CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the experimental results are analysed. The effects of sample weight on TPO spectrum are presented in section 5.1. The effects of metal and support on coke combustion are reported in section 5.2. Section 5.3 demonstrates the coke accumulation on $Pt\text{-}Sn/A_2O_3$ catalyst. Finally, section 5.4 exhibits the effect of coke deposition on the pore structure of $Pt\text{-}Sn/Al_2O_3$ catalyst.

In general, the activity of a propane dehydrogenation catalyst decreases with time on stream due to the deactivation by coking. Figure 5.1 presents the monitoring of $Pt\text{-}Sn/Al_2O_3$ catalyst activity on propane dehydrogenation which is carried out under the temperature of 600°C and atmospheric pressure. No hydrogen exists in the feed stream in order to minimize the parameters for a reaction proceeding. From the result, $Pt\text{-}Sn/Al_2O_3$ catalyst has very high initial activity followed by high deactivation rate. After that its activity sharply drops. After 40 minutes on stream, the conversion is very low, surprisingly being always more than zero. Even though, the activity decreases gradually, it has never disappeared for entirely length of run.

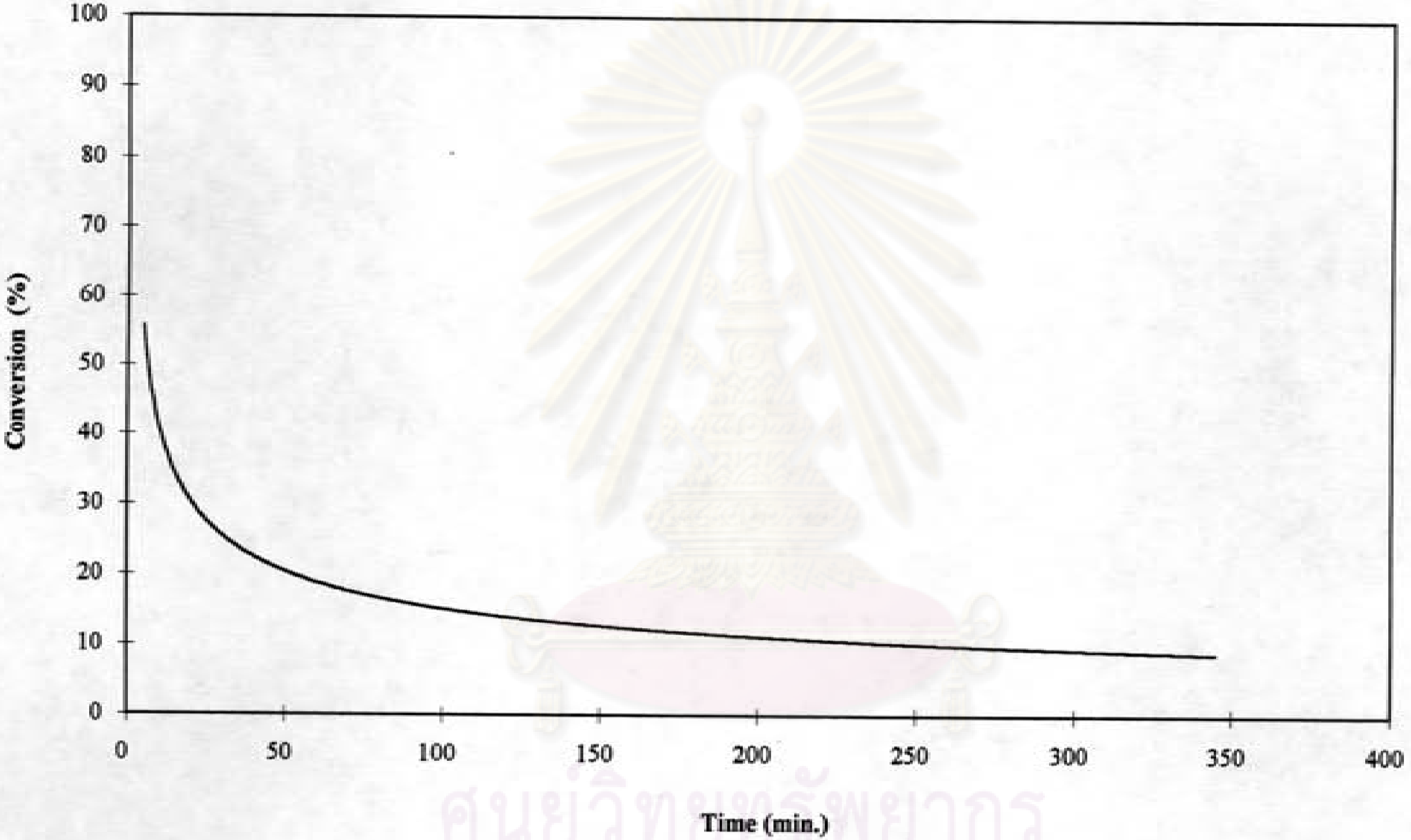

Figure 5.1 Typical deactivation pattern of a Pt-Sn/Al_2O_3 catalyst on propane dehydrogenation reaction at 600°C, H_2/HC=0 , GHSV = 22570/hr

According to the aims of this work, the deposited coke is the object of considerable material to be characterized for more understanding of the coke nature in order to find a way to reduce coke deposition. Prior to analysis, coked catalysts are usually prepared by propane dehydrogenation reaction. The feed stream is 20% propane-nitrogen mixture flowing through a catalyst bed at 30 cc/min. The coking conditions are 600°C at atmospheric pressure and 22570/hr gas hourly space velocity (GHSV). No hydrogen exists in the feed stream. Three hour coked sample was analyzed by TPO technique.

The Temperature-Programmed Oxidation technique is an effective method to determine the total amount of carbon containing in a sample by measuring the amounts of carbon dioxide produced. In order to determine the carbon weight , the calibration curve of carbon dioxide is required as shown in the appendix A. It is expressed in the term of gram of carbon or percent of carbon in a sample as requirement. Typical Temperature-Programmed Oxidation result from deactivated propane dehydrogenation catalyst is illustrated in figure 5.2.

Figure 5.2 generally shows two significant oxidation zones. The first peak locates at about 480°C , and the second is at about 550°C. It has been shown that (Atchara, 1995) the peak at 480 °C belongs to coke deposit on metal sites and the second one belongs to coke deposit on acidic sites. In conclusion, both peaks locate in high combustion temperature region. The summation of area on TPO curve corresponds to approximately 5.96 mg carbon or 6.62 wt.% carbon based on 90 mg of coked catalyst sample.

