CHAPTER V

RESULTS AND DISCUSSION

The coke formations for dehydrogenation were investigated within the varieties of alkanes and alkenes. The discussion herein effects of reactants in the terms of conversion, selectivity of coke formation, and productivity. Finally, the model of coke formation is proposed.

5.1 The effect of reactants in dehydrogenation reaction.

A variety of alkanes and alkenes were used as reactants to investigate the formation of coke. Alkanes were used in this work because they were one of the most important reactants in dehydrogenation to increase chemical feedstocks, i.e. propene is a monomer to manufacture polypropylene. It is obvious that alkene is a main product in alkane dehydrogenation. In order to understand the further phenomena of alkane dehydrogenation, dehydrogenation of alkene was studied as well.

5.1.1 Thermal cracking effects over an operating condition.

Dehydrogenation was carried out at the temperature condition of 500°C. At this condition, thermal cracking, one of the side reactions, would occur simultaneously especially for long chain hydrocarbons. A blank test then was studied. In the blank test, 0.1 g γ-Al$_2$O$_3$ was placed inside the reactor instead of Pt-Sn-K/γ-Al$_2$O$_3$ in order to quantify the influence of support on thermal cracking. The test was run at 500°C. At the condition set, thermal cracking was found around 5-30 % for C$_5$-C$_8$ reactants, while C$_3$ did not show any thermal cracking product. From this result, the temperature of dehydrogenation would be reduced depending upon hydrocarbon type. It was found that hydrocarbons with carbon atom 5, 6, 7, 8 showed thermal cracking insignificantly at 350°C, 300°C, 250°C, and 200°C, respectively.

5.1.2 Activity and coke selectivity.

Different reactants showed their activities and amount of coke formed over Pt-Sn-K/γ-Al$_2$O$_3$ differently. Therefore the comparison of coke amount for each reactant converted might not be applicable. It was better to define a new terminology related to selectivity named percent selectivity of coke formation. It was defined as follows:

$$\% \text{ selectivity of coke formation} = \frac{\text{atom of carbon deposited on catalyst}}{\text{carbon atom of hydrocarbon feed converted}} * 100$$

According to the effect of thermal cracking, it was preferred to classify hydrocarbon into short and long chain hydrocarbon.

5.1.2.1 Short chain hydrocarbon.

A pair of propane and propene was used to represent short chain hydrocarbon. The dehydrogenation of these reactants were carried out at 500°C. The activities of light hydrocarbons along time on stream are shown in Figure 5.1. It can be observed that for the initial time interval, the dehydrogenation of propane hydrocarbon is high, approximately 40%. However, it decreases rapidly with time on stream. Finally, the deactivation gradually decreases. In the same figure, the dehydrogenation of propene shows activity much lower (only 3%) than that of propane. As these results, propene reacted more difficult than propane did. This can be explained using thermodynamic calculation, which shows that the Gibbs free energy (ΔG) of propene dehydrogenation (116.49 kJ/g mole) was higher than that of propane dehydrogenation (59.38 kJ/g mole).

Two products were found via propane dehydrogenation. Propene was a main product while propadiene (0.056 wt%) was detected within moderate amount. For propene dehydrogenation, propadiene (0.2596 wt%) became a main product. By its
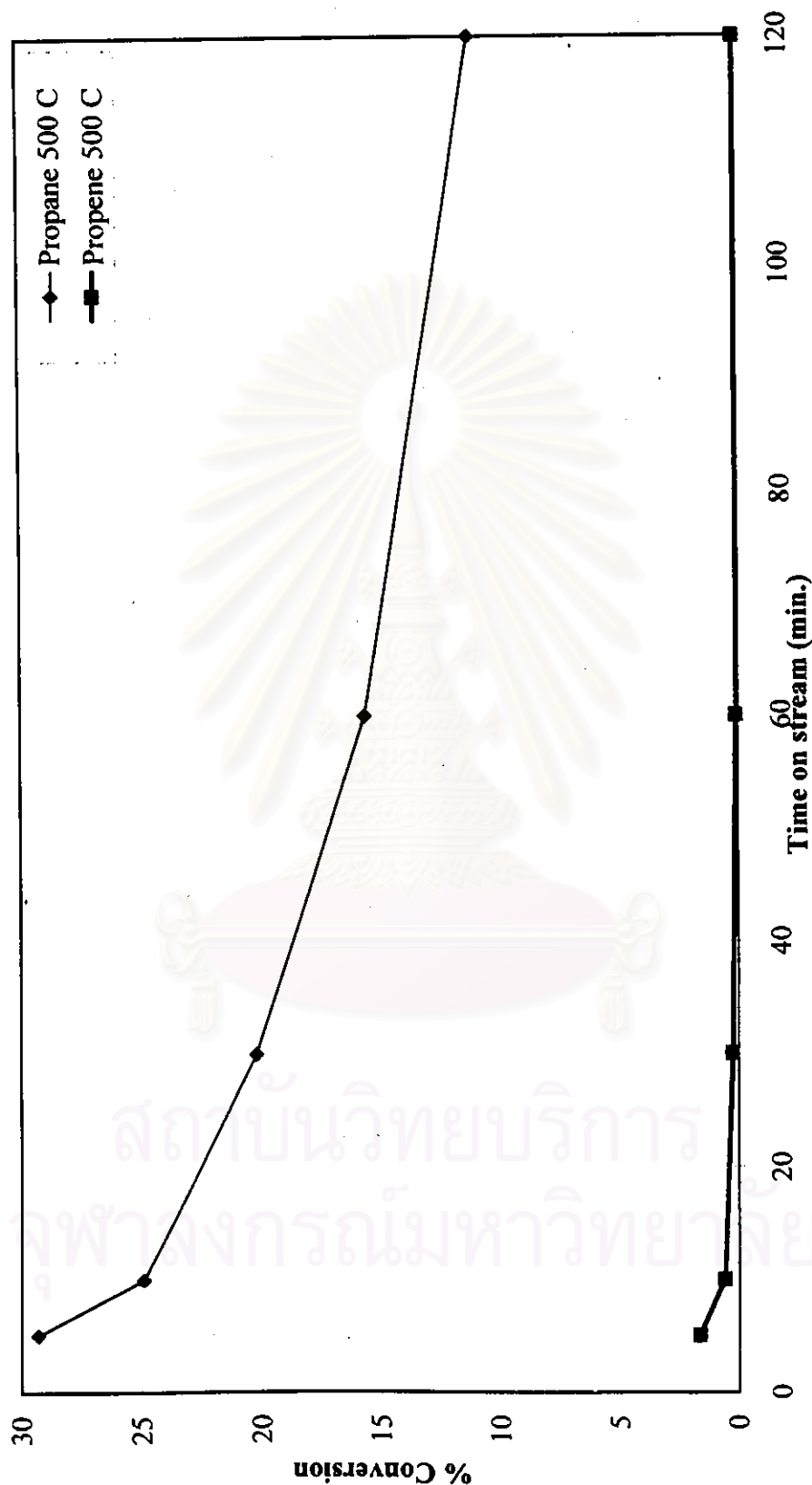
Figure 5.1 % conversion on propane and propene dehydrogenation over 0.3wt%Pt 0.3wt% Sn 0.6wt%K /Al_2O_3 as a funtion of time: GHSV =22500 hr^{-1} .

nature, propadiene exhibits extremely high reactivity [71]. It can easily react with other chemicals in the system, for example polymerization and/or cyclization, to form complexes. Compared to propane and propene, propadiene is the most active. It is then reasonable to presume that propadiene is likely to be a main participant in the formation of coke for both dehydrogenations.

Percent selectivity of coke formation for propane and propene dehydrogenation are shown in Table 5.1. One can notice that percent selectivity of coke formation for propene dehydrogenation is higher than that for propane dehydrogenation. The reason is that propene dehydrogenation produced propadiene, which is a main species to form coke, higer than propane dehydrogenation does. Additionally, propadiene also was produced directly from propene dehydrogenation while propane dehydrogenation required one more step to form propadiene.

Table 5.1 % Hydrocarbon conversion, coke content, and coke selectivity for 2 hour (TOS) over 0.3wt%Pt-0.3wt%Sn-0.6wt%K/Al_2O_3 operated with variety of reactants

Reactant	Reaction temperature (°C)	% HC conversion (at 5 min.)	Coke content (wt%)	% Selectivity of coke formation
Propane	500	29.30	0.80	0.002
Propene	500	1.64	2.30	0.185
n-Pentane	350	0.55	2.35	0.922
1-Pentene	350	39.92	1.83	0.006
n-Hexane	300	0.88	1.61	0.393
1-Hexene	300	21.32	1.64	0.010
n-Heptane	250	0.50	0.22	0.080
1-Heptene	250	21.24	1.31	0.016
n-Octane	200	0.46	0.16	0.020
1-Octene	200	32.41	0.63	0.002

5.1.2.2 Long chain hydrocarbon.

Alkanes and alkenes having 5-8 carbon atoms were investigated. They were considered as long chain hydrocarbon representatives. The activities of each dehydrogenation are shown in Figures 5.2 through 5.5. It was found that the activities of alkene dehydrogenation were higher than those of their conjugated alkene (alkane) dehydrogenation. Similar to propane dehydrogenation, the activities in each reaction decreased rapidly at the initial time interval and gradually decreased after some period of time. In addition, many products were detected from dehydrogenation of long chain hydrocarbon, especially operation at high temperature. It was expected that these side reaction products came from the thermal cracking process.

The consideration of the percentage of coke selectivity for dehydrogenation of long chain hydrocarbon are also shown in Table 5.1. It was found that the percentage of coke selectivity for alkene dehydrogenation was lower than that for their conjugated alkene (alkane) dehydrogenation. On the other words, coke selectivities for long chain hydrocarbon were not consistence to their activities, considered each pair of the same carbon atom.

