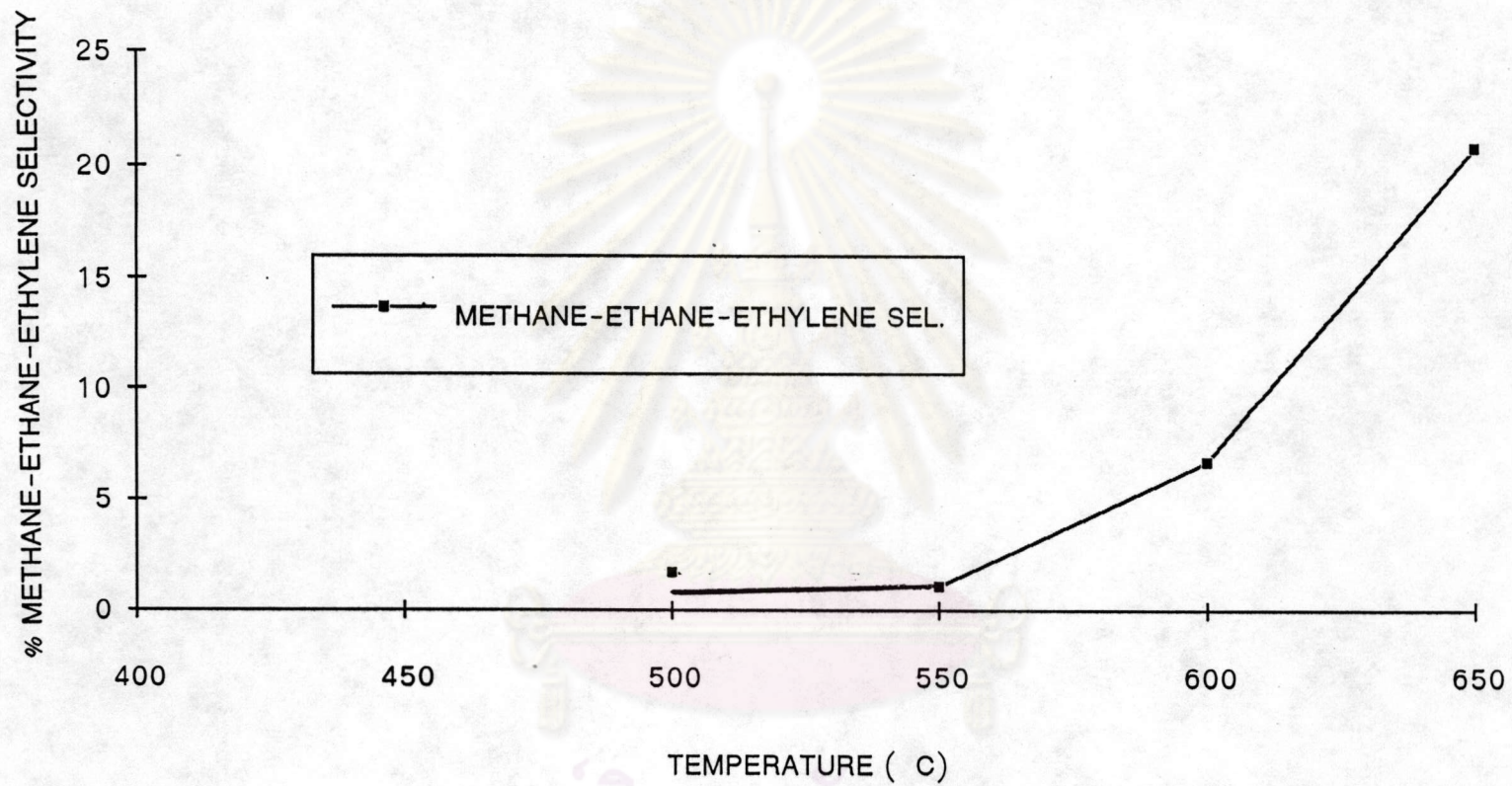
**Figure 5.7** % Methane, Ethane-Ethylene selectivity VS. Temperature
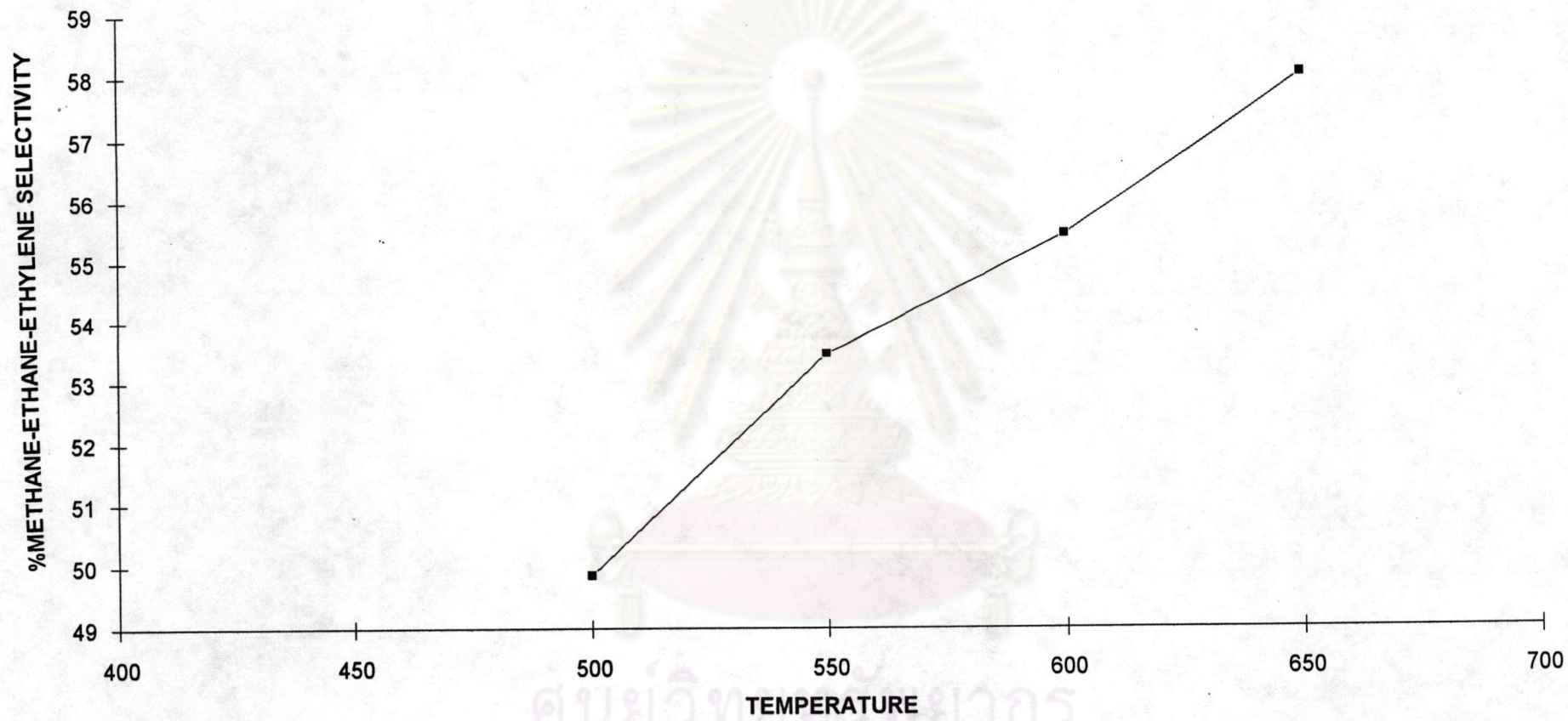
**Figure 5.8** % Methane, Ethane-Ethylene selectivity (Alumina) VS. Temperature.

Catalyst Deactivation

Coke formation was an undersible side effect of many chemical operations because it leaded to costly decoking steps, reduced efficiency of operation, and increases rate of metal corrosion. There is, therefore, a tremendous incentive to decrease the rate of catalyst coking or at least better understand the phenomena of coke deposition. The first aim was mentioned above (see effect of catalyst composition). Understanding phenomena of coke deposition was suggested as follow.