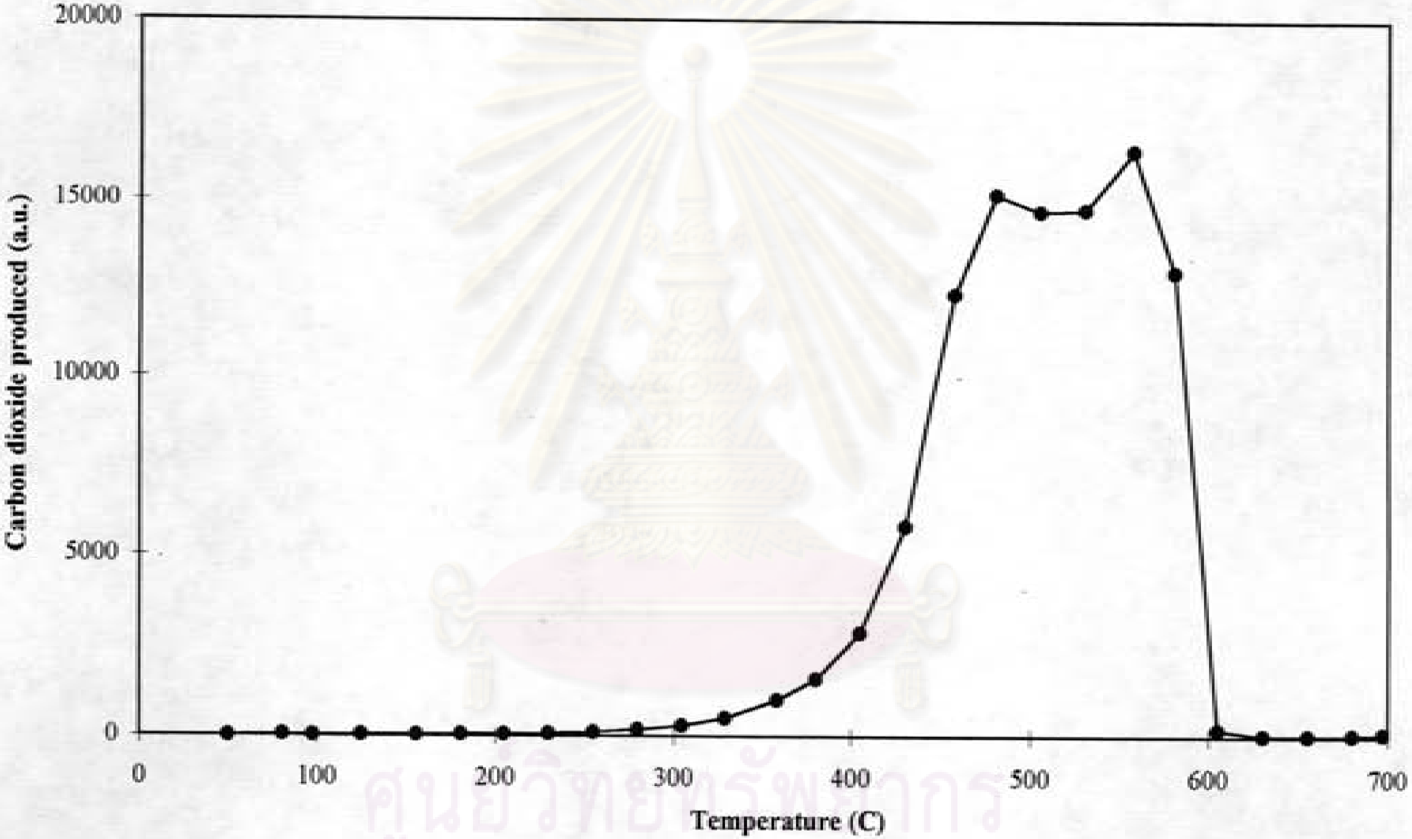

Figure 5.2 TPO profile of coked Pt-Sn/Al_2O_3 catalyst after 3 hr for dehydrogenation of propane at 600°C , coked sample 90 mg

5.1 Effect of Sample Weight on TPO Spectrum

5.1.1 Coked catalyst

Varying the sample weight on TPO technique was carried out so as to study its role on the combustion characteristics of coked catalyst samples. For coked Pt-Sn/Al_2O_3 catalyst, sample weight influence on TPO spectrum is clearly observed as demonstrated in figure 5.3. The results were obtained from 6 hr coked catalyst which contains a large amount of carbon in this study. The normal sample sizes, 90 mg, used for TPO technique did not achieve the actual combustible temperature analysis for this sample. Thus, a smaller sample weight, 35 mg, was used. The case of 35 mg coked catalyst allows a good resolution of the two peaks: one of which is around 500°C and the other is around 550°C. The estimated total amount of carbon of both samples are 9.77 mg or 10.86 wt.% carbon and 3.46 mg or 9.9 wt.%carbon for 90 mg and 35 mg coked catalyst, respectively, which is nearly equal. However, the combustible properties found for 6 hr coked catalyst are considered to be the highest temperature in the study.

The study has shown the limitation of TPO technique which depends upon the amount of carbon containing in the samples. Thus, the coke loading in samples should be account for the interpretation of TPO results.