The gathering of reaction rate and coke selectivities for all studied hydrocarbon species are presented in Figure 5.6. It can be seen that conversion was not proportional to percent selectivity of coke formation. All studied species had tendency which was whenever activity went down, coke selectivity would increase. This conclusion might easily be found an argument of using data which was not operated at the same temperature. The explanation in was this tredency was precisely correct just in the case of thermal cracking excluded, even at different operating temperature. This deduction will be ultilized such a coke formation mode in section 5.2.3.
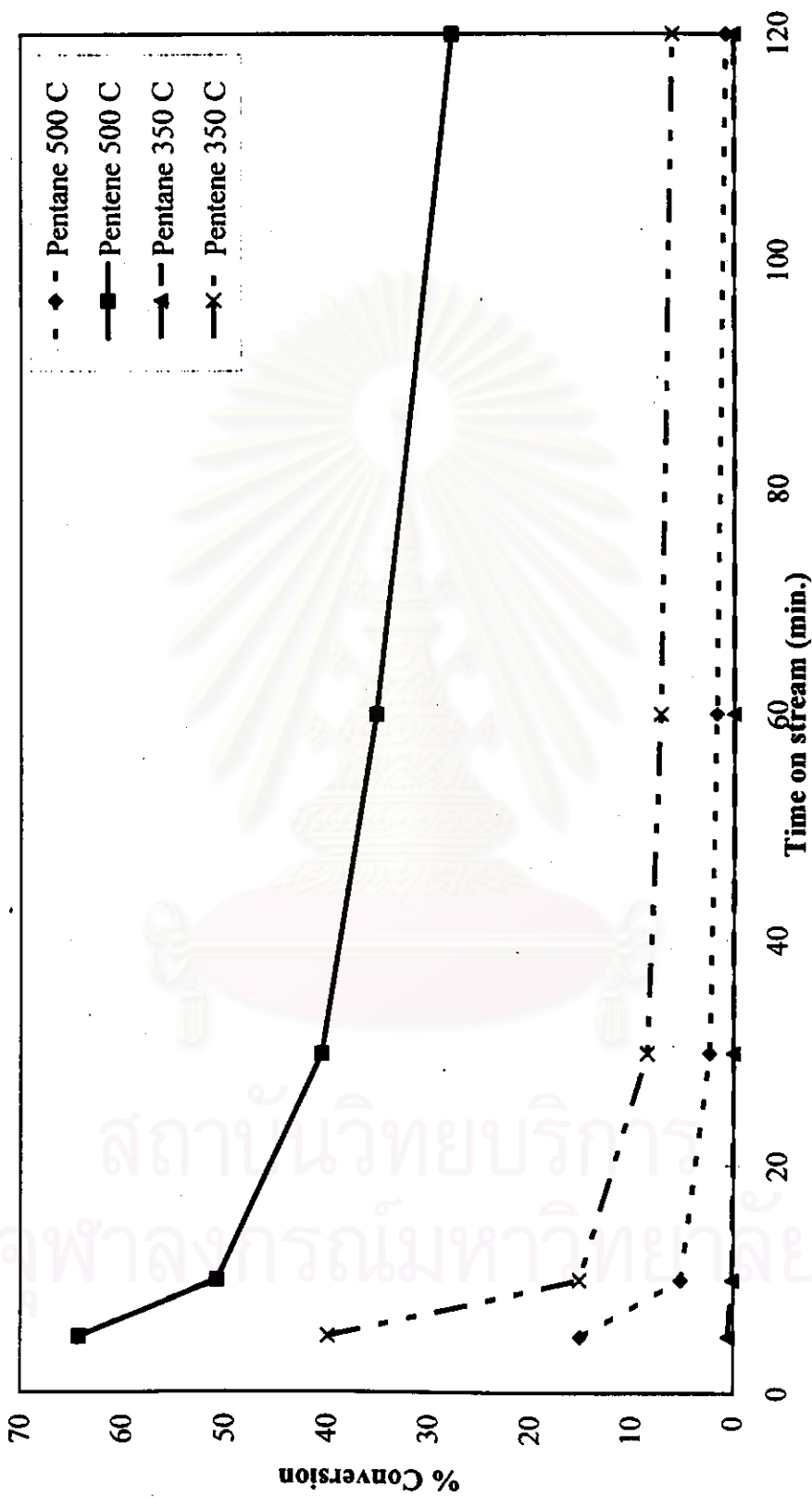
Figure 5.2 % conversion on pentane and pentene dehydrogenation over 0.3wt%Pt 0.3wt% Sn 0.6wt%K /Al$_2$O$_3$ as a funtion of time: GHSV =22500 hr^{-1} .
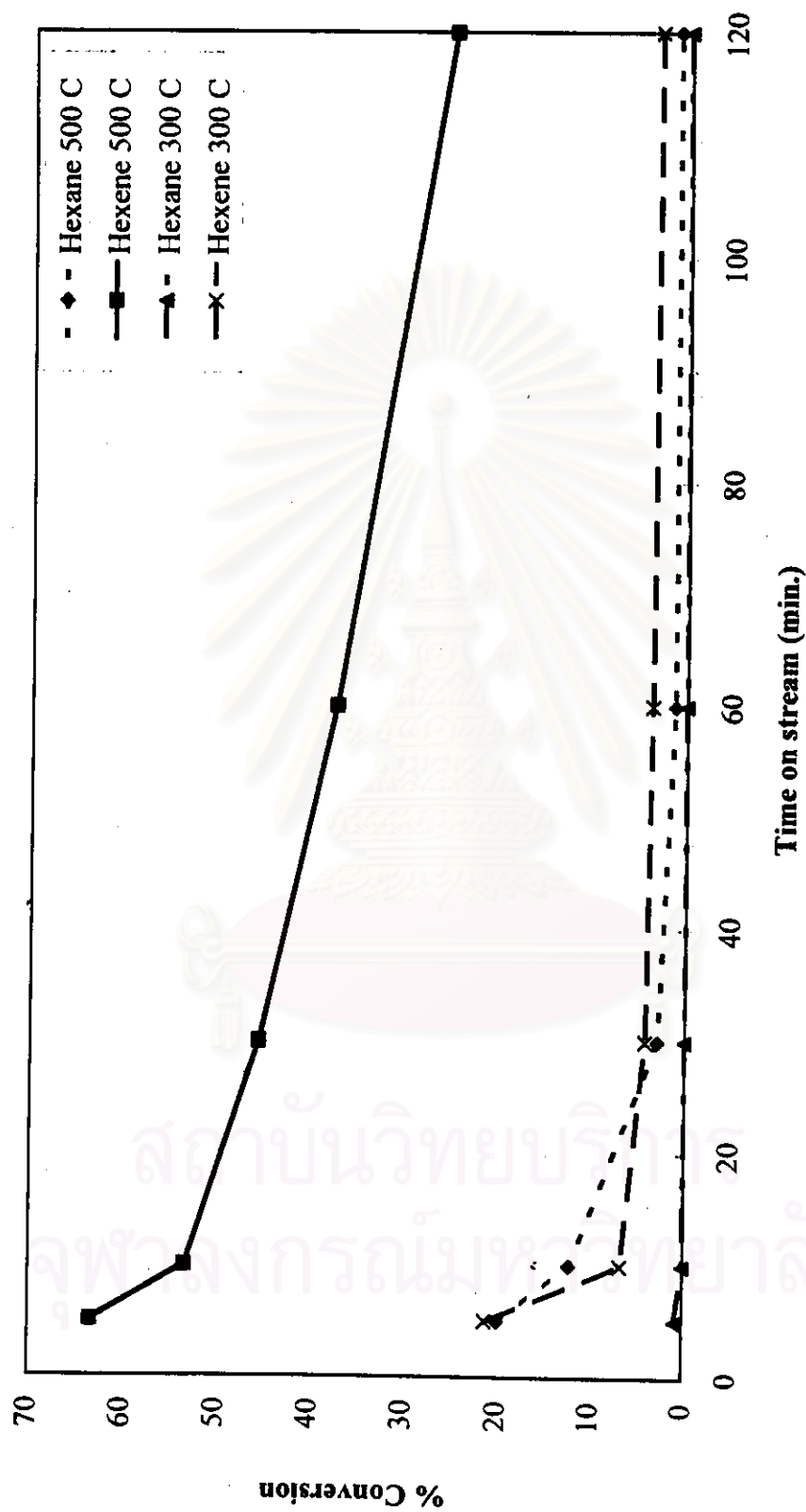
Figure 5.3 % conversion on hexane and hexene dehydrogenation over 0.3wt%Pt 0.3wt% Sn 0.6wt%K'/Al$_2$O$_3$ as a funtion of time: GHSV =22500 hr^{-1}.
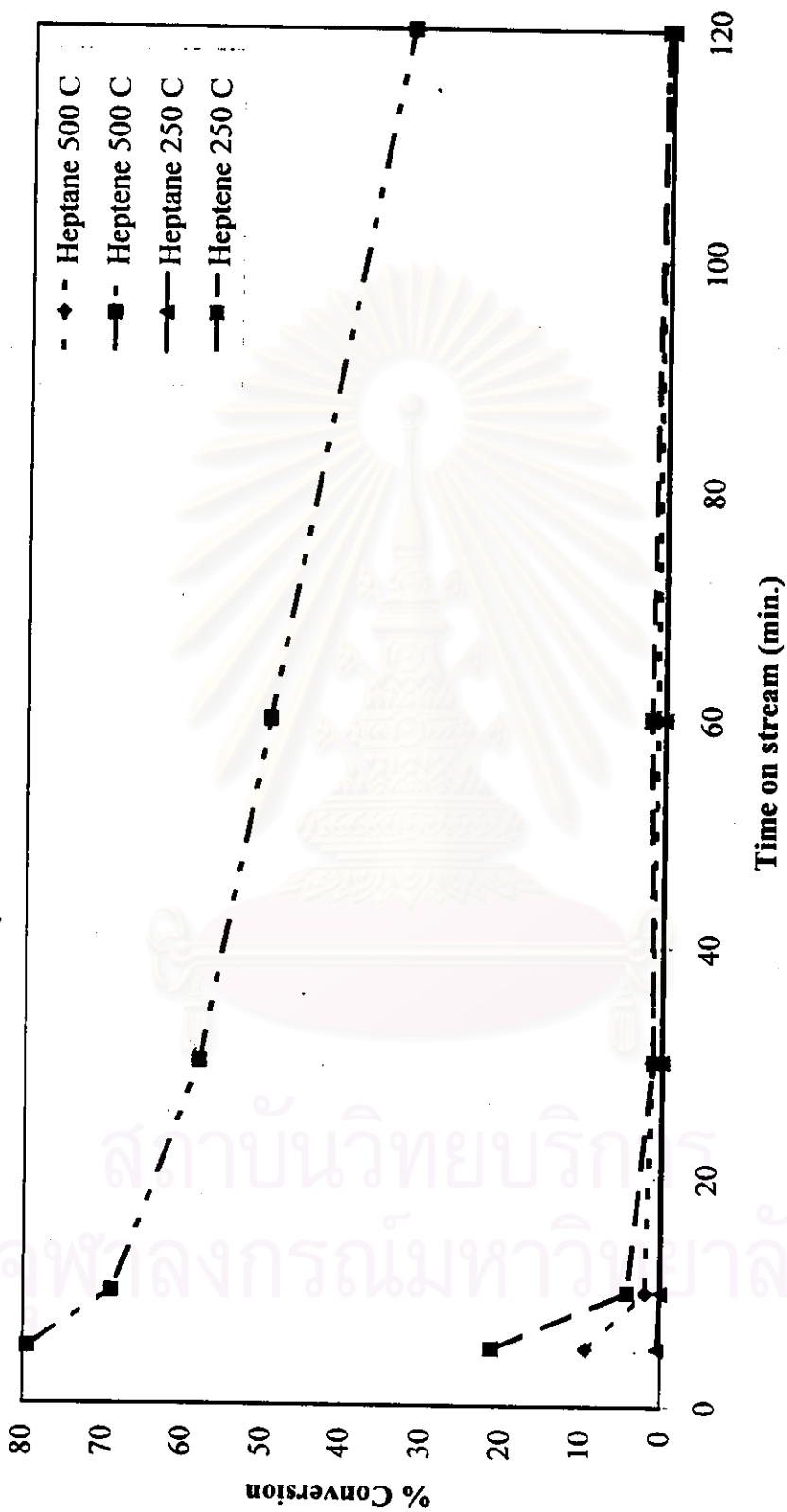
Figure 5.4   % conversion on heptane and heptene dehydrogenation over 0.3wt%Pt 0.3wt% Sn 0.6wt%K / Al$_2$O$_3$ as a funtion of time: GHSV =22500 hr^{-1} .
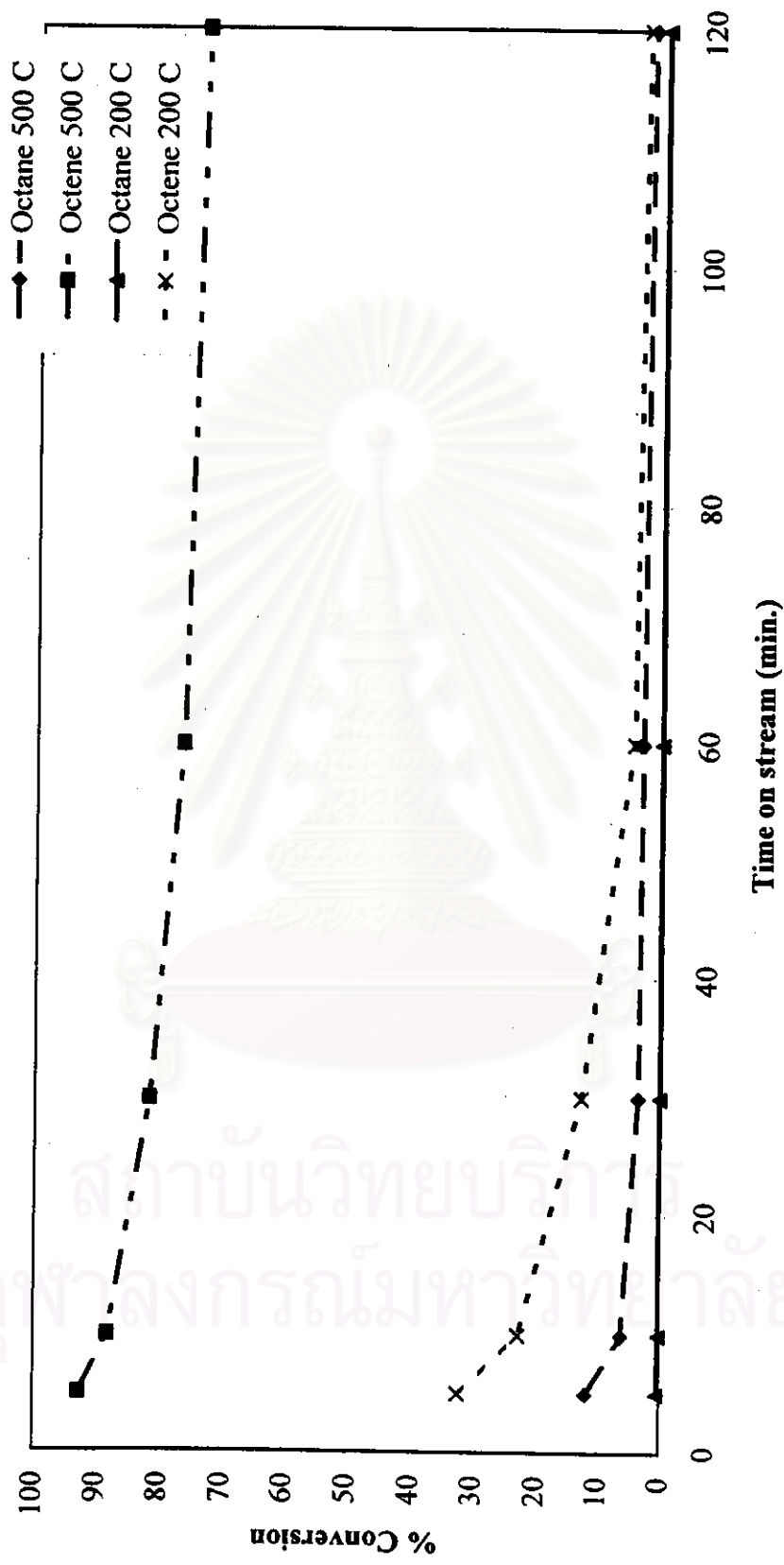
Figure 5.5   % conversion on octane and octene dehydrogenation over 0.3wt%Pt 0.3wt% Sn 0.6wt%K /Al$_2$O$_3$ as a funtion of time: GHSV =22500 hr^{-1}.
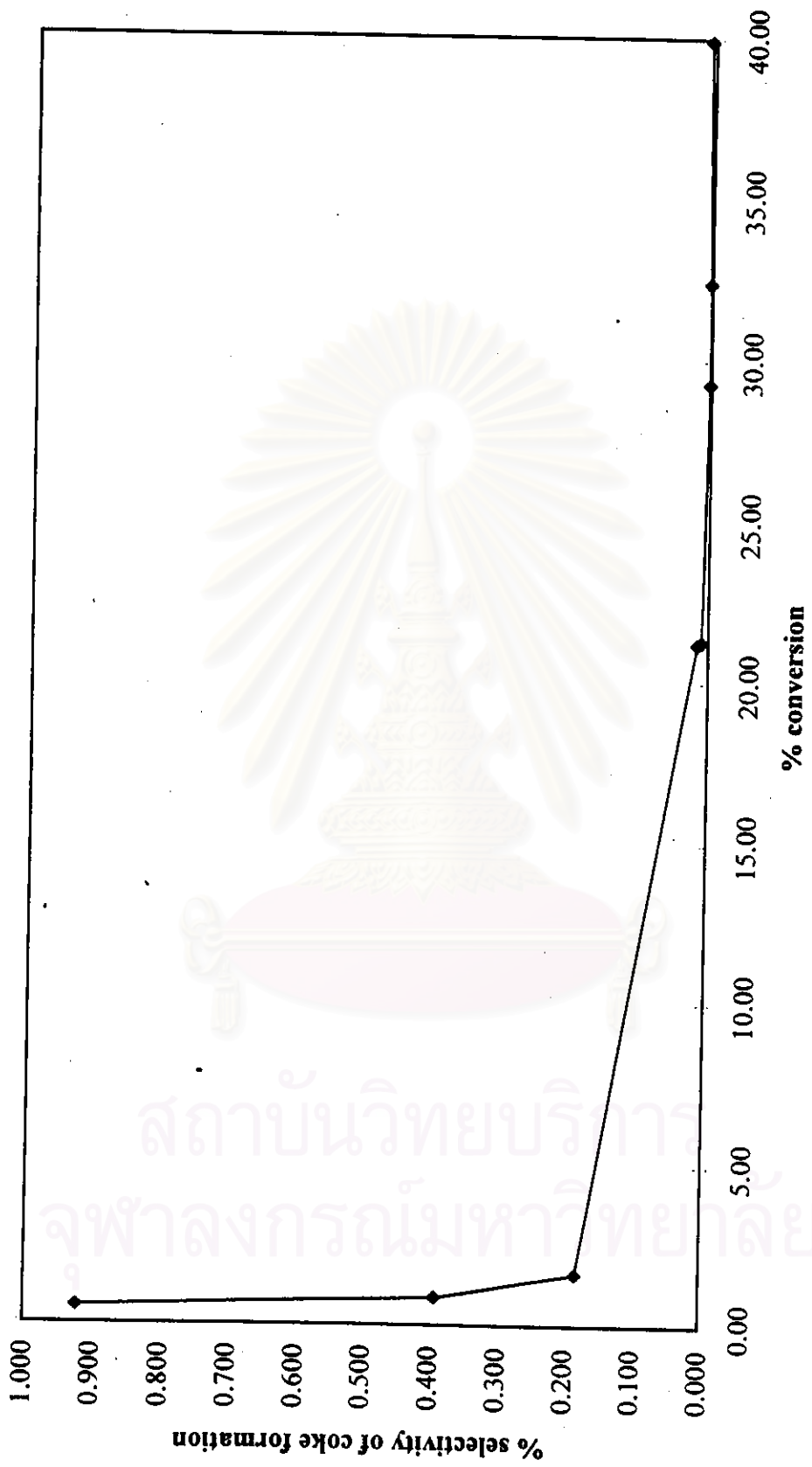
Figure 5.6 Relationship between % conversion and % selectivity of coke formation on dehydrogenation over 0.3wt%Pt 0.3wt% Sn 0.6wt%K /Al$_2$O$_3$. GHSV = 22500 hr^{-1}.