1. Scanning Electron Microscopy of Catalysts.

Scanning Electron Micrograph (SEM) of fresh and coked catalysts ,after deactivation by propane dehydrogenation for 40 min. 600 $^\circ$C, are compared in Figures 5.9-5.13. The fresh catalyst was clean crystalline structure. After 40 min. of time on stream, there are many small particles deposited on the surface of catalysts but fresh and spent alumina have clean support.
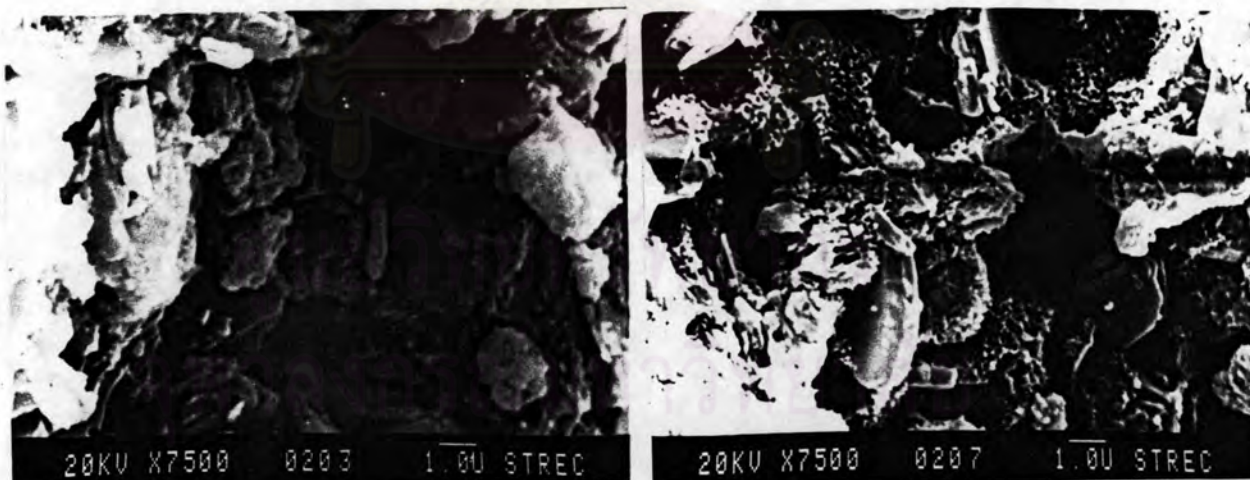


(A)　　　　　　　　　　　　　　　　(B)

**Figure 5.9** Scanning Electron Micrograph (SEM)

(A) Fresh alumina and (B) Spent alumina

(A)

(B)
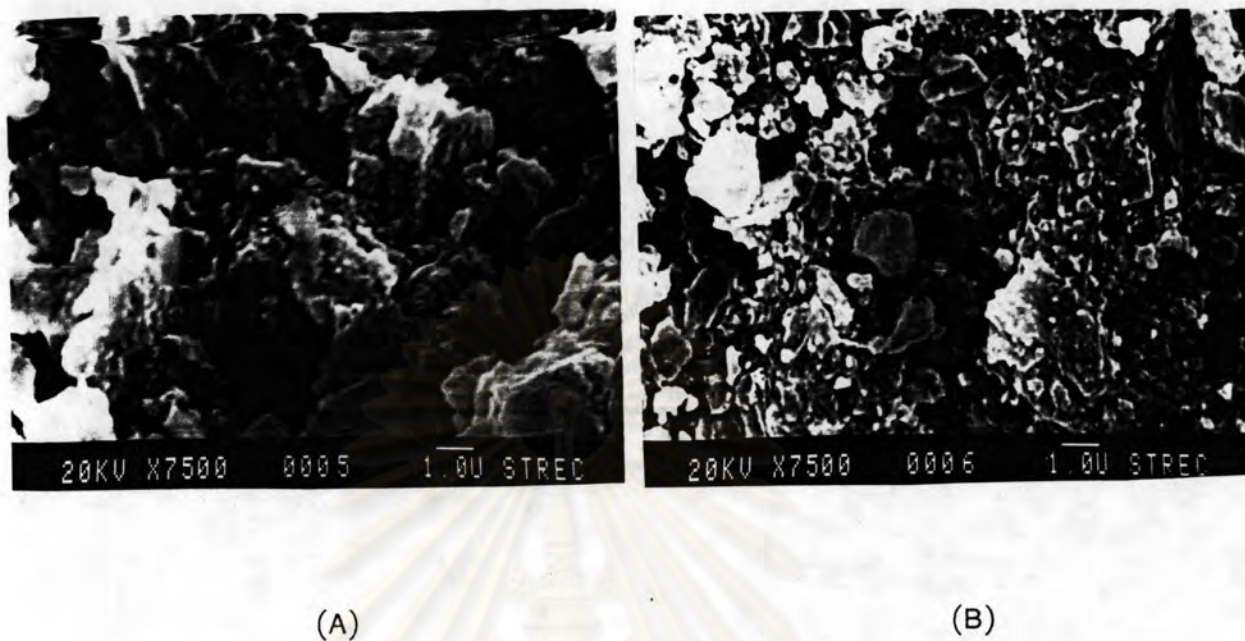
**Figure 5.10** Scanning Electron Micrograph (SEM) of Pt-Sn catalyst

(A) Fresh catalyst and (B) Coked catalyst



(A)

(B)

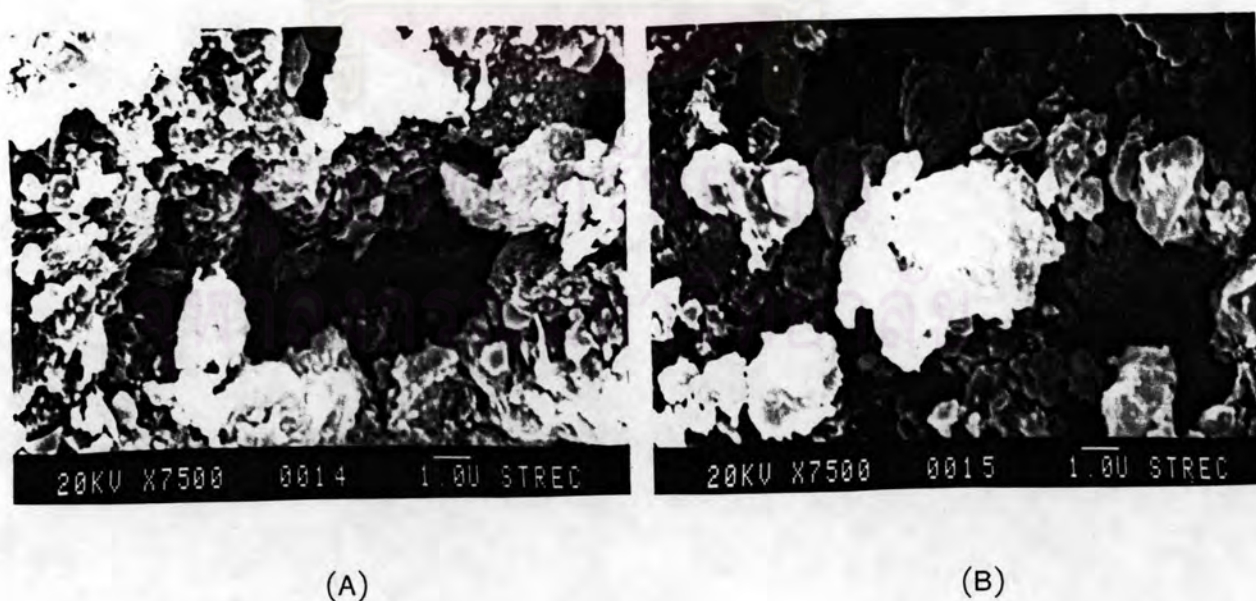**Figure 5.11** Scanning Electron Micrograph (SEM) of Pt-Sn-Li catalyst
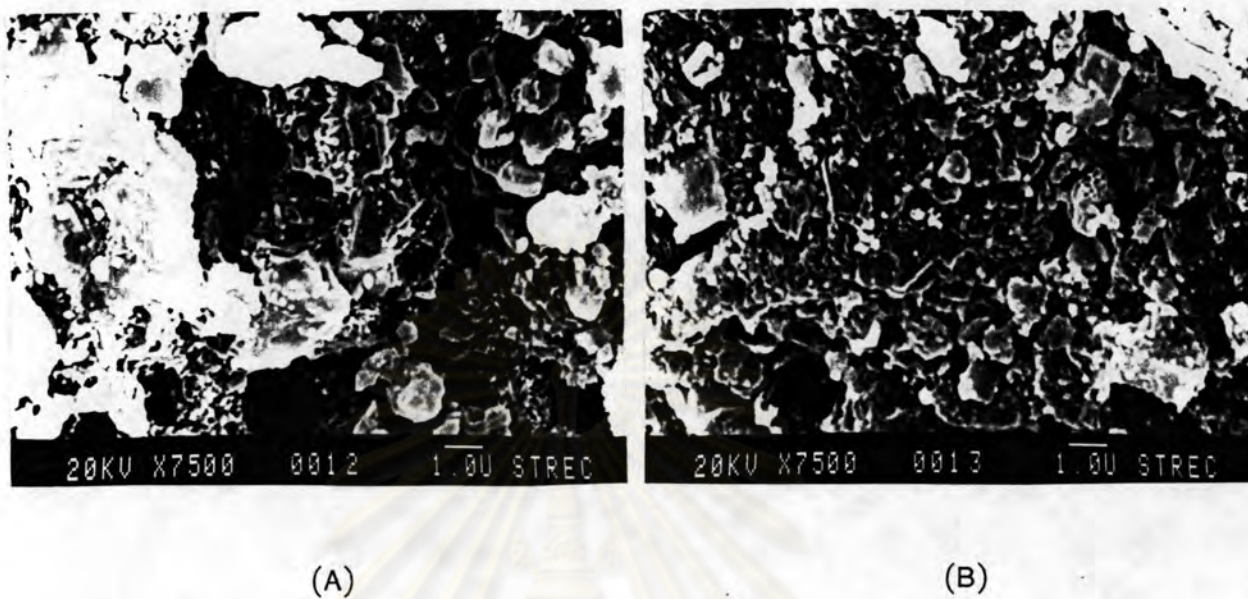
(A) Fresh catalyst and (B) Coked catalyst