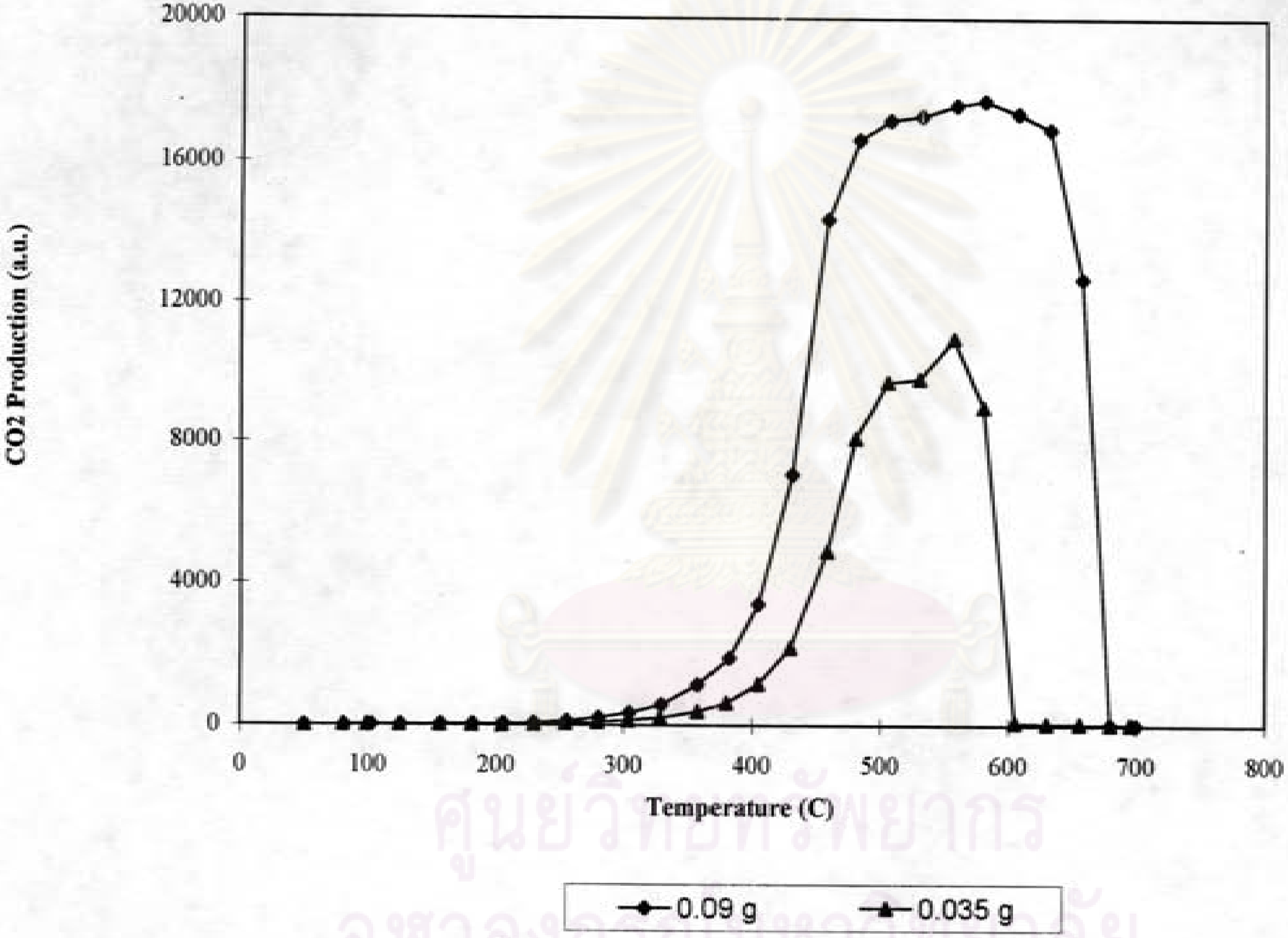

Figure 5.3 Influence of coked catalyst weight on TPO spectrum

5.1.2 Coke from catalyst digestion

In this section, coke was separated from coked catalyst sample by metal and support digestion. In figure 5.4 the coke samples from catalyst digestion are divided into three different sample weight, 2.9 ,5.1 and 8.7 mg of coke samples. From the results, all TPO curves show the similarly combustion pattern. One peak was observed for all three samples and it was found that the peaks located at nearly range which are 580°C, 608°C and 608°C for 2.9, 5.1 and 8.7 mg of coke samples, respectively. If higher sample weight is used, it certainly will not completely burnt within a short time. The proper sample weight will provide the actual characteristic of TPO spectrum. This result indicates that in order to minimized the role of sample weight on TPO spectrum the amount of sample should not too high, e.g. less than 10 mg in this case. However, too small sample weight will cause difficulty in handling.

In figure 5.5 the initial range of coke combustion is illustrated. The figure shows that the three sample sizes have the same patterns of combustion characteristic on TPO curves. A little declines are also observed at 380°C. Then, carbon dioxide produced increases rapidly for all three samples. Unfortunately, no adequate experimental data are obtained to interprete more details.

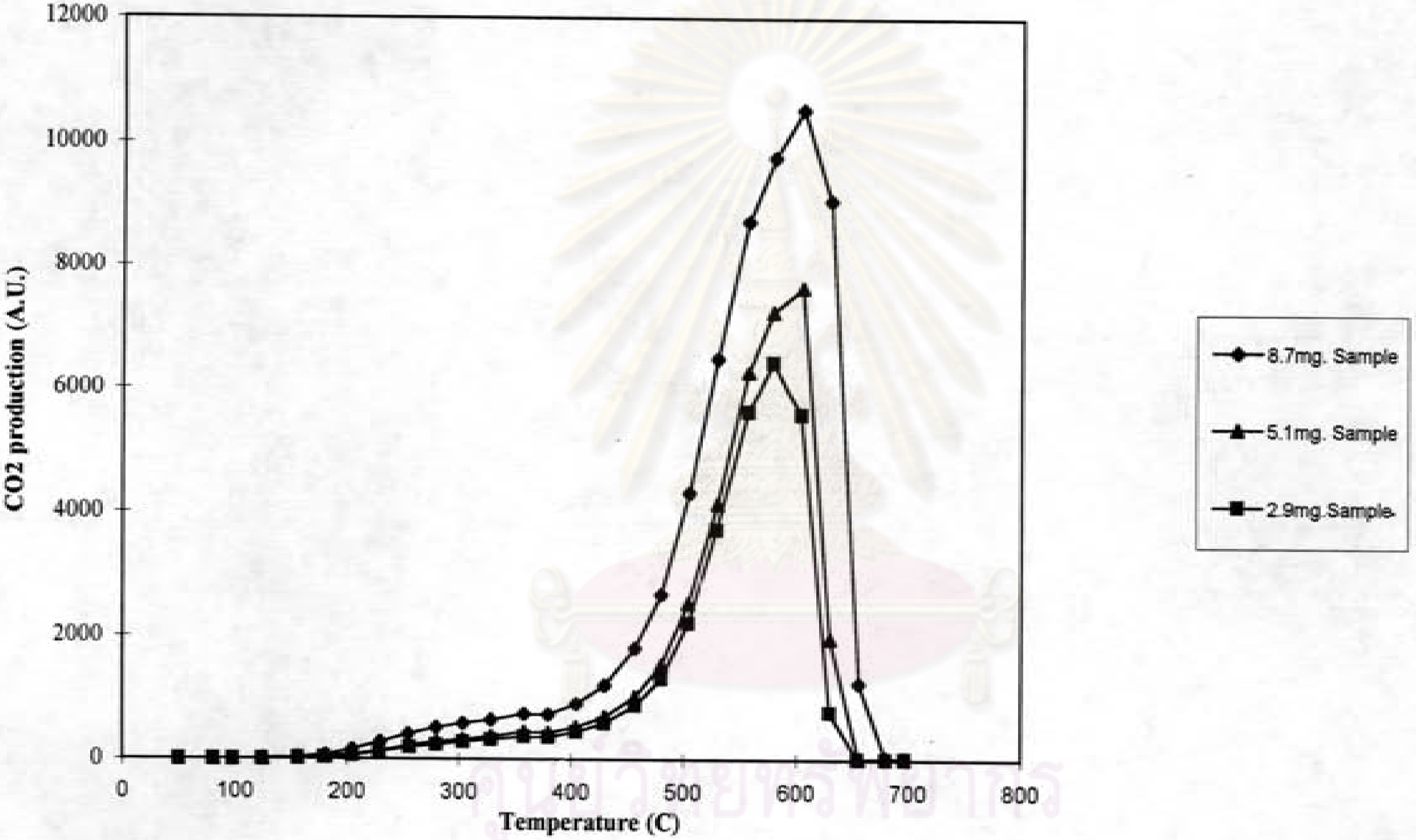

Figure 5.4 Effect of weight of coke from catalyst digestion on TPO spectrum, coke from 3 hr and 600°C propane dehydrogenation reaction