5.2 Proposed mechanism of coke formation

5.2.1 Modified mechanism of series and parallel coke formation.

Hughes [49] suggested that coking would occur in a reaction either in parallel or in consecutive (series) to the main reaction. The parallel or consecutive reactions for coking could be written as follows:

$$A \longrightarrow B$$
$$A \longrightarrow C \qquad \text{Parallel coke formation}$$
$$A \longrightarrow B \longrightarrow C \qquad \text{Series coke formation}$$

He explained on the series coke formation model that the amount of coke increases with increasing the main product. For alkane dehydrogenation, alkene is considered as a main product. To prove Hughes's model, alkenes were used as reactants for this research. His model suggests that if, the amount of coke which is formed by using alkene as a reactant is higher than that formed by using alkane as reactant, the coke formation will mode in series pattern. However, parallel model of Hughes has a constraint and can not explain the coke formation which is occurred from the different reactants. The following model of coke formation is modified as shown in Figure 5.7. It can be used to explain for entire studied reactants.
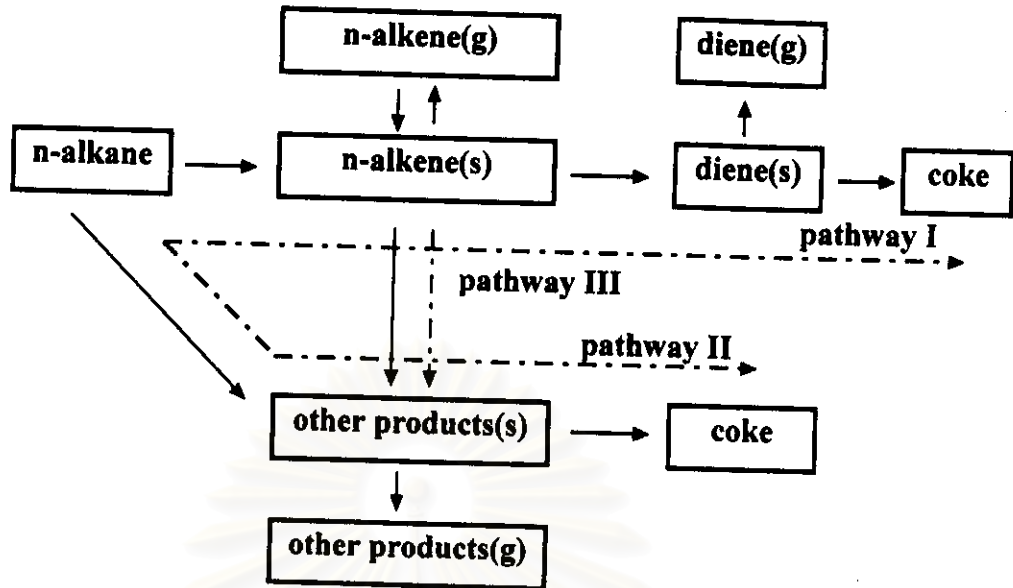
Figure 5.7 Mechanism of coke formation. ((g) = gas phase, (s) = surface species)

This mechanism explains the possibility of coke formation into three different directions. The coke formation of all alkanes consists of all pathways. Pathway I and pathway III provide a series coke formation, while pathway II leads to a parallel coking formation. The coke formation of alkene contains the mechanisms through pathway I and III. Unlike alkane, pathway III will perform differently as a parallel model, while pathway I still is in a series model. The following paragraphs give details of each pathway.

Pathway I

Consider n-alkane as a reactant, hydrogen atoms are detached from n-alkane to form n-alkene on the surface of catalyst. Some of n-alkene is desorbed to be main product in the gas phase, and some is still around on the surface which would eliminate more hydrogen atoms to form diene. Diene also performs similar to n-alkene. Some diene desorbs to be by-products, and the rest diene would develop a complex structure leading to coke. If a starting reactant is n-alkene, on this pathway it will have a similar mechanism as described above, excepted there was no discharging step of hydrogen atoms from n-alkane.

Pathway II

This pathway describes some possibility that n-alkane would produce other intermediate (except n-alkene). Side reactions such as catalytic cracking, cyclization, and aromatization cause variety of products. The amount of carbonaceous deposit on catalyst depends upon the nature of products whether they would like to desorb or grow complexes.