(A)                                                    (B)

**Figure 5.12** Scanning Electron Micrograph (SEM) of Pt–Sn–Na catalyst
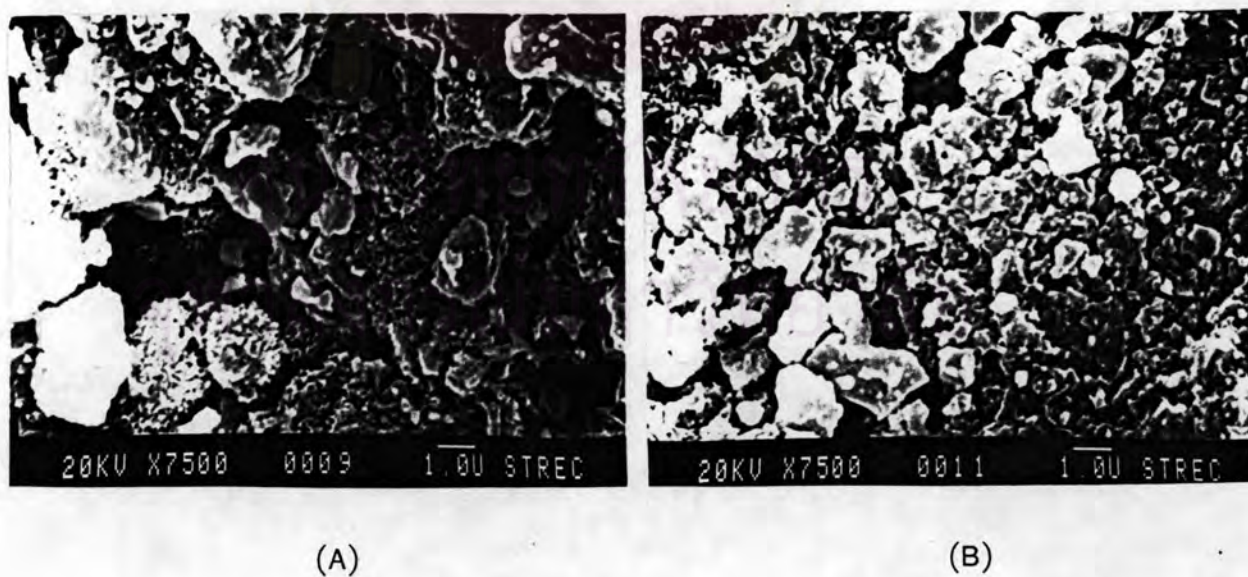
(A) Fresh catalyst and  (B)  Coked catalyst



(A)                                                    (B)

**Figure 5.13** Scanning Electron Micrograph (SEM) of Pt–Sn–K catalyst

(A) Fresh catalyst and  (B)  Coked catalyst

2. Coked catalyst characterization

Temperature programmed oxidation (TPO) was used to determine the amount of coke formation in propane dehydrogenation. Gas chromatograph was used to measure the amount of $CO_2$ produced from coke combusion (by setting programmed rate heating) which indicated the total amount of coke. In previous work, coke that could be easily oxidized was found at metal site was referred to as reversible coke whereas one that could be hardly oxidized was found at support was called irreversible coke [7,8]. However, in commercial process, the long term deactivation of catalysts caused by irreversible coke had the effect on productivity and also profit. Thus the improvement of catalyst performance and the change of coke formation characteristics might be understand. This research developed the new method which could determine not only the amount of coke as measure by TPO but also it indicated coke covered on metal active site which was to elucidate how the coke deposition behavior covered the metal active site.