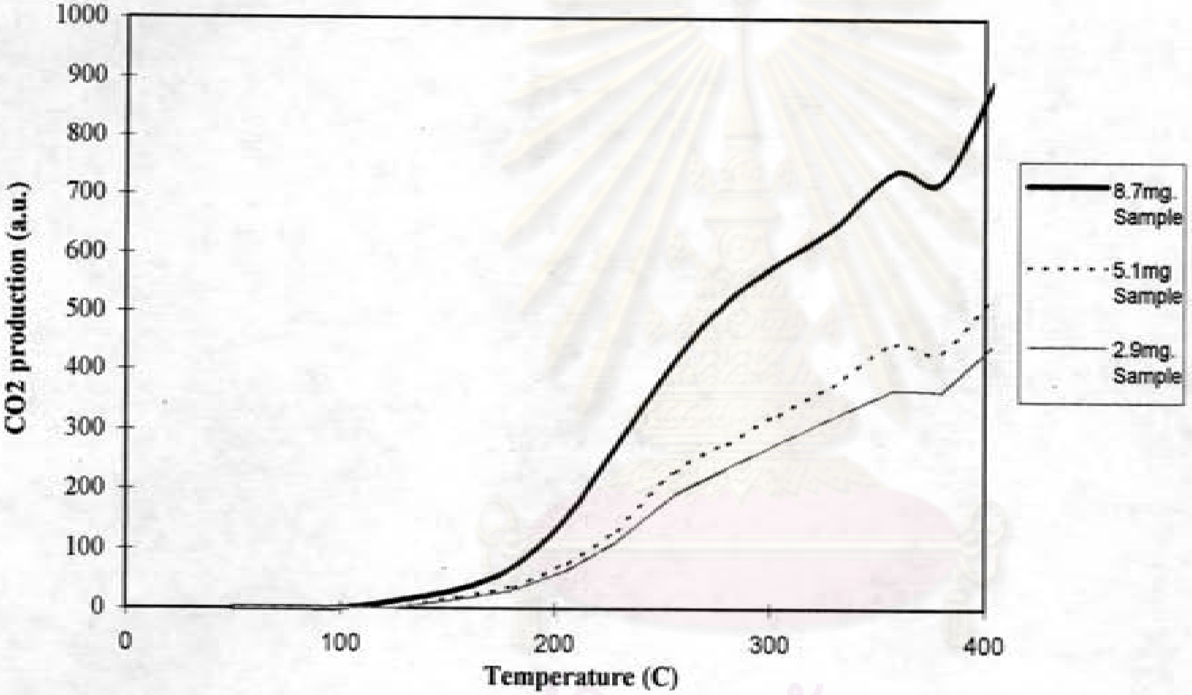

Figure 5.5 Effect of weight of coke from catalyst digestion in the range of 0-400°C of figure 5.4

5.2 Effect of Metal and Support on Coke Combustion

Refer to Atchara (1995) and the other workers, they have never mentioned about coke combustion system without metal and support presence. The kinetic parameters of coked combustion approximated by Atchara (1995) did not expressed clearly the detail of mechanism on coke combustion.

In case of metal and support disappearance it is of interest to investigate the combustion characteristic of coke samples by means of TPO technique. Two coke samples are prepared by two different ways. One is coked catalyst and the other is coke from catalyst digestion. In figure 5.6, comparison between TPO result, obtained from coked catalyst and coke from catalyst digestion, is demonstrated. The figure shows that disappeared metal and support have obviously effect on the characteristic of coke combustion. A high temperature coke is observed on the coke sample from catalyst digestion. On the other hand, two types of high temperature coke are found on TPO results. It means that the two peaks observed are caused by metal and support. It is probably that high surface area and porosity properties of support promote the coke combustion by increasing coke surface area contacted to oxygen and Pt may catalyze the oxidation. The starting point of carbon dioxide production can reasonably confirm the role of Pt in catalytic oxidation for the case of coke sample from catalyst digestion, while the first oxidation zone of coked catalyst were able to be detected earlier. Hence, coke could be removed easily if the metal and support are present.

Estimated amount of carbon on coked catalyst sample and coke sample from catalyst digestion are 5.96 mg or 6.62 wt.% carbon, and 2.15 mg or 42.25 wt.% carbon, respectively. These suggest that both of them contain the amount of carbon in the acceptable range and they were completely burnt. However, TPO spectrum was able to be normalized in order to be compared the quantity of total carbon in case of different coke containing. In addition, it is worth noting that coke from catalyst digestion and coked catalyst have their own combustion characteristic as shown in figure 5.7 which focuses on the comparison between TPO results in the range of 50-400°C.