Pathway III

This pathway gives a chance of n-alkene to form coke. n-Alkene is formed after the dehydrogenation of n-alkane. It would convert to other products (except diene) via different side reactions. Side reactions and amount of coke could somewhat refer to pathway II.

To make this proposed model reliably, the comparisons between proposed model with experimental data were proclaimed into four aspects.

1.<u>Three carbon atoms on coke formation.</u>

The dehydrogenations of propane and propene were considered. Both reactions give products similarly. Products consisted of n-alkene and diene. Byproducts obtained from reactions were very small. This gave very little chance for coke formation via pathway II and III, and the behavior of coke formation should follow by the first pathway.

According to the model (pathway I), it presents percent selectivity of coke formation from alkene as a reactant should higher than that using alkane as a reactant. This mechanism is then appropriate to the experimantal results.

2.<u>Five and six carbon atoms on coke formation.</u>

Refer to the experimental results that the coke formation from pentane was smaller than pentane and the coke formation from hexene was equal to hexane, the results obviously were not corresponds to pathway I since in this pathway, the coke formation from alkene, main product of alkane, should be larger than from alkane. The behavior of coke formation then should rely on parallel model controlling steps. Either pathway II or III could be suited, relied on the starting reactant.

3.<u>Seven and eight carbon atoms on coke formation.</u>

The experimental results of this reactants group was consistent with pathway I, which responded that coke produced from alkane is less that from alkene. However, the experimental results gave that percent selectivity of coke formation of alkane is higher than that of alkene which conflicted with the model. Thus, the first pathway was ruled out. The coke formation from this reactant group, seven and eight carbon atoms, pursued the parallel model.

From this reactant group, it was found to be having low conversion. There are two reasons for these results. One is catalyst deactivation by huge amount of coke. The other is caused by appropriate conditions. Compared the two reasons, the low conversion originated from the first reason cause possibly causes a lot of coke deposit on catalyst, whereas, a little amount of coke forms from the second reason. Therefore the low conversion of heptane and octane related to the second cause.

4.Effect of thermal cracking on coke formation.

Table 5.2 and Figures 5.2 through 5.5 show that alkene gives activity and the amount of coke higher than alkane, if the reaction includes thermal cracking effect. In spite of that percent selectivity on coke formation of alkene is lower than alkane for some studied chemicals (C5-C8).

Table 5.2 % Hydrocarbon conversion, coke content, and coke selectivity for 2 hour (TOS) over 0.3wt%Pt-0.3wt%Sn-0.6wt%K/Al_2O_3 operated with variety of reactants

Reactant	Reaction temperature (^oC)	% HC conversion (at 5 min.)	Coke content (wt%)	% Selectivity of coke formation
n-Pentane	500	15.09	2.17	0.016
1-Pentene	500	64.17	4.82	0.003
n-Hexane	500	20.00	1.92	0.120
1-Hexene	500	63.26	5.99	0.004
n-Heptane	500	9.40	1.28	0.019
1-Heptene	500	79.40	5.11	0.003
n-Octane	500	11.81	0.30	0.004
1-Octene	500	92.74	9.31	0.003

In seven and eight carbon atoms reactant group, it is noted here that thermal cracking effect initiated more other products. Hence, it have more chance for the coke formation following by pathway II and III in the proposed model. The pathway II and III become significant for coke formation while pathway I shows a little influence.

5.2.2 Analysis of coke by temperature programmed oxidation technique.

According to the model, it can be concluded that the type of reactant has effect on the coke formation mechanism. In this section, the detail of coke formed from different reactant was studied. TPO is a general technique to fulfill that thought. In general TPO spectra, it is accepted that the low temperature peak (280-370 °C) corresponds to coke deposited on or in contract with metal sites. The intermediate temperature peak 445 °C, is associated with the coke on acid sites close to the metal. The 570 °C peak is produced by coke on the acid sites far away from any metal sites [72].

5.2.2.1 Short chain hydrocarbon.

Figure 5.8 shows the TPO patterns of spent catalysts from propane and propene dehydrogenations operated at 500°C. The spectrum received from propane dehydrogenation contained two peaks. The first peak was clearly at 275°C and the other was somewhat ambiguous broadened. This peak occupied in a big temperature range of 350-450°C. Besides, the first peak was little higher than the second peak. Considering a TPO pattern received from propene dehydrogenation, it could not be identified clearly as two peaks. The peak showed a sharp one at 425°C containing a shoulder around 500°C.

Location of peak generally indicates structure of coke formed during its deactivation. Higher temperature used to burn coke completely will cause peak shifting. It also leads coke structure to be more complicate. The peak at 275 °C was only found from spent catalyst in propane dehydrogenation. It was explained that coke deposit via propane dehydrogenation was a low temperature coke and contained a simple structure while, TPO pattern of propene dehydrogenation did not remain such a simple structure. Moreover, the sharper second peak obtained from propene dehydrogenation showed the coke structure would contain more complexity.
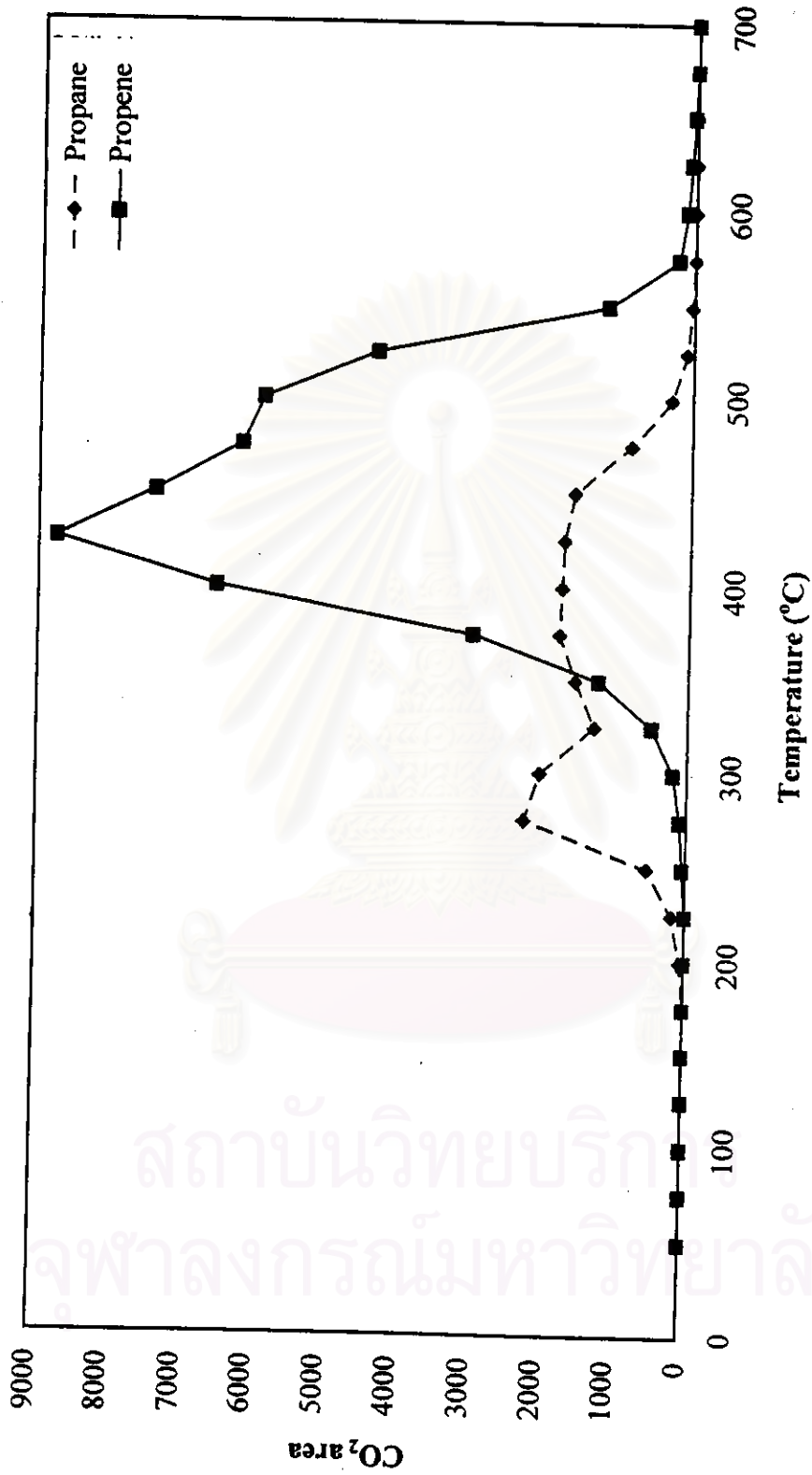
Figure 5.8 TPO spectra for propane and propene dehydrogenation over 0.09 g. of 0.3wt%Pt 0.3wt% Sn 0.6wt%K /Al$_2$O$_3$ at 500 °C, 120 min., GHSV= 22500 hr^{-1} ,

The study of coke formed along time on stream(TOS) was studied. Propene dehydrogenation was chosen to study in order to understand whether it caused the shifting of peak on TPO spectra. Coke deposited on catalyst at four different TOS (10, 20, 30, 120 min) were investigated. Figure 5.9 shows percent weight carbon as a function of time. It was found that the rate of coking rather constantly increased over 2 hours. The results of TPO spectra were shown in Figure 5.10. Two peaks were observed at the initial time interval (10-30 min). Propene dehydrogenation produced coke faster than propane dehydrogenation. Coke amount under 20 minutes via propene dehydrogenation seemed to be equal to that under 120 minutes via propane dehydrogenation. Area under the peak got larger with time on stream. Considering the first peak of spectra, it gradually shifted with temperature conditions. However, under the TOS of 120 minutes, only one peak was found and the area under the peak was very large compared to coke found at the initial time interval. The peak found at 120 minutes TOS appeared almost at the same temperature which found for the second peak at the initial time interval. It could take into account that coke started to contain more complex in structure along TOS. Finally, there was not found simple structure on this coke at all. It was believed that coke over 120 minutes was hardly to deposit on the such a small site of metal. Besides, the structure got clumsy could be an other supported reason. Therefore, they moved to deposit over support close to metal sites, instead. It can be concluded here that coke structure varies as time on stream.