Such result are shown in Figures 5.14-5.18. At the reaction temperature of 500 $^{o}$C, it was found that total, reversible and irreversible coke deposition on the metal active sites are represented as %TC, %IRC, and %RC (APPENDIX B.1) as illustrated in Figure 5.15. Initially, %TC and %IRC increased linearly with time on stream, whereas, %RC slightly decreased, yet, higher than %IRC in the first 30 min. Once the steady state was reached (about 1 hours), three types of coke deposition approached the constant value as follows: %TC = 47.01, %IRC = 42.00, and %RC = 5.00. At reaction temperatures between 480-520 $^{o}$C, the phenomenon of coke deposition on metal active site was similar to that of 500 $^{o}$C but the amounts of %TC and %IRC were totally different. This indicated that increasing reaction temperatures between 480-520 $^{o}$C would lead to higher %TC and %IRC as shown in Figures 5.19,20 respectively. At 600 $^{o}$C, however, %IRC, and %TC are higher than %RC throughout-time on stream. Like the earlier temperature, all 3 values converted after 1 hr. For every temperature total amount of coke , irreversible coke and reversible coke deposited on the metal active sites were found to asymtote in a certain value inidicating the equilibrium between irreversible coke and reversible coke which deposited on the metal active sites. Furthermore during the equilibrium, no matter what temperature it was, the coverage of total coke on the metal site was not throughly complete.
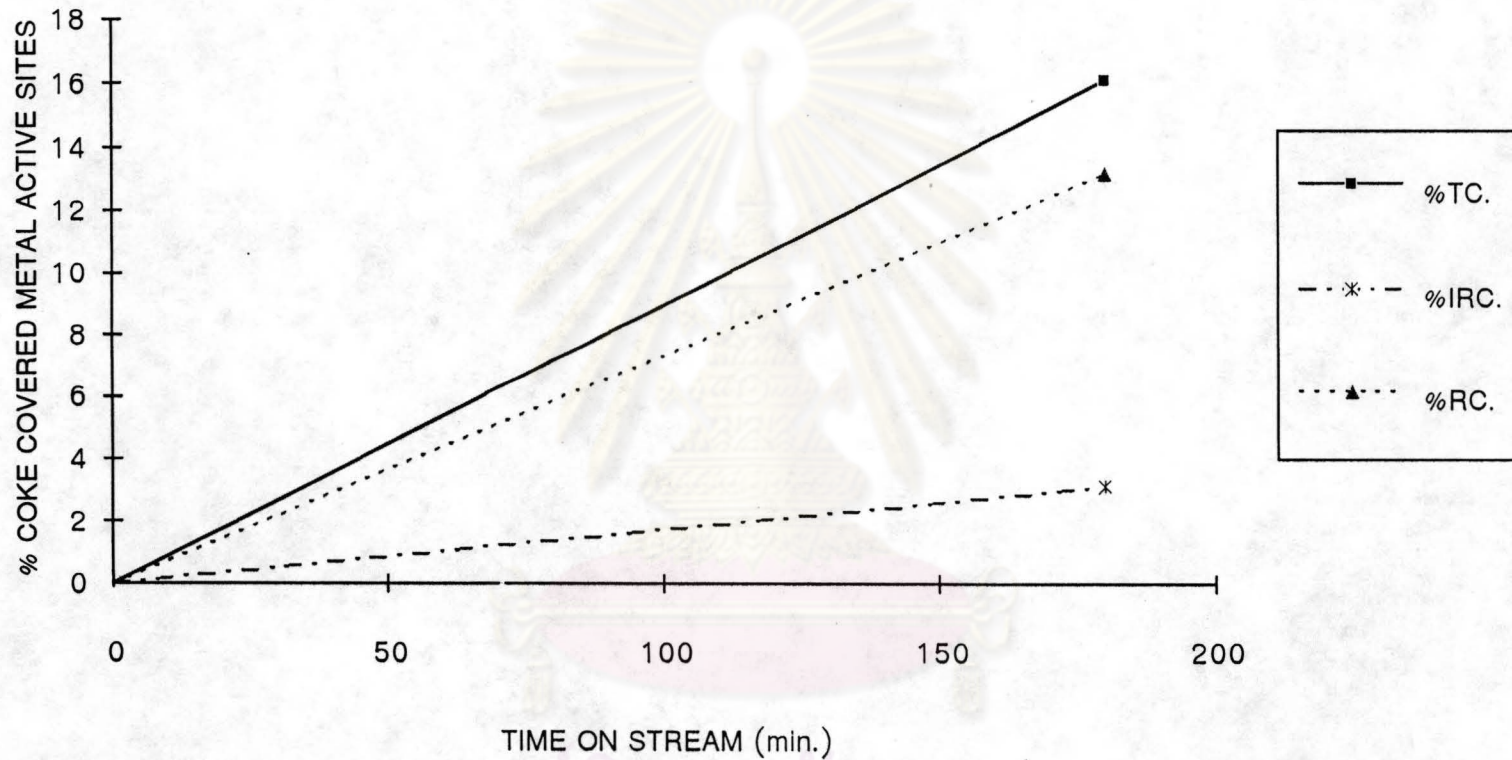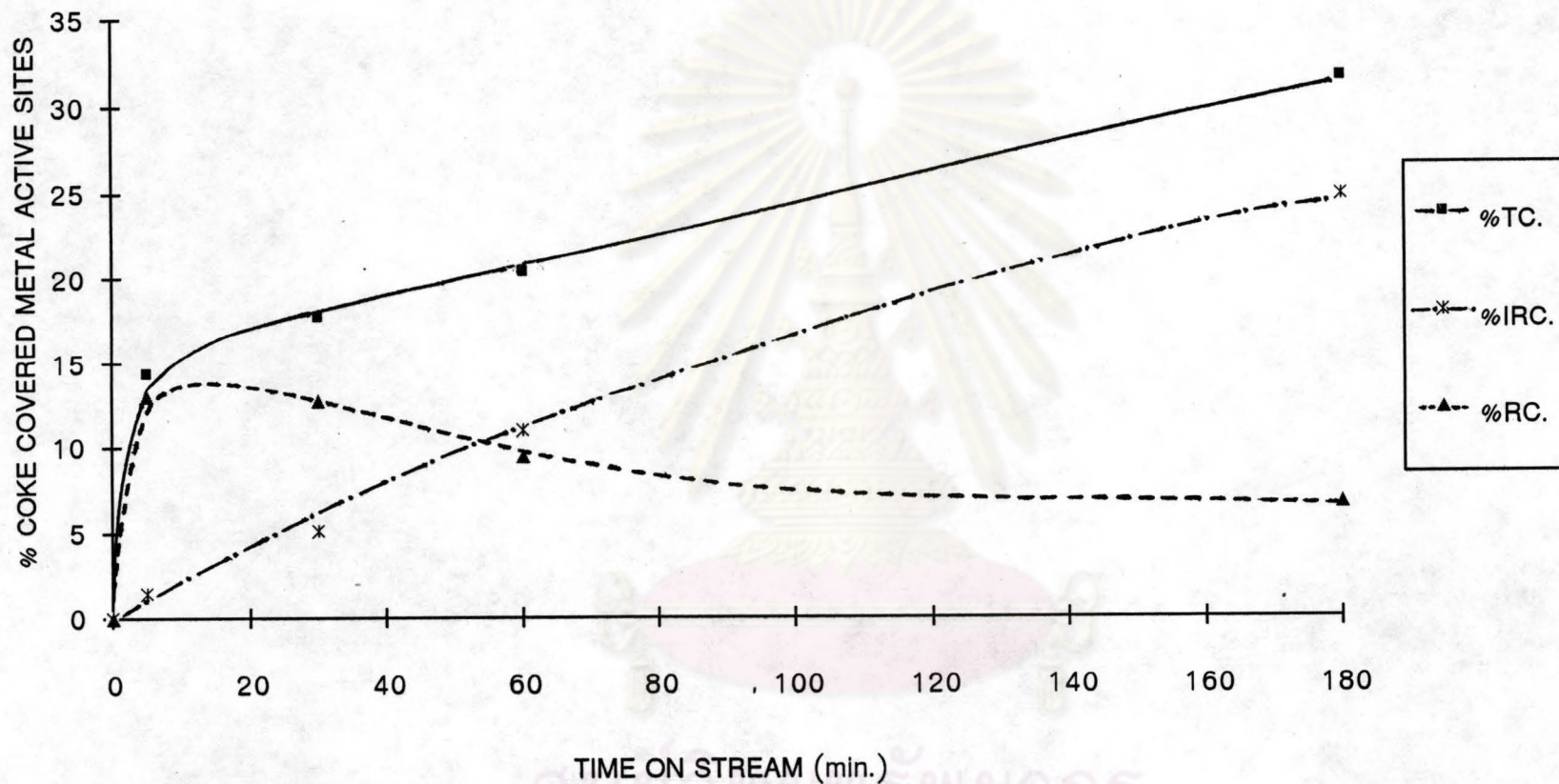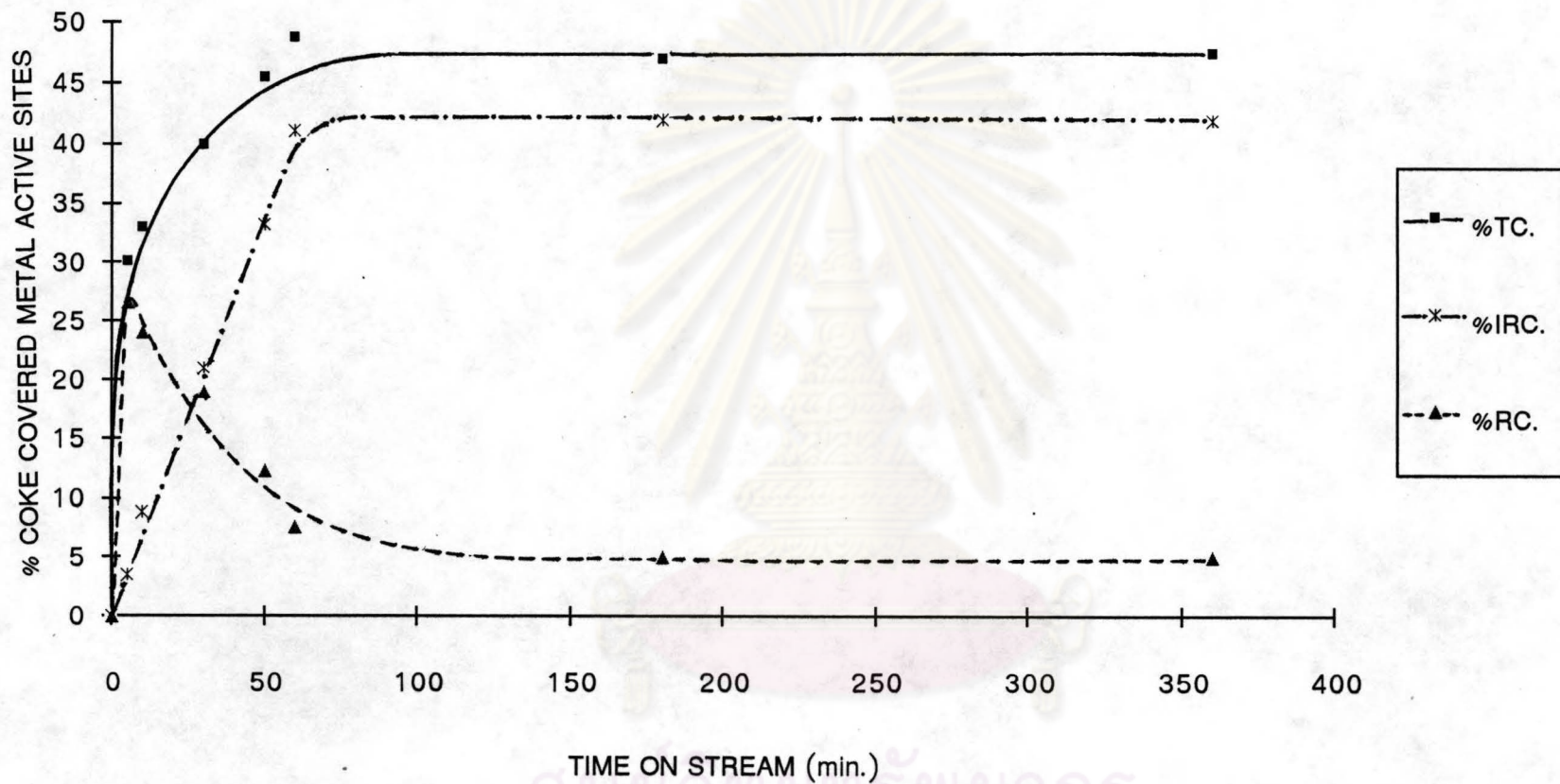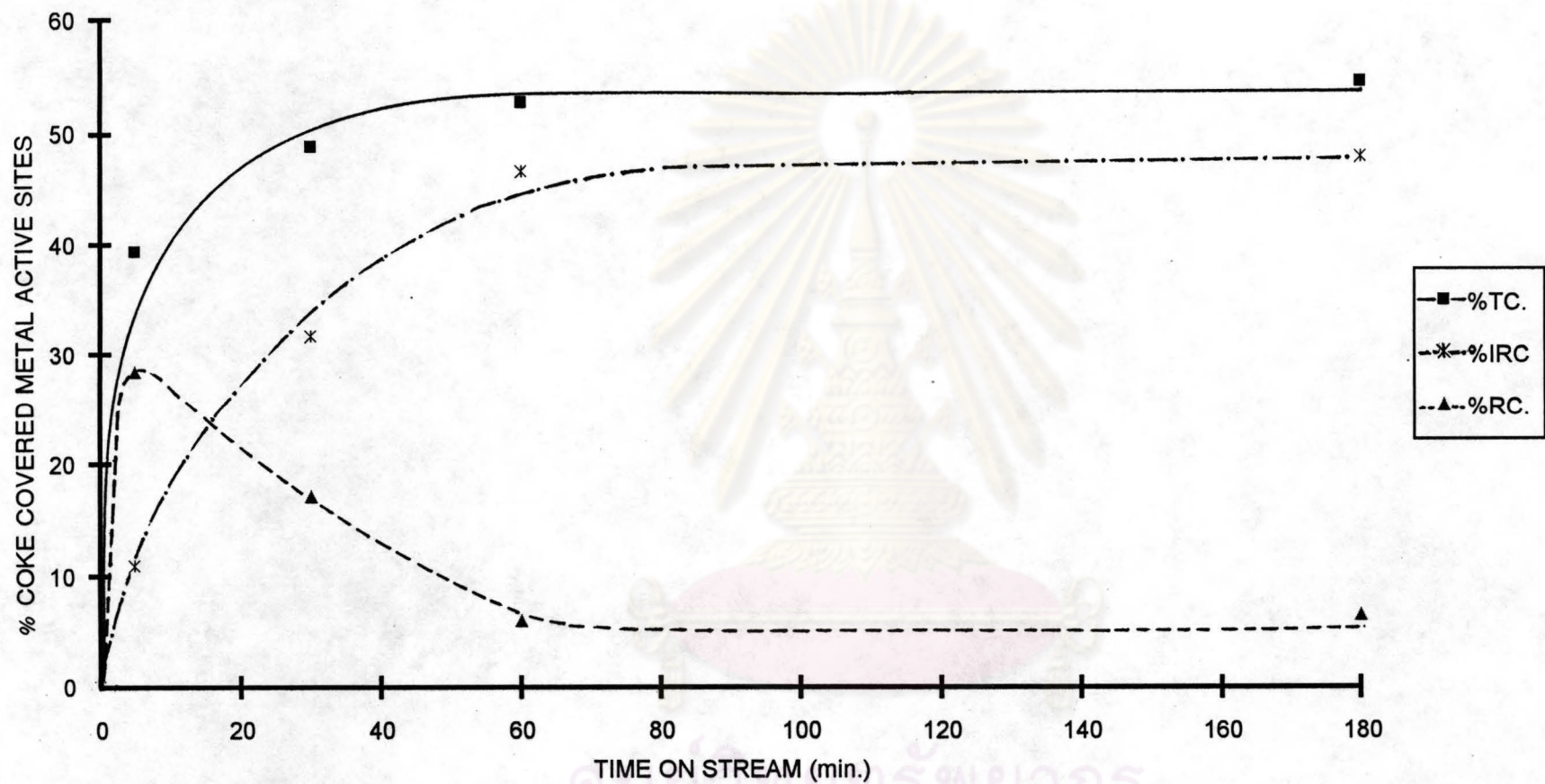
**Figure 5.14** % Coke covered metal active site VS. Time on stream (min.)