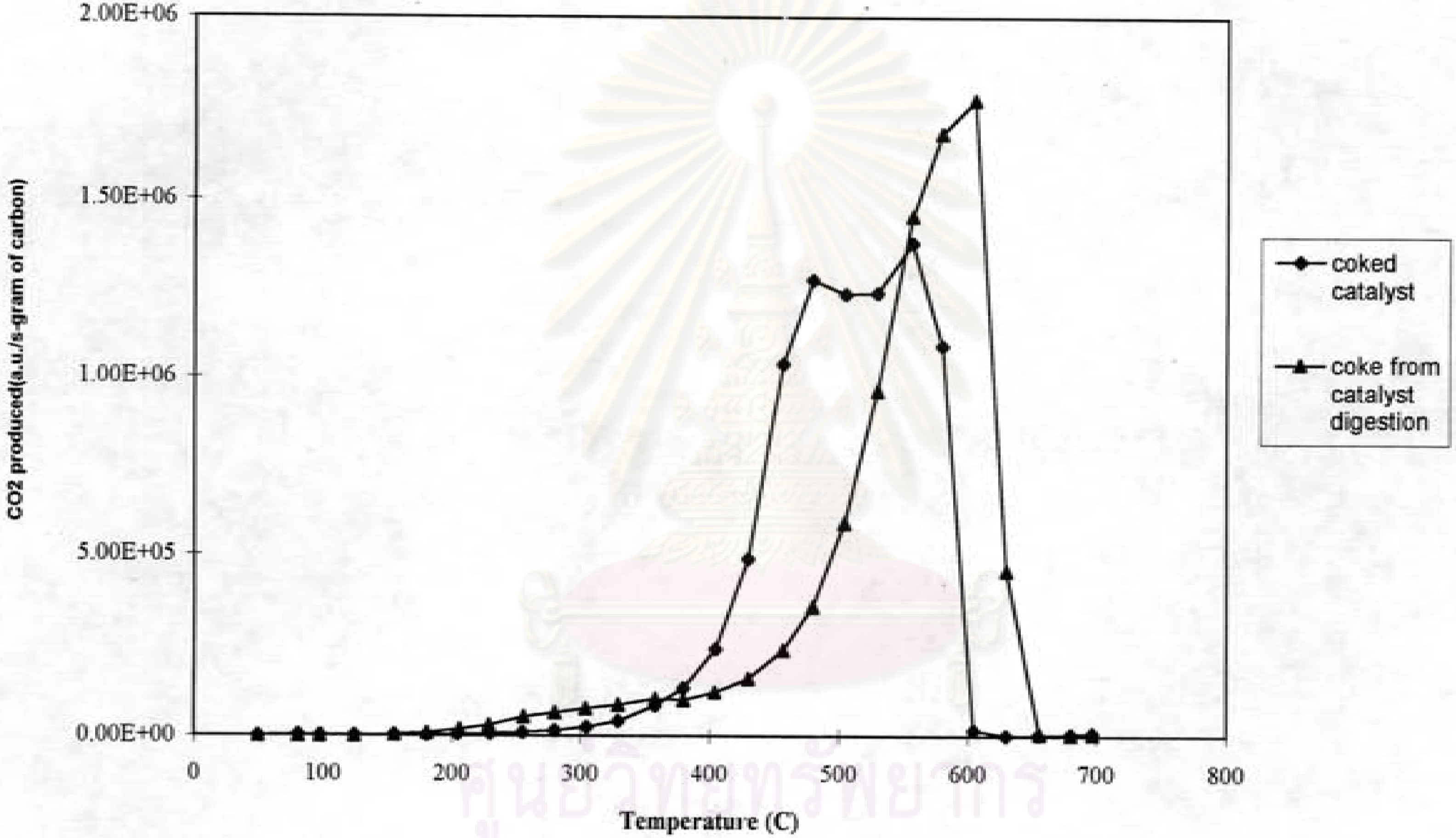

Figure 5.6 Normalized TPO curve of coke from catalyst digestion and coked Pt-Sn/Al_2O_3 catalyst, 3 hr and 600°C on propane dehydrogenation reaction

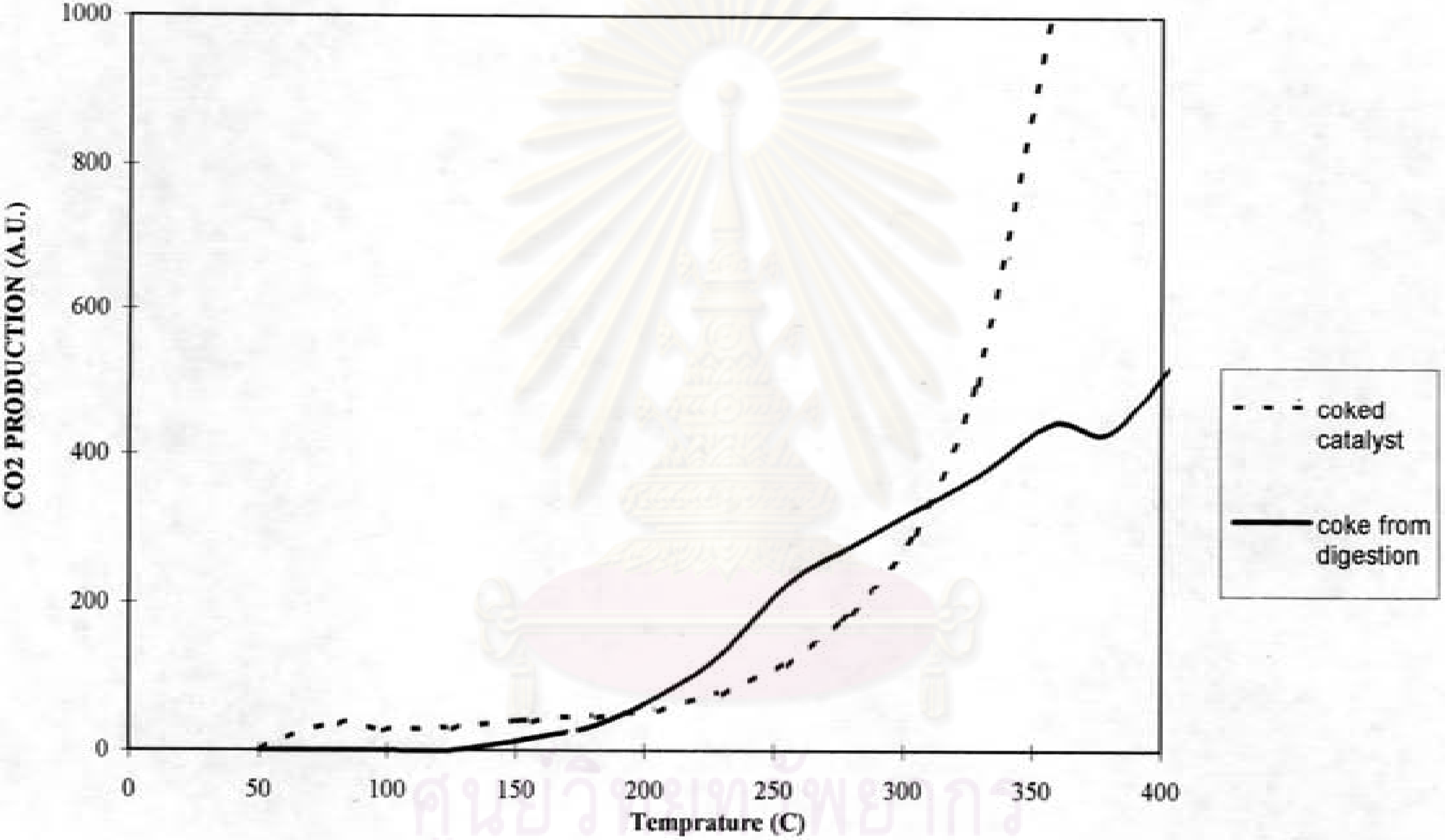

Figure 5.7 Comparison of coke from catalyst digestion and coked Pt-Sn/Al_2O_3 catalyst 3 hr and 600°C on propane dehydrogenation reaction

5.3 Coke Accumulation on Pt-Sn/Al_2O_3 Catalyst

The coke accumulation on the catalyst was investigated in this study. All samples in the experiment were prepared by varying process time on propane dehydrogenation at 600°C and atmospheric pressure. The total flow rate of gases in the feed was 22,570/h gas hourly space velocity (GHSV). The fundamental research using a fixed bed reactor is practical for laboratory scale. Temperature-programmed oxidation was the technique employed for the quantity and quality of the various types of coke deposits.