The same study was done with propane dehydrogenation. As known, the amount of coke after 120 minutes (0.80 %wt) TOS was equal to that obtained from propene dehydrogenation in 20 minutes (0.75 %wt). The TPO results of them were presented in Figure 5.11. They provided in the same pattern, but they did not match as one finger print. The first peak as the coke on the metal site via propane dehydrogenation was higher than that from propene dehydrogenation. However, it showed in the opposite side to the second peak. The second peak of propene dehydrogenation was higher than that of propane. The explanation of each TPO pattern depended on how fast and how much propadiene generated in each reaction. As understood that propadiene was a main product from propene dehydrogenation, the
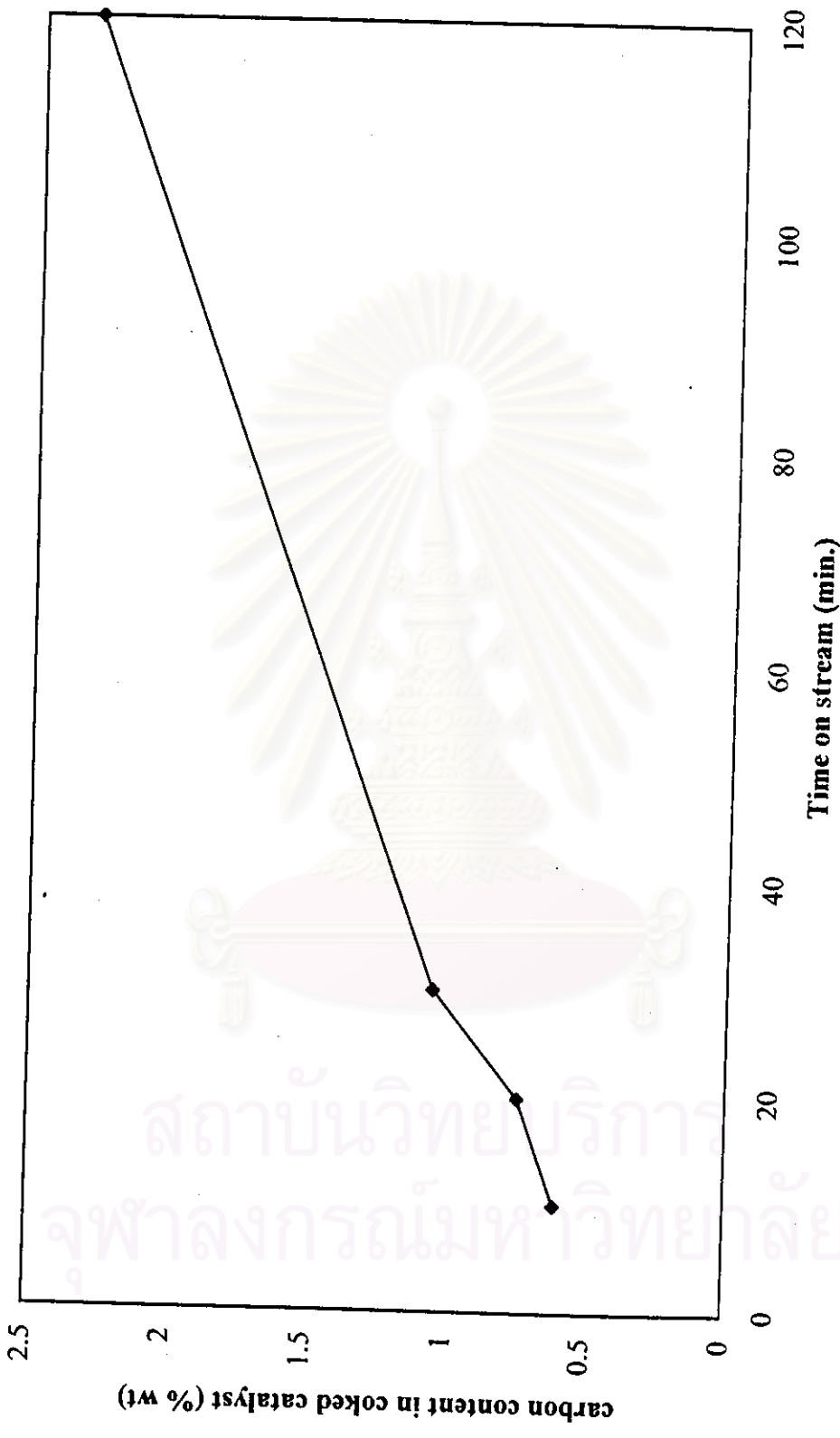
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Figure 5.9 Coke content from propene dehydrogenation for different values of time on stream, operated at 500 °C.
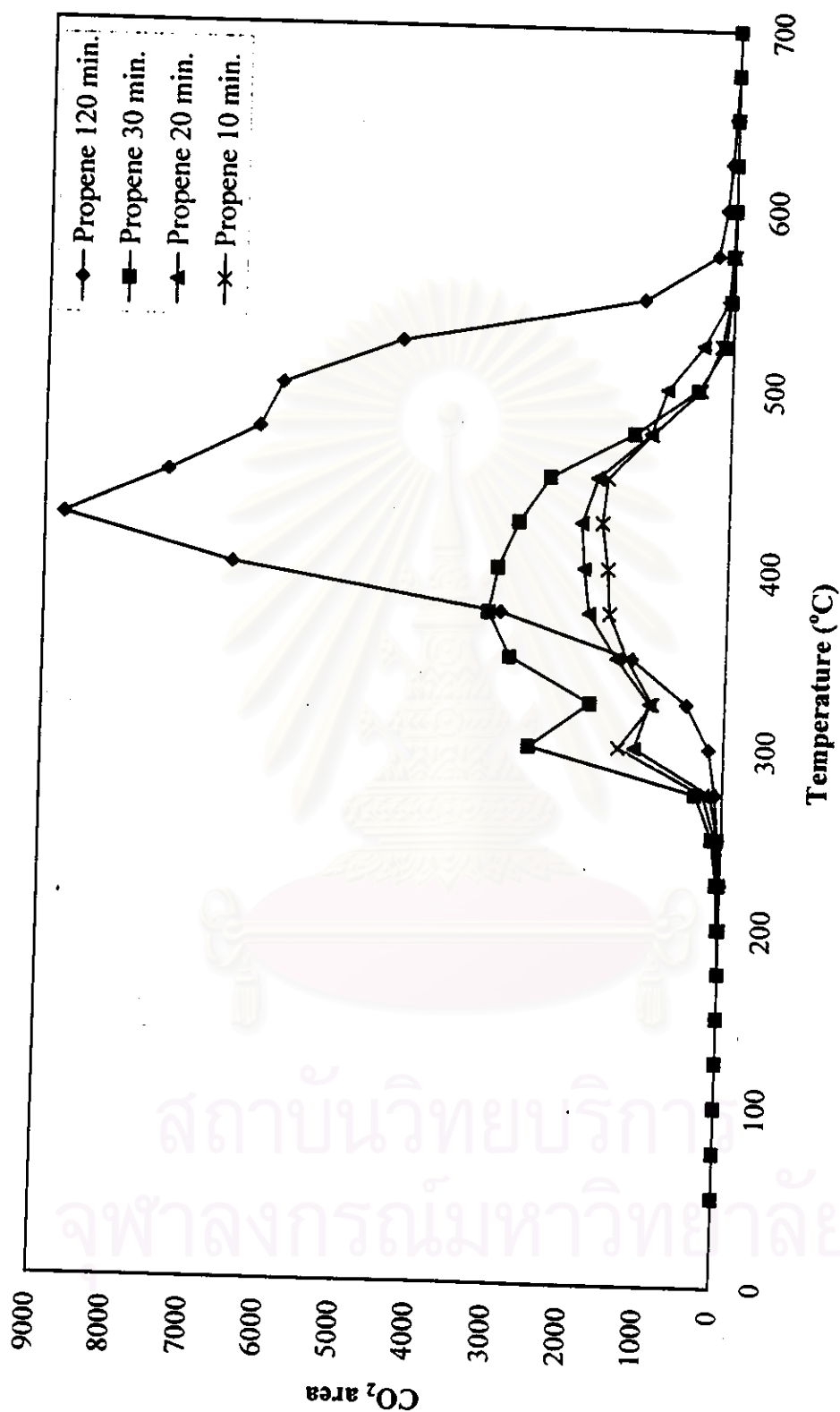
Figure 5.10 TPO spectra for propene dehydrogenation over 0.09 g. of 0.3wt%Pt 0.3wt% Sn 0.6wt%K /Al$_2$O$_3$ at 500 °C, GHSV= 22500 hr^{-1} .
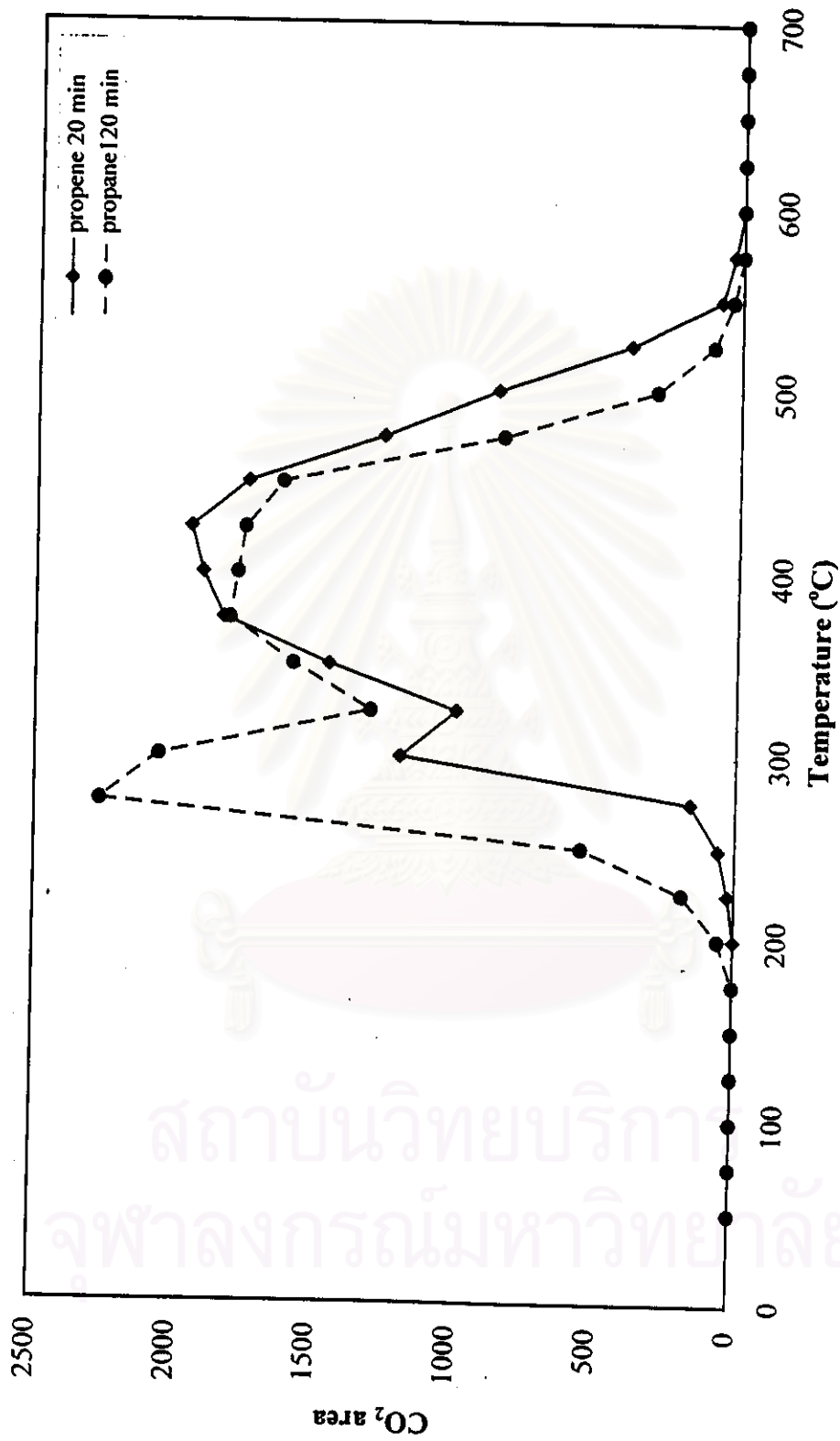
Figure 5.11 TPO spectra for propane and propene dehydrogenation over 0.09 g. of 0.3wt%Pt 0.3wt% Sn 0.6wt%K / Al_2O_3 at 500 °C, GHSV= 22500 hr^{-1} .

complex coke on metal site could be developed rapidly until it was drained off to the support. Therefore in the first step of reaction, the coke could increase rapidly. That means the hard coke also increases. Hard coke via propene dehydrogenation then was more than that via propane dehydrogenation.