Catalyst : (0.3 wt%) Pt-(0.3 wt %)Sn-(0.6 wt%)Na/Al$_2$O$_3$,

Temperature : 460 $^{\circ}$C, Feed = H$_2$+20% propane in N$_2$, H$_2$:HC ratio=1.0

**Figure 5.15** % Coke covered metal active site VS. Time on stream (min.)

Catalyst : $(0.3 \text{ wt\%})$ Pt-$(0.3 \text{ wt \%})$Sn-$(0.6 \text{ wt\%})$Na/Al$_2$O$_3$,

Temperature : 480 $^{\circ}$C,Feed = H$_2$+20% propane in N$_2$, H$_2$:HC ratio=1.0
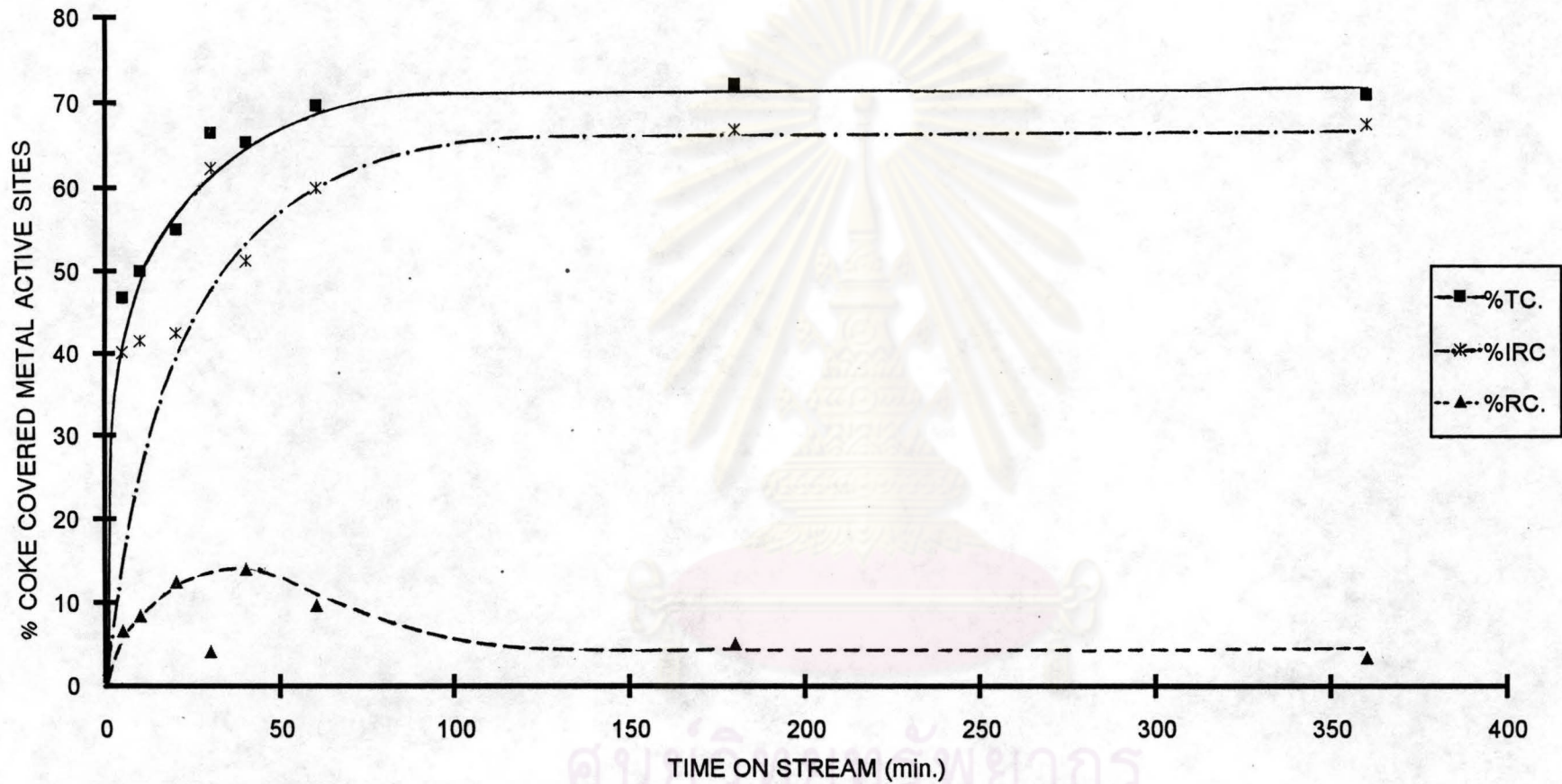
70