Based on the same coked catalyst sample weight, 90 mg, the TPO result provides the discrepancy of burning characteristics and coke content among 6 coked catalyst samples as illustrated in figure 5.8. Barbier(1988) reported that the accumulation of carbonaceous deposits on the support was the result of polymerization on the acidic sites of the alumina support. Metal promoted coke accumulation on the catalyst by limitation of hydrogen, yielding stable dehydrogenated carbonaceous deposits. In figure 5.8, the higher combustion temperature can be inferred to the more stable dehydrogenated carbonaceous deposits than that lower one.

Certainly, the amount of coke in samples usually increase with process time as demonstrated in figure 5.9, while there are justly alternation between the various types of coke sample. These mean that the property of each samples is different. 5 min. coked sample is well defined soft coke which can be removed at the lowest combustion temperature while the others burnt at higher temperature are defined as harder coke in this paper. The results show that the position of two peaks are shifted toward higher temperature for the higher process time.

From figure 5.8, one can see that the first peak, superimposes on the second peak and indicates the amount of soft coke, rapidly develops during the initial period of reaction but slightly changes after 40 minutes. This phenomenon is not observed for the second peak, which indicates the amount of coke on the support. The second peak becomes higher with increasing process time and the total carbon of the coked samples seems to be increase linearly after 40 minutes in figure 5.9.

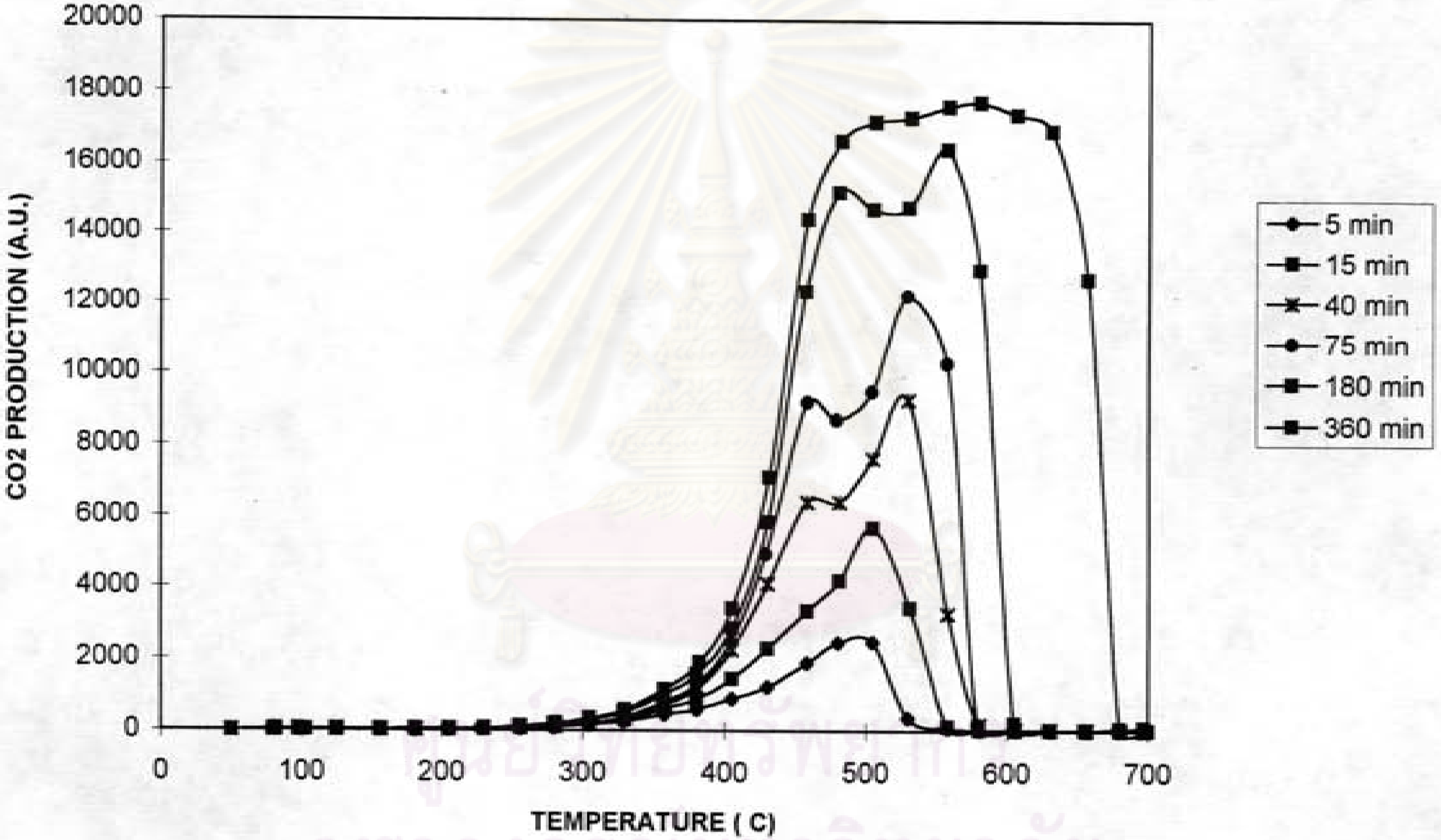

Figure 5.8 TPO profile of coked Pt-Sn/Al_2O_3 catalyst, 600°C reaction, weight of coked sample = 90 mg.