5.2.2.2 Long chain hydrocarbon.

As known that C_6 could possibly react over this type of catalyst in both dehydrogenation and cracking depending upon operating condition, conditions at 300°C and 500°C then were used to operate C_6. Figure 5.12 presents TPO patterns obtained via hexane and hexene dehydrogenation at 300°C over 2 hours TOS. Both spectra gave an interesting aspect that they both had similar finger print. Another experiment was also done at the similar fashion, but operated at 500°C. It was found that even TPO patterns were similar, the peak area were different. The peak area of hexane dehydrogenation was less than that of hexene dehydrogenation, as shown in Figure 5.13. The reason was obviously come from the difference in coke amount during the test. It came up with whether the same amount of coke from both reactions would give same finger print.

Using amount of coke obtained from hexane dehydrogenation of TOS 2 hr. as a reference 1.88 %wt., the experiment in this section was to determine TOS of hexene dehydrogenation which would give the same amount of coke. Considering TPO results at four different TOS in Figure 5.14, they differed from the TPO results of propene dehydrogenation. These results showed only one peak even at the initial time interval. There was no shifting of peak along TOS. This concluded that coke formed by long chain hydrocarbon generated only hard coke.

Figure 5.15 shows amount of coke generated during the reaction at 500°C. It was observed in two facets. The first one was TOS of 25 minutes for hexene dehydrogenation would obtain 1.88 %wt., same amount as reference. Same amount of coke obtained from hexane and hexene dehydrogenation generated TPO spectra which
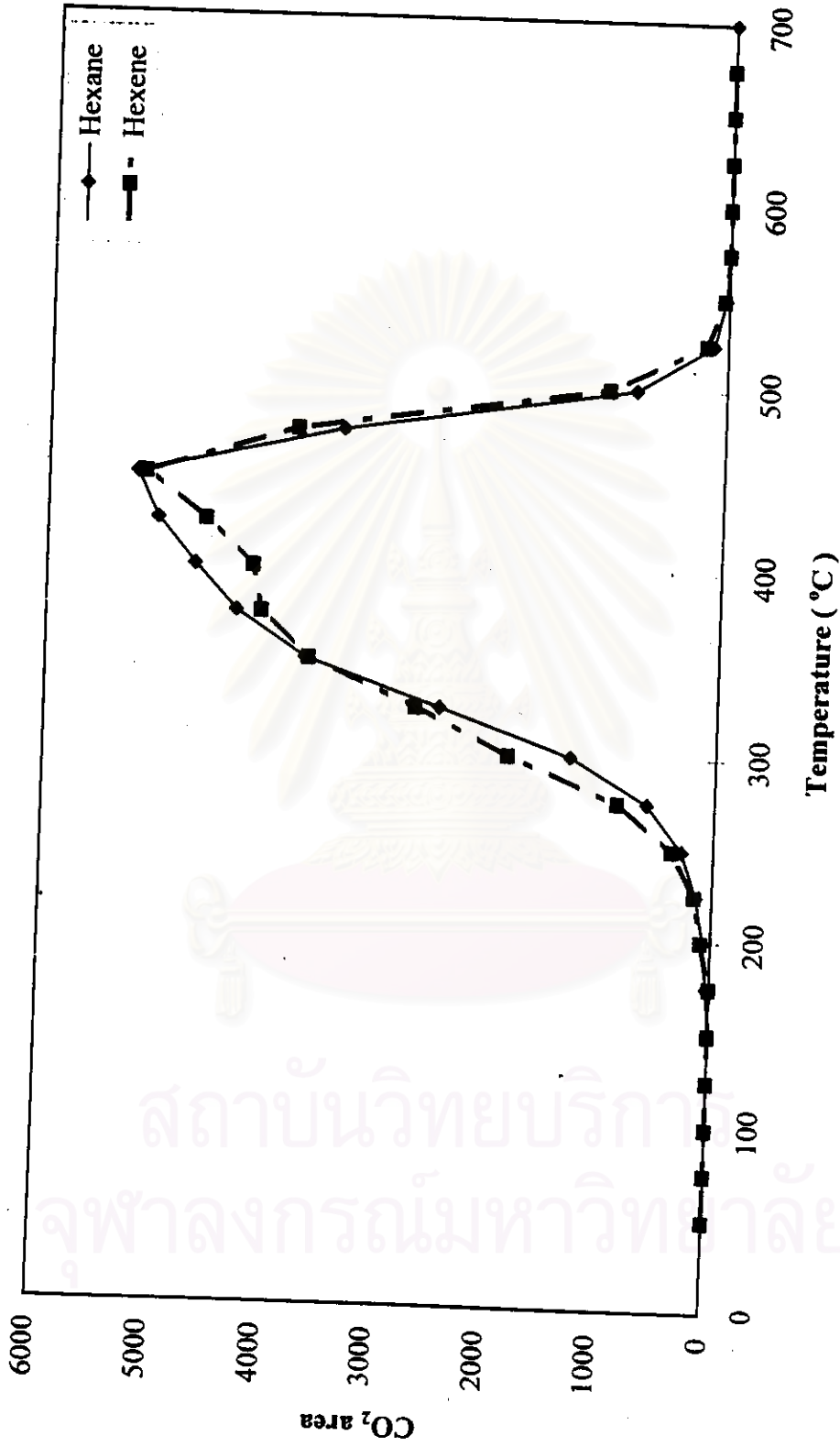
Figure 5.12 TPO spectra for hexane and hexene dehydrogenation over 0.09 g. of 0.3wt%Pt 0.3wt% Sn 0.6wt%K /Al2O3 at 300 °C, 120 min., GHSV =22500 hr^{-1}
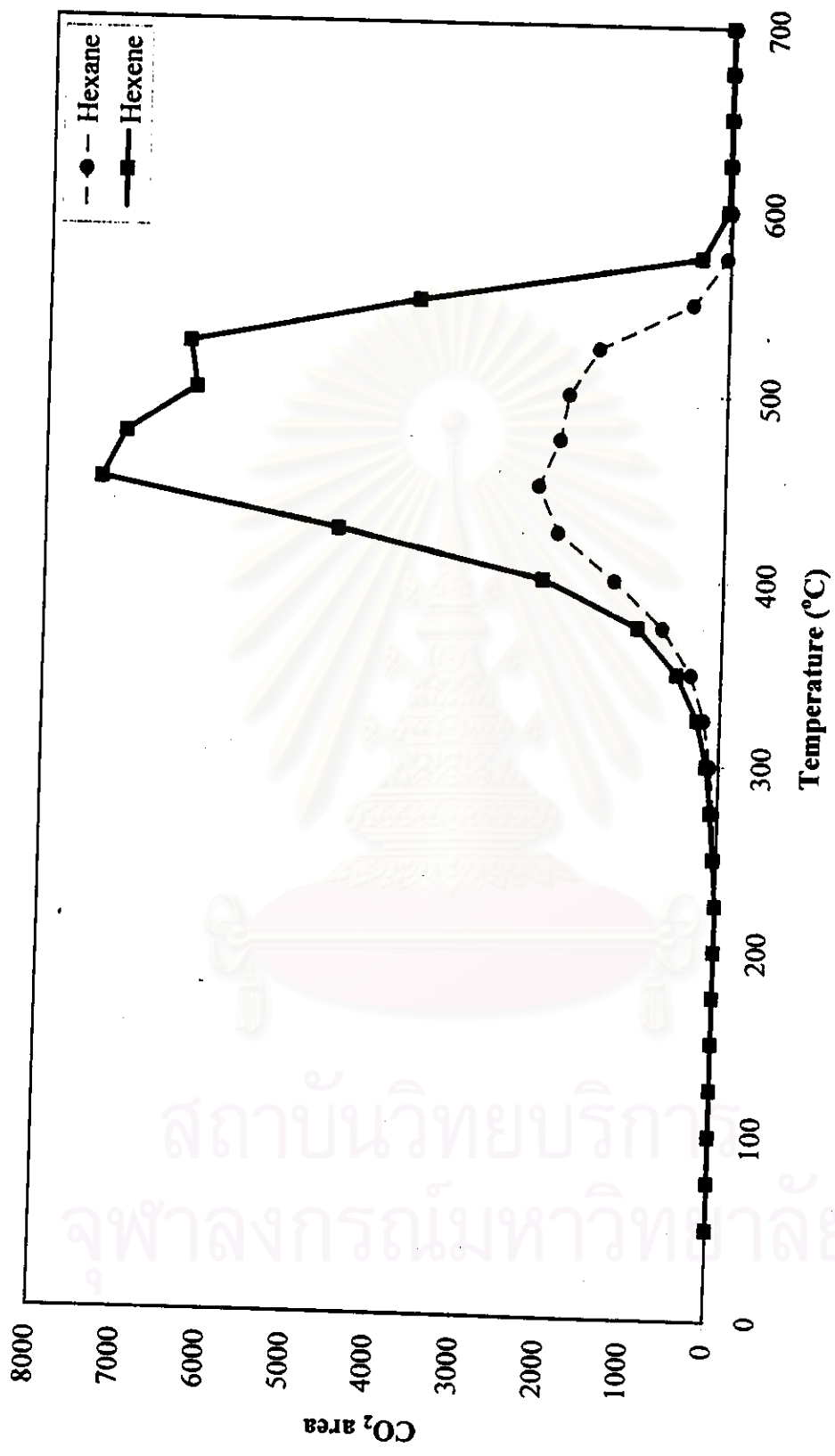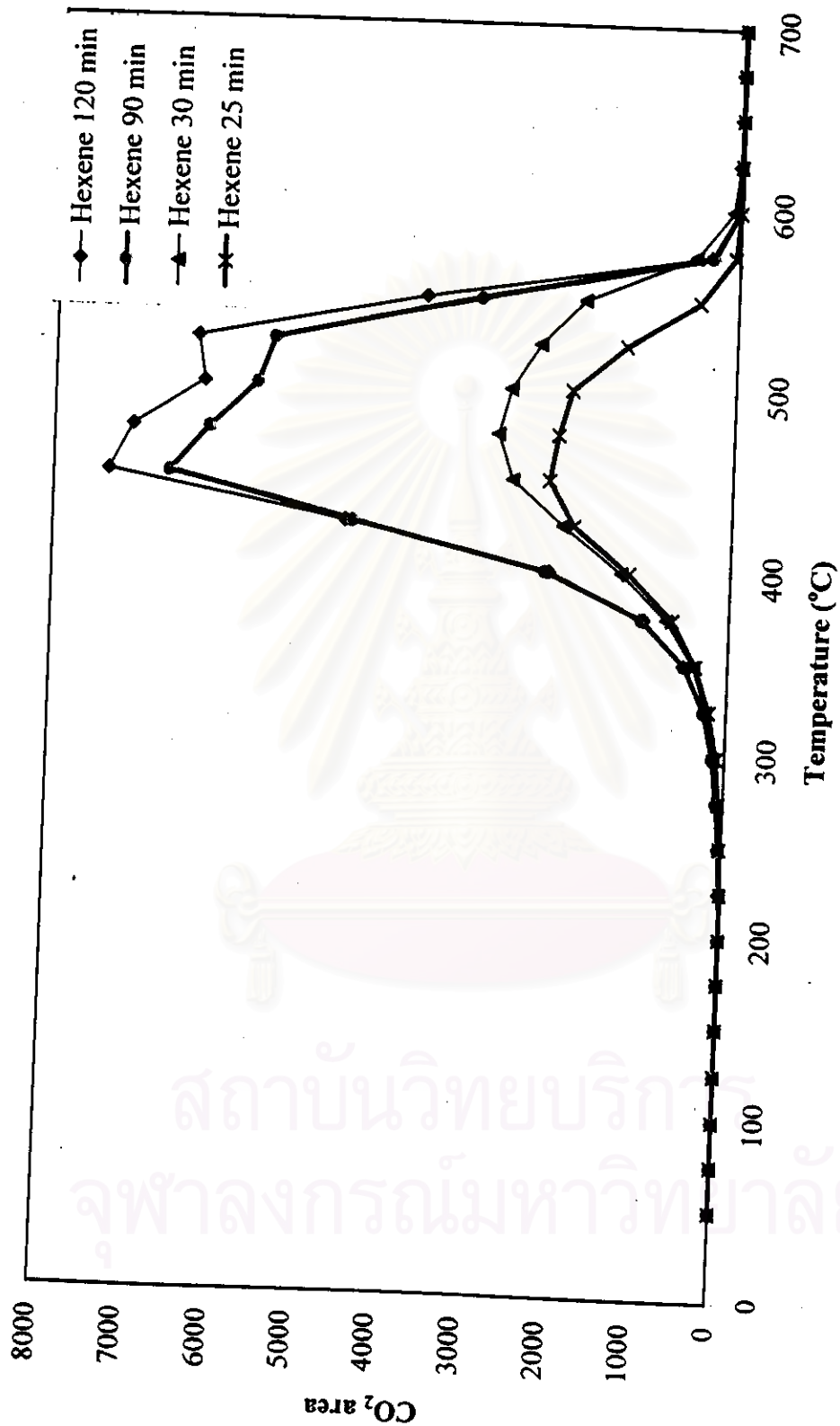
Figure 5.13 TPO spectra for hexane and hexene dehydrogenation over 0.09 g. of 0.3wt%Pt 0.3wt% Sn 0.6wt%K /Al$_2$O$_3$ at 500 °C, 120 min., GHSV= 22500 hr^{-1} .