**Figure 5.16** % Coke covered metal active site VS. Time on stream (min.)

Catalyst : (0.3 wt%) Pt-(0.3 wt %)Sn-(0.6 wt%)Na/Al$_2$O$_3$,

Temperature : 500 $^{\circ}$C,Feed = H$_2$+20% propane in N$_2$, H$_2$:HC ratio=1.0

71

**Figure 5.17** % Coke covered metal active site VS. Time on stream (min.)

Catalyst : (0.3 wt%) Pt-(0.3 wt %)Sn-(0.6 wt%)Na/Al$_2$O$_3$,

Temperature : 520 $^\circ$C,Feed = H$_2$+20% propane in N$_2$, H$_2$:HC ratio=1.0

**Figure 5.18** % Coke covered metal active site VS. Time on stream (min.)

Catalyst : (0.3 wt%) Pt-(0.3 wt %)Sn-(0.6 wt%)Na/$Al_2O_3$,

Temperature : 600 $^{\circ}$C,Feed = $H_2$+20% propane in $N_2$, $H_2$:HC ratio=1.0
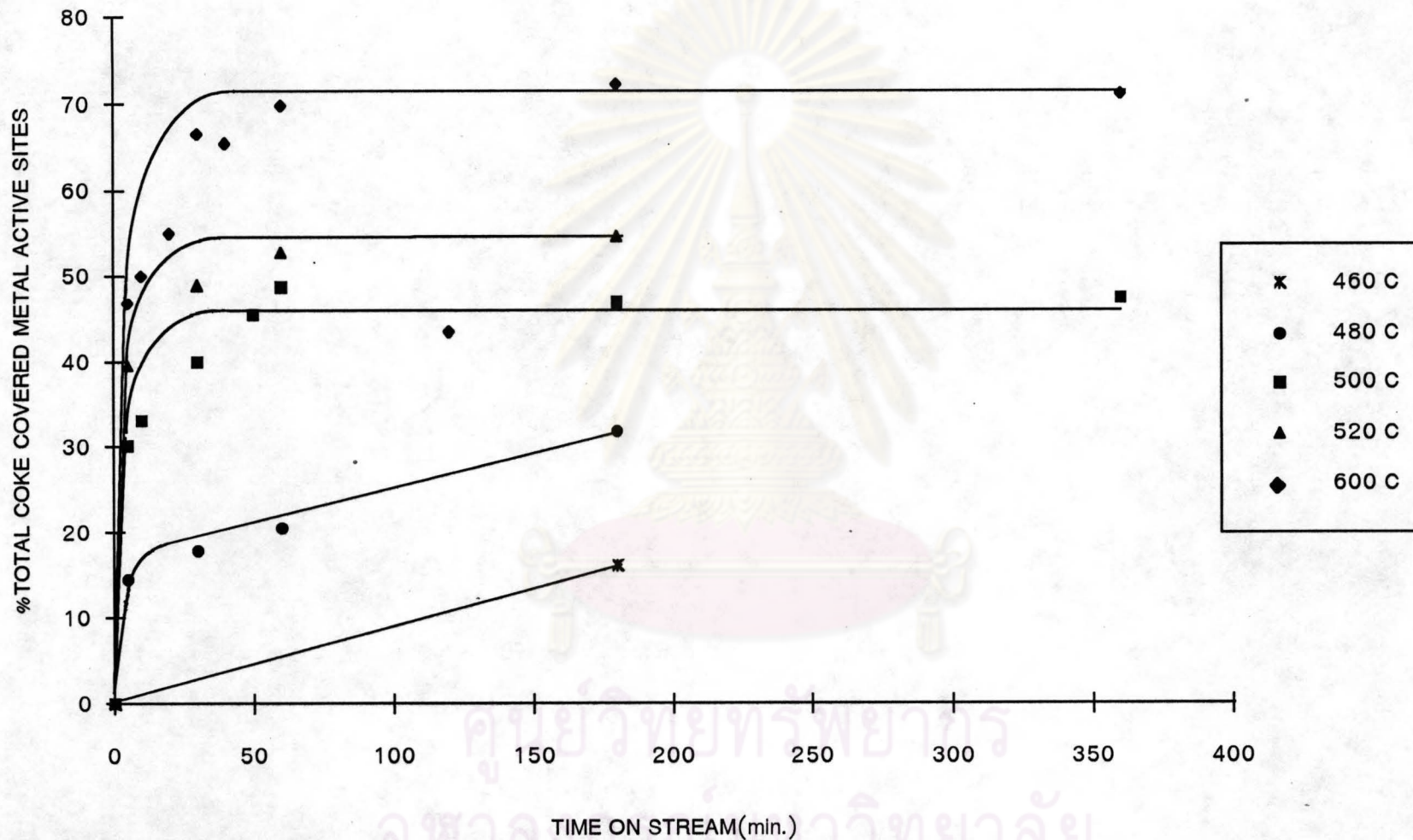
**Figure 5.19** % Total coke covered metal active sites VS. Time on stream (min.)

Catalyst : (0.3 wt%) Pt-(0.3 wt %)Sn-(0.6 wt%)Na/Al$_2$O$_3$,

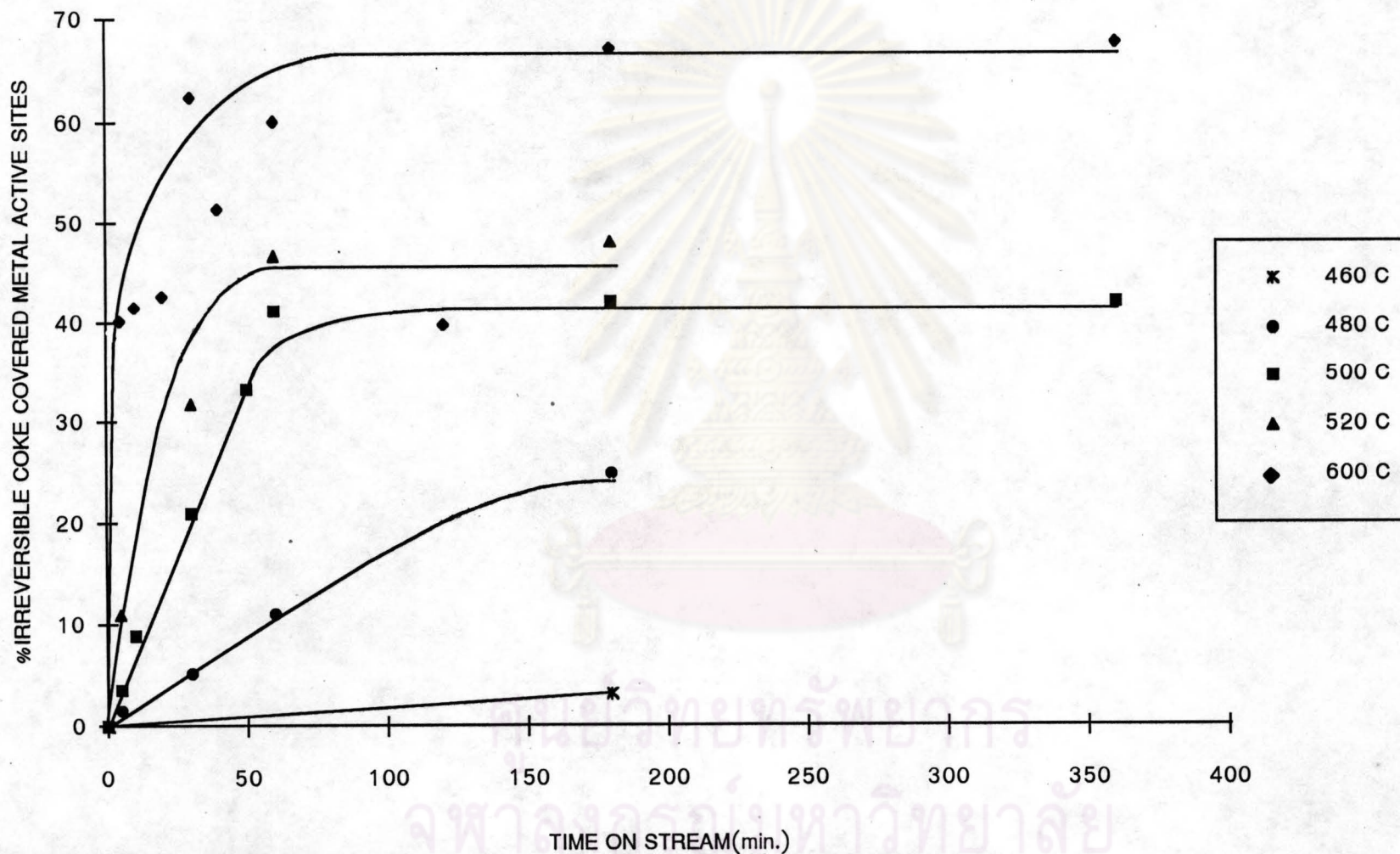Feed = H$_2$+20% propane in N$_2$, H$_2$:HC ratio=1.0