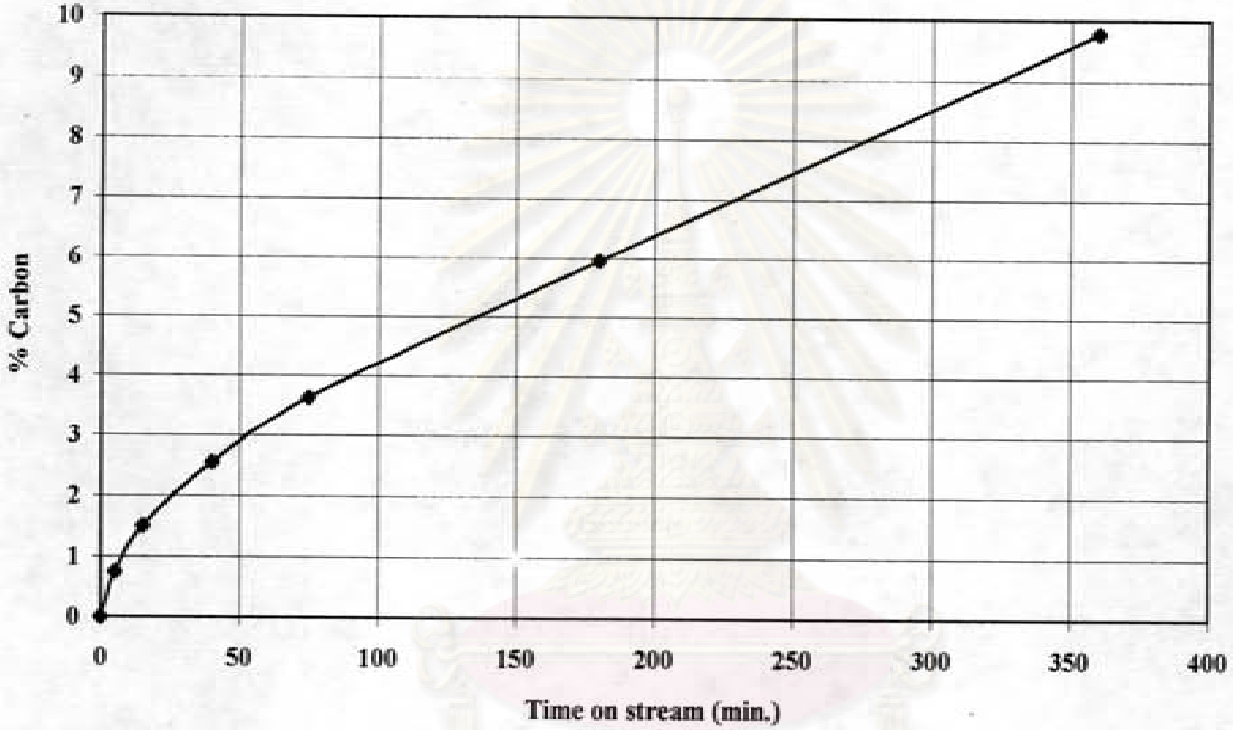

Figure 5.9 Carbon content on deactivated Pt-Sn/Al_2O_3 catalyst, propane reaction at 600°C, GHSV = 22570/hr, H_2/HC = 0

5.4 Effect of Coke Deposition on Pore Structure of Pt-Sn/Al_2O_3 catalyst

Coke deposition affect the transport of reactants and products in porous catalyst. Whether deposition of coke restricts the pore openings or blocks these of completely is still a subject of uncertainty and will depend on the extent of coke formation, the morphology of the coke forming reaction and the structure of the catalyst itself (Al-Bayaty, 1994). Thus, this section present the investigation of effect of coke deposition on pore structure of Pt-Sn/Al_2O_3 catalyst which was mostly used for propane dehydrogenation reaction.

Fresh (uncoked) Pt-Sn/Al_2O_3 catalyst

BET surface area and pore size distribution for two samples of fresh Pt-Sn/Al_2O_3 catalyst were first measured to check the repeatability of the measurement technique. The results obtained shown in figure 5.10 indicate that Pt-Sn/Al_2O_3 catalysts have a wide range of pore radii from 20 °A to 1100 °A and high surface area of 290 sq.m./g. The maximum number of pore size are 60-70 A. The results in figure 5.10 exhibit that the pore size distribution of the two samples were repeatable. Total pore volume of both samples are 0.524 and 0.521 cc./g.

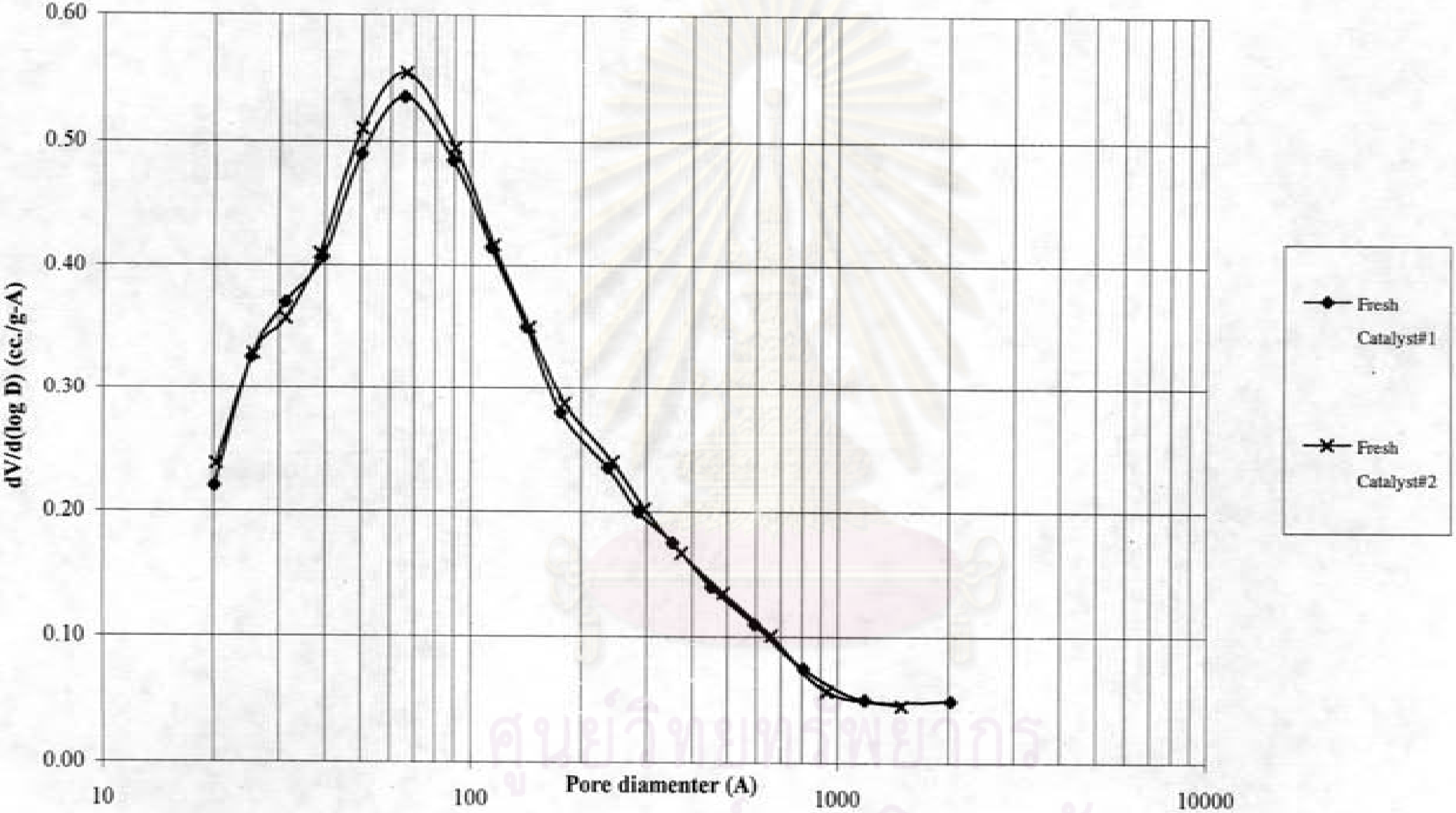

Figure 5.10 Pore size distribution of fresh Pt-Sn/Al_2O_3 catalyst

Coked catalyst

BET surface area and pore size distribution measurements following coking of the propane dehydrogenation catalyst were performed in this study. The results illustrated in figure 5.11 are the pore size distribution curve of various coked catalyst. The amount of coke observed is between 2-10 wt.% and the coked samples were prepared by varying time on stream. The pore size distribution data demonstrates that the total pore volume reduces because of coke deposition. This phenomenon was categorized as pore plugging. Coke from propane dehydrogenation reaction seems to uniformly spread over the surface in pores of the catalyst, whatever the time on stream are.