Figure 5.14 TPO spectra for hexene dehydrogenation over 0.09 g. of 0.3wt%Pt 0.3wt% Sn 0.6wt%K /Al$_2$O$_3$ at 500 °C, GHSV= 22500 hr^{-1} .
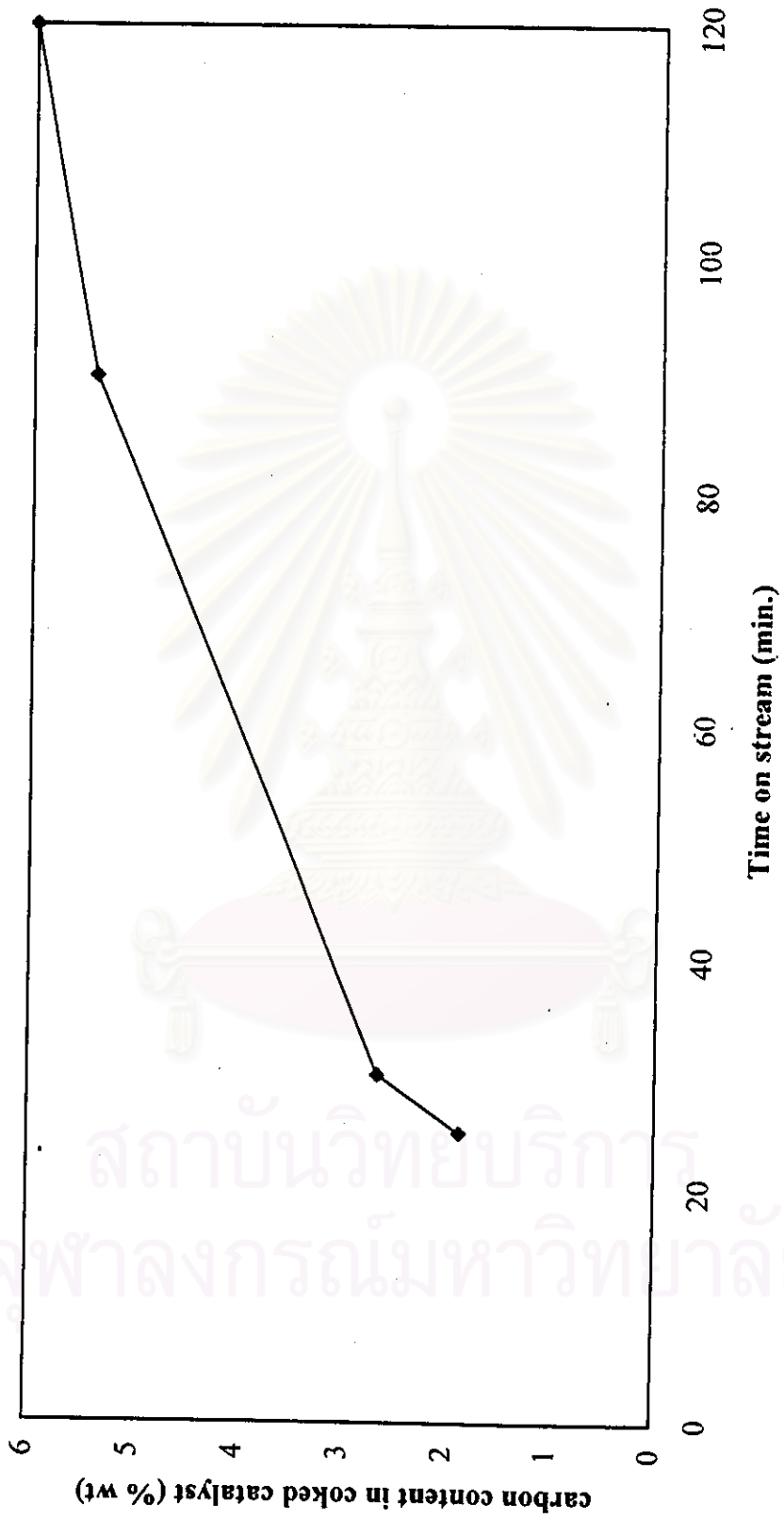
Figure 5.15 Coke content from hexene dehydrogenation for different values of time on stream, operated at 500 °C.

matched completely as shown in Figure 5.16. Both hexane and hexene dehydrogenation included thermal cracking gave the perfect match in TPO pattern of coke, like what was considered before for thermal cracking was excluded (compare Figure 5.12 and Figure 5.16). This could be concluded that coke formation was not affected by thermal cracking neither on metal nor support. This results agree to the conclusion of parallel mode to this long chain hydrocarbon. The second aspect showed coke formed by long chain hydrocarbon (6%) over 2 hr. was about three times coke formed by short chain hydrocarbon (2.3%) over the same TOS. The conclusion then provides long chain hydrocarbon could generate coke in many ways, such as thermal cracking, catalytic cracking, cyclization, and aromatization, compared to short chain hydrocarbon.
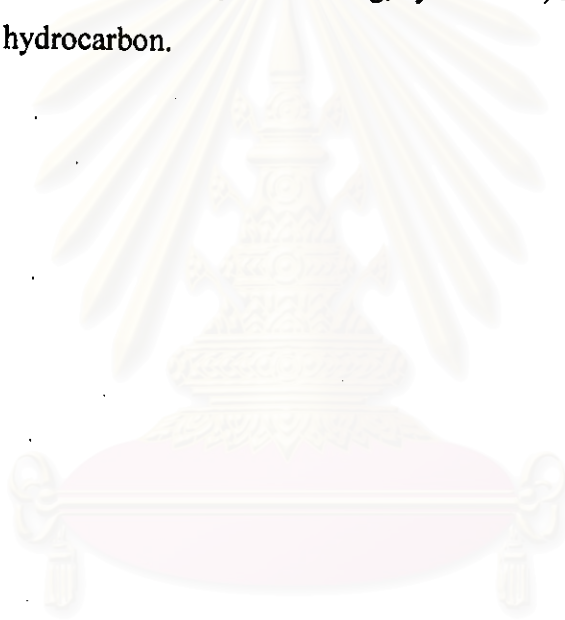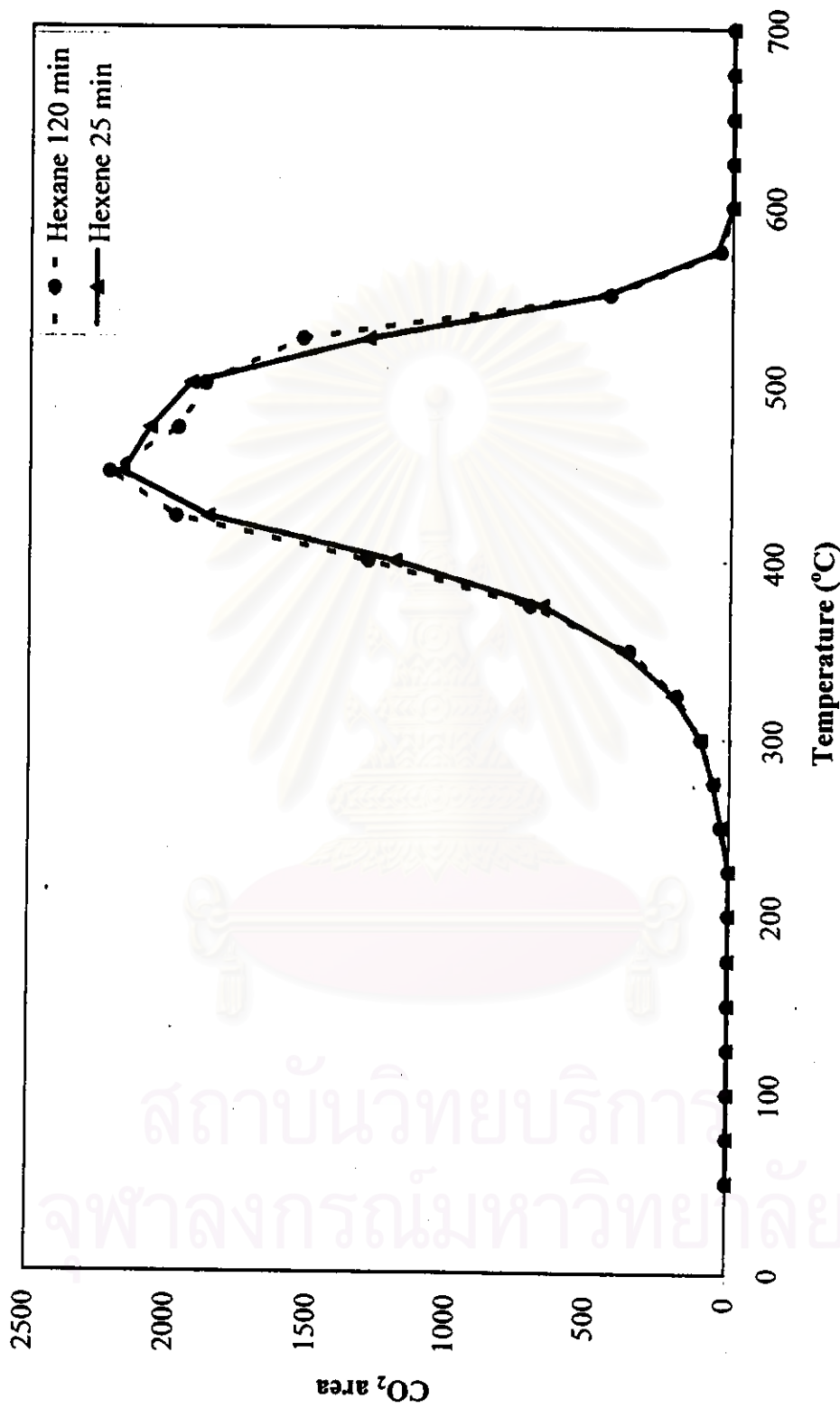
Figure 5.16 TPO spectra for hexane and hexene dehydrogenation over 0.09 g. of 0.3wt%Pt 0.3wt% Sn 0.6wt%K /Al$_2$O$_3$ at 500 °C, GHSV= 22500 hr^{-1} .