**Figure 5.20** % Irreversible covered metal active sites VS. Time on stream (min.)

Catalyst : (0.3 wt%) Pt-(0.3 wt %)Sn-(0.6 wt%)Na/Al$_2$O$_3$,

Feed = H$_2$+20% propane in N$_2$, H$_2$:HC ratio=1.0

Such an equilibrium could possibly be represented by the following models:

**PRECURSOR**



○   reversible coke deposited on metal active sites

●   irreversible coke deposited on metal active sites
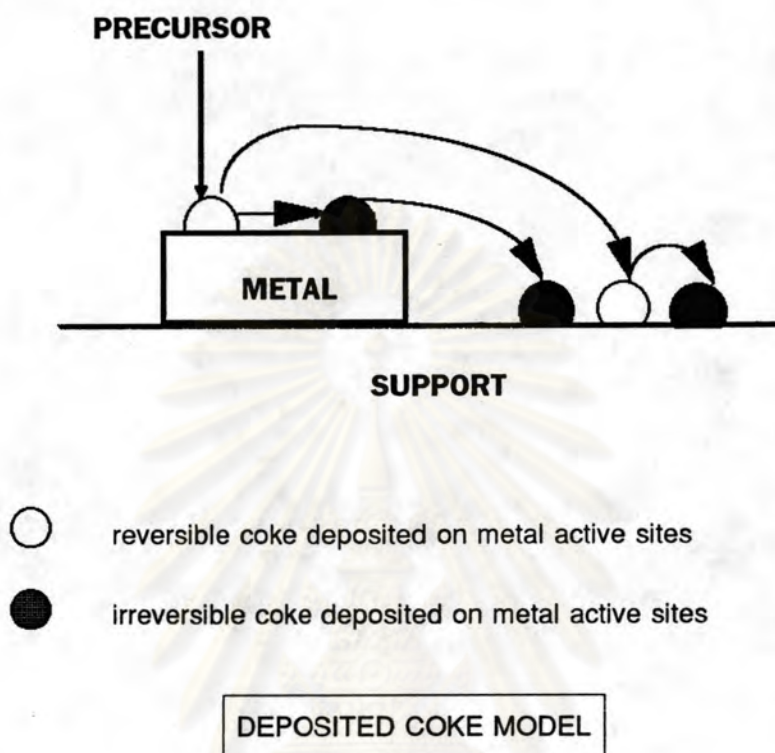
DEPOSITED COKE MODEL

**Figure 5.21**  Deposited coke model.

Deposited coke model was described that feed adsorbed on Pt-site and dehydrogenated to coke precursor until that changed to reversible coke covered on metal active sites.  After,  the reversible coke deposited on metal  active sites was polymerized or  dehydrogenated  onto irreversible coke covered on metal active sites. Finally, covered-irreversible  coke metal active sites were drain off to acidic support. On the other hand, the reversible coke covered on metal sites were drain off to alumina support. Consequently, the reversible coke on acidic site convert to irreversible coke on support.

It was valid provided that the measured active sites decreased due to coke deposition and there was no sintering occured during the experiment.  Upon this limitation, it is probably able to compare the active sites of fresh catalyst and regenerated catalyst by calculating the percentage of error (APPENDIX B.2) as shown in Table 5.8. The active sites of fresh and regenerated catalysts were rather close as the percentage of  error was too small.

**Table 5.8** % error from fresh and regenerated catalysts

| Temperature | Time on stream | % error |
|:---:|:---:|:---:|
| 600 $^{\circ}$C | 5 min | 3.59 |
| | 10 min | 3.88 |
| | 20 min | 3.84 |
| | 30 min | 6.32 |
| | 40 min | 6.88 |
| | 1 hr | 8.30 |
| | 2 hr | 10.91 |
| | 3 hr | 11.35 |
| | 6 hr | 12.01 |
| 520 $^{\circ}$C | 3 hr | 8.03 |
| 500 $^{\circ}$C | 3 hr | 7.88 |
| | 6 hr | 9.34 |
| 480 $^{\circ}$C | 3 hr | 2.38 |
| 460 $^{\circ}$C | 3 hr | 2.12 |

This model, similar to the theory of Gate et al.[2] and Biswas et al.[51], clearly indicated that the irreversible coke on metal active site migrate to acidic sites of the alumina; called "The drain off effect". Coke on metal sites drained off to suport during the course; it could generally be considered as the total coke formation as depicted in Figure 5.22. As time on stream proceeded, the amount of total coke on both metal site and support increased, particularly irreversible coke, [7,57] but total amount of reversible coke had reduced value implying the irreversible coke (convert from deposited reversible coke metal active site) drain off from metal to support did occur. Alternatatively reversible coke drained off to support and converted to irreversible coke, thus leading to an equilibrium state, coke covered on the metal sites.