5.2.3 Simplify mechanism of coke formation.

From the results above, it was observed that the results of propane and propene dehydrogenation differed from the other pairs of alkane and alkene. For example, conversion of propene was very lower, but percent selectivity of coke formation high. In contrast, the other pairs of hydrocarbon conversion of alkene was higher than conversion of alkane while selectivity showed opposite.

In this section, a simplified mechanism of coke formation is established. This mechanism is simplified by the same experimental data by eliminating some effects such as operating temperature and types of reactants. The mechanism can be ultilized in practices, which differs from the previous model which ultilizes in scientific applications.

In propane and propene dehydrogenation, propadiene was found in both of reactions. As known, propadiene was an active substance, and the hypothesis that propadiene presents as a coke precursor was established. Propadiene was found in such a small amount out of whole gas products, averaged 1.14%. This result indicated that adsorbed propadiene was hardly to desorb to the gas phase nor desorb into a trace. For that reason, the adsorbed propadiene could develop to form coke.

According to very low activity on propene dehydrogenation compared to propane dehydrogenation, it then was hardly used to study in further. It was agreed to study the activity on propane dehydrogenation over different gas hourly space velocities in order to clearify the relationship of coke selectivity and reaction rate.

Three space velocities (11,250, 22,500 and 45,000 hr^{-1}) were carried out in the reaction. It was already proven that these conditions already excluded mass transfer limitation region. Figure 5.17 shows the general information that lower volumetric flow rate will increase the conversion of the reaction. The results were due to longer contact time between reactant species and catalyst surface. The computations were
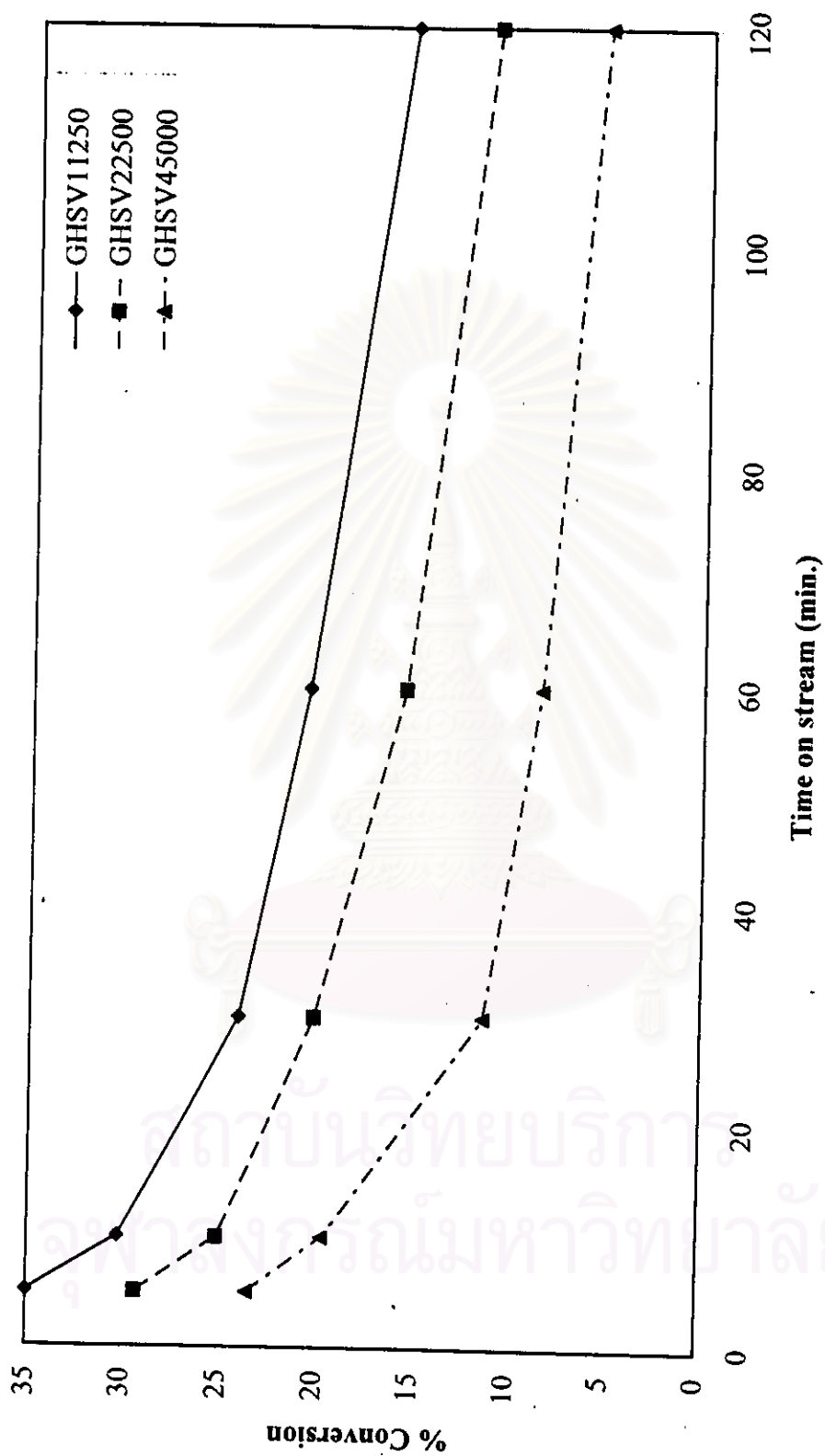
Figure 5.17 % conversion on propane dehydrogenation over 0.3wt%Pt 0.3wt% Sn 0.6wt% K /Al$_2$O$_3$ as a funtion of time, at 500 °C.
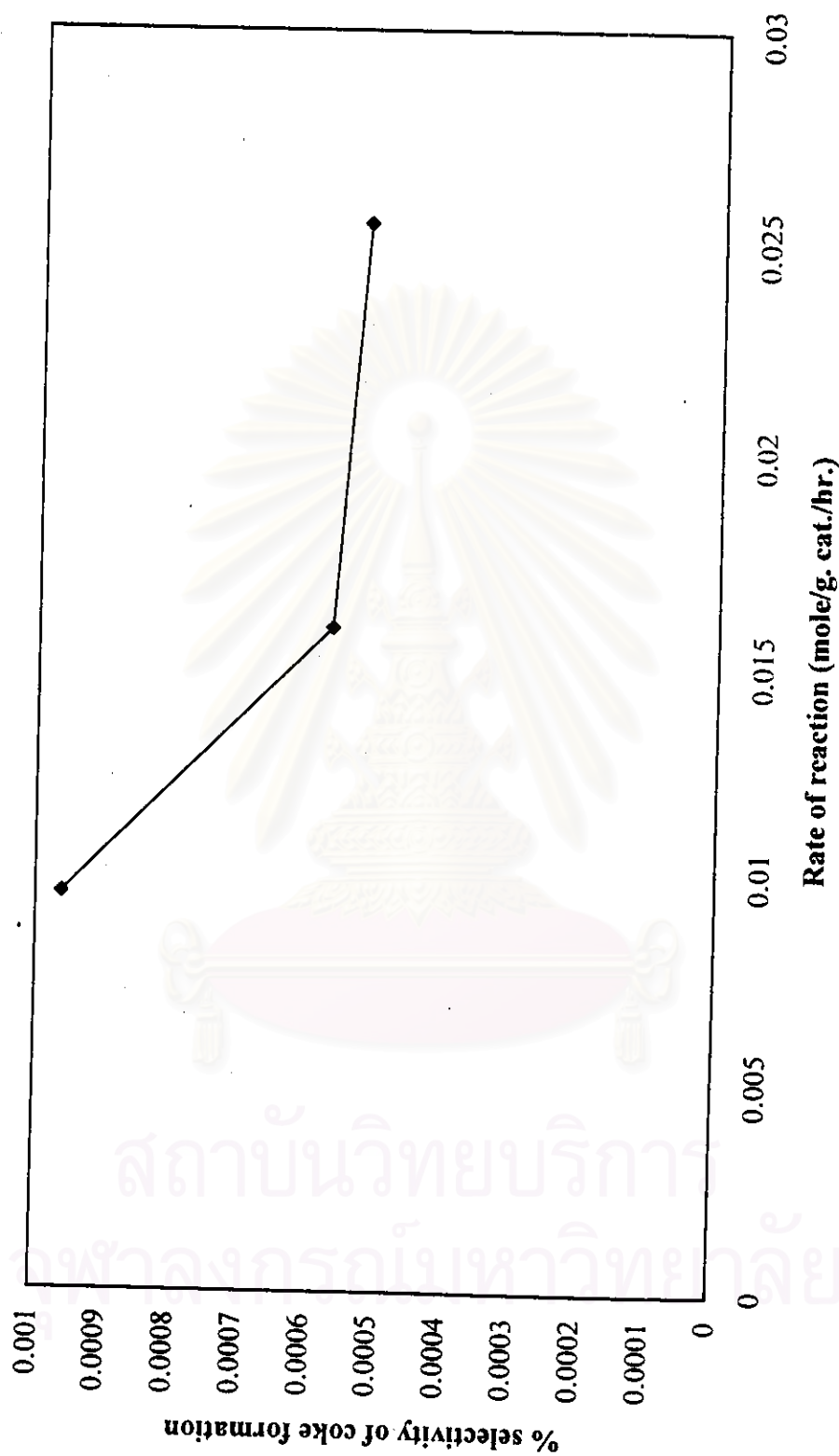
Figure 5.18 Relationship between rate of reaction (5 min.) and % selectivity of coke formation on propane dehydrogenation over 0.3wt%Pt 0.3wt% Sn 0.6wt%K /Al₂O₃ at 500 °C, 120 min. .

contact time between reactant species and catalyst surface. The computations were done over coke selectivity and reaction rate. Lower rate of reaction provided higher selectivity of coke formation as shown in Figure 5.18. From the results above, it provided a new simple mechanism of coke formation. This mechanism shown in Figure 5.19 claimed that the higher production rate of coke precursor appeared in the gas products, the lower coke deposited on the catalyst surface is. On the other hand, if the deactivation is found significantly, product of coke precursor would be found in a amount of trace. This mechanism can also suit to explain any reactions. It also suits for each pair of alkane and alkene not matter thermal cracking effects the reaction. What is found from the relationship between coke selectivity and reaction rate can be useful in practice. The data could suggest roughly the condition which gave low coke deposition. In this study, only propane dehydrogenation was determined. The (roughly) recommended condition provided low selectivity of formation will be at any rate of reaction higher than 0.0158 mole/g. catalyst/hour.
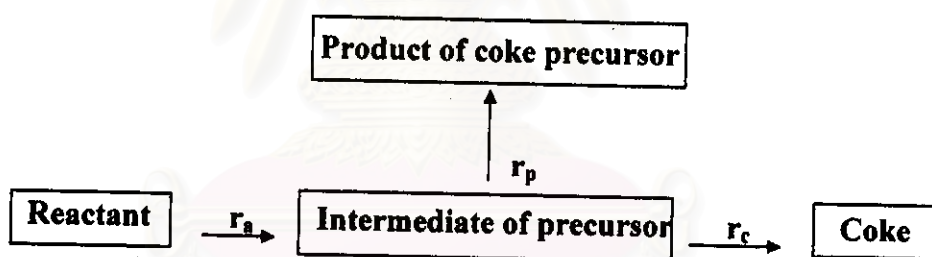

Figure 5.19 Simplify mechanism of coke formation.