According to the above mentioned effect, reversible coke on metal site did not change with temperature rather it leveled off as illustrated in Figure 5.23.
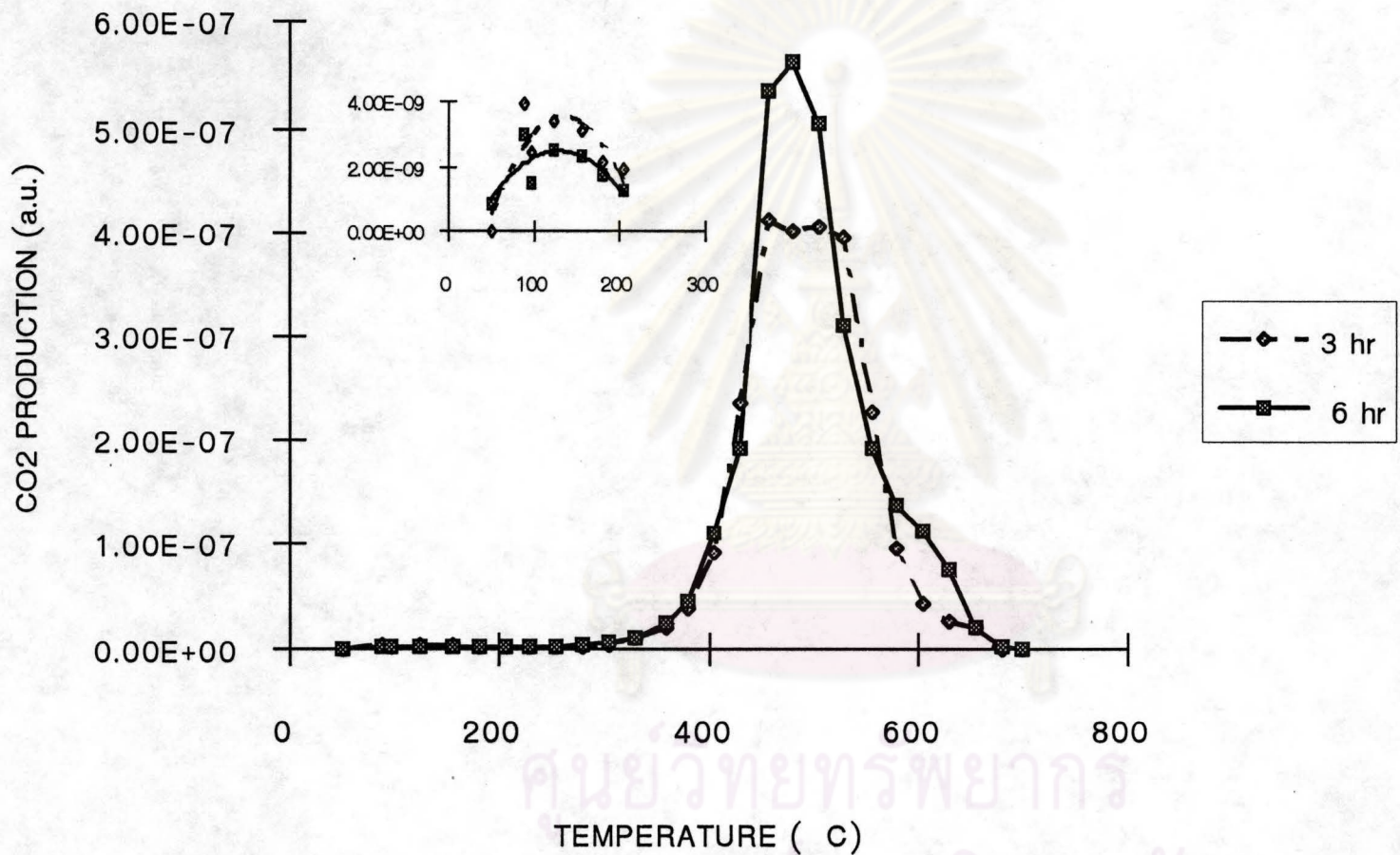
**Figure 5.22** Temperature Programmed Oxidation of various time on stream of coke catalysts
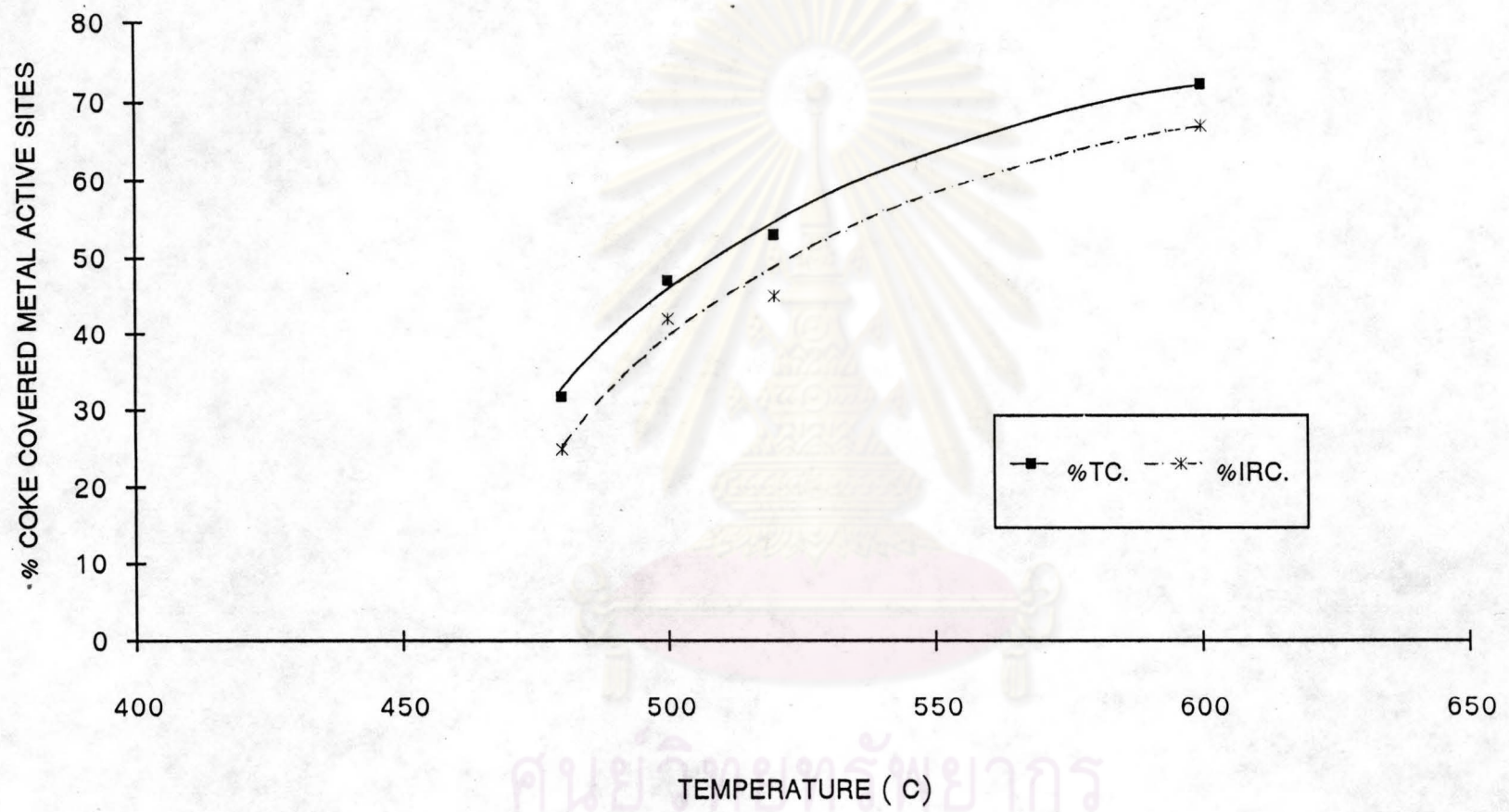
**Figure 5.23** % Reversible coke covered metal active site VS. Temperature (°C)

The initial time on stream, irreversible coke deposited on metal active sites was found linear could extrapolate to zero order reaction whence referred to rate constant (k) was shown in Figure 5.24. Finally plot ln k versus 1/T that had slope was Ea/R illustrated in Figure 5.25. Then, Ea of irrevesible coke deposited on metal active sites = 280 kJ/mol with reaction temperature range between 460 $^\circ$C to 520 $^\circ$C.
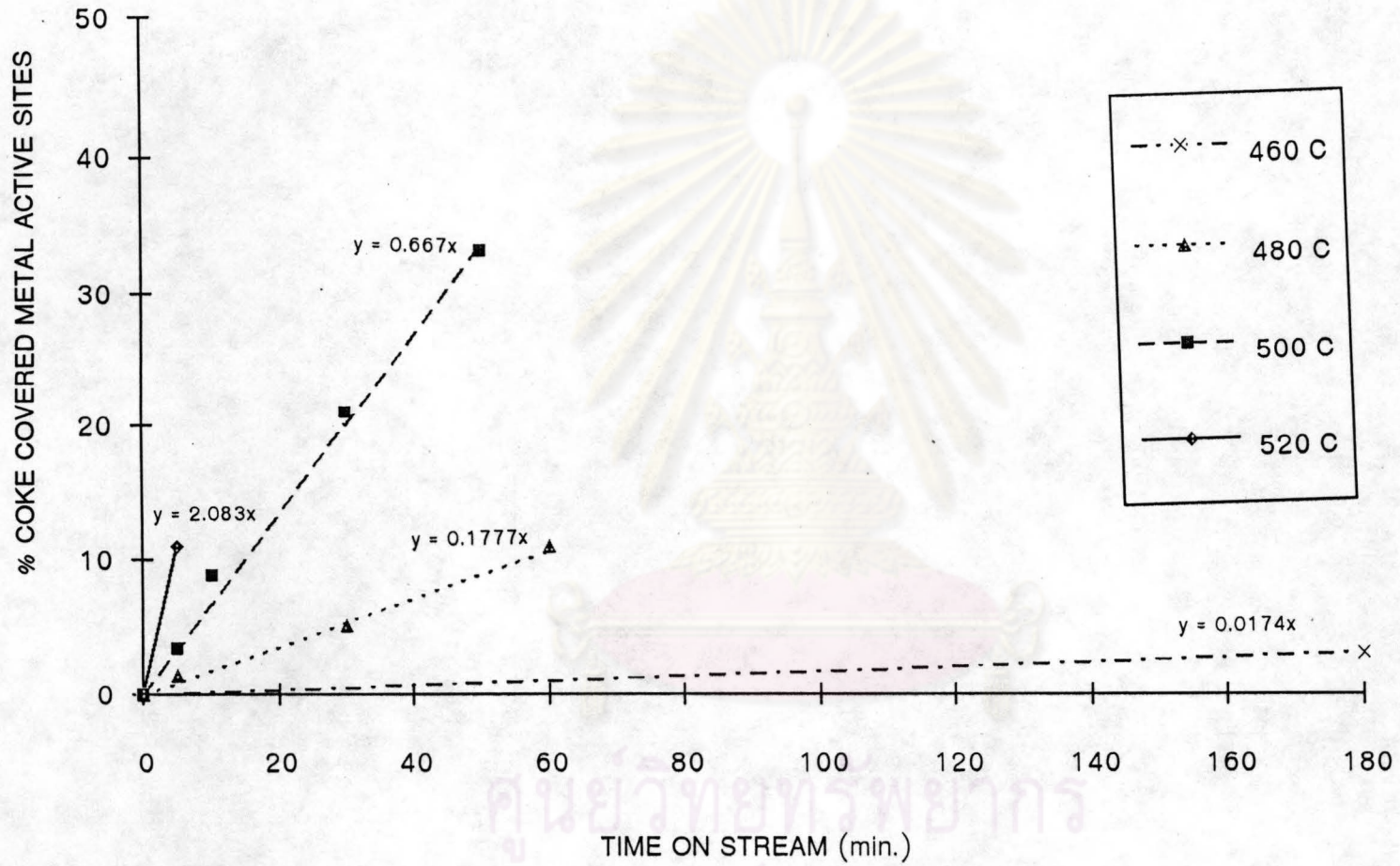
**Figure 5.24** % Coke covered metal active site VS. Time on stream (min.)

**Figure 5.25** ln k (sec$^{-1}$) VS. 1/T (K$^{-1}$)