From table 5.1, a reduction of total pore volume are about 1.92% occurs in 30 min. coked sample at a coke deposition of 2.2 wt.% carbon, whereas the pore volume of 60 min. coked sample is reduced rapidly by 10.75 % at a coke level of 4.03 wt.% carbon. The comparison between fresh catalyst and 30 min. coked catalyst demonstrates that coke accumulated and mainly blocked the small pore whose radii are between 20-40°A. After 60 minutes of operation, wide range of mesopores were blocked as pore size distribution data and these cause the significant drop of pore volume. The 180 min. coked catalyst sample shows a little drop of pore volume. The 360 min. coked catalyst sample was deactivated by coke which accumulated and obviously blocked the huge pores on the catalyst. Therefore, the most reduction of total pore volume, 23.22 %, was found for 360 min. coked catalyst containing 9.9 wt.% carbon. It means that 70% of pore volume on the catalyst is exist after prolong operation and there are a large amount of void volume for reactant diffusion. However, the pore size distribution and BET surface area data correspond to the deactivation curve, figure 5.1, which shown the constant remaining of catalytic activity.

The possibility of pore collapse occurring was negligible here, consequently, it was verified by treating Pt-Sn/Al_2O_3 catalyst in Ar at the conditions of this study. The pore size distribution data of the later sample are reported accompanied with of fresh catalyst data in figure 5.12.

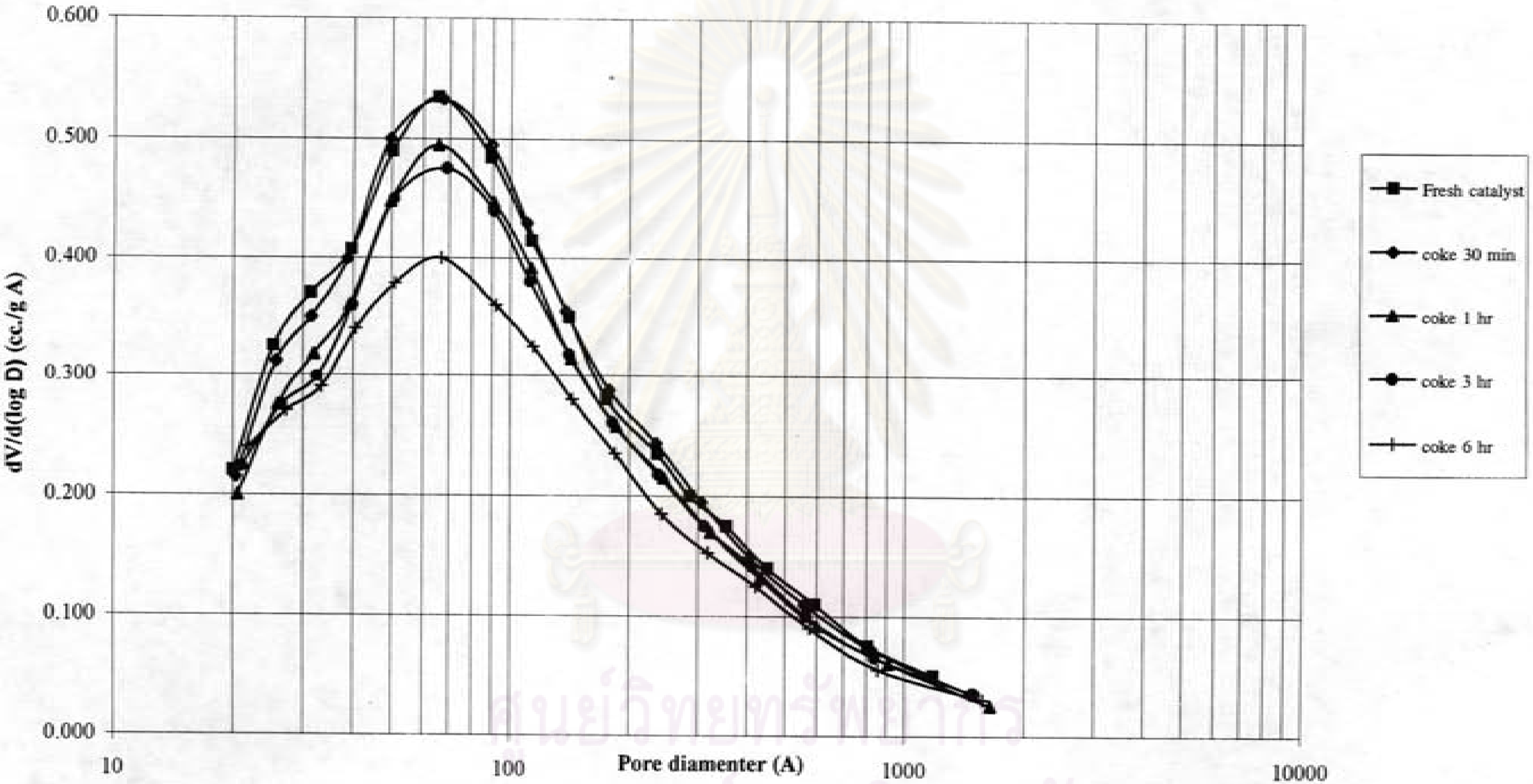

Figure 5.11 Pore size distribution of coked Pt-Sn/Al_2O_3 catalyst

Table 5.1 BET surface area, total pore volume and carbon content of coked samples

SAMPLE	BET surface area (sq.m./g)	Total pore volume(cc/g)	% reduction of volume	% carbon
Fresh Pt-Sn catalyst	287.17	0.521	-	-
30 min. coked sample	279.82	0.511	1.92	2.2
60 min. coked sample	258.27	0.465	10.75	4.03
180 min. coked sample	256.60	0.456	12.48	6.62
360 min. coked sample	238.51	0.400	23.22	9.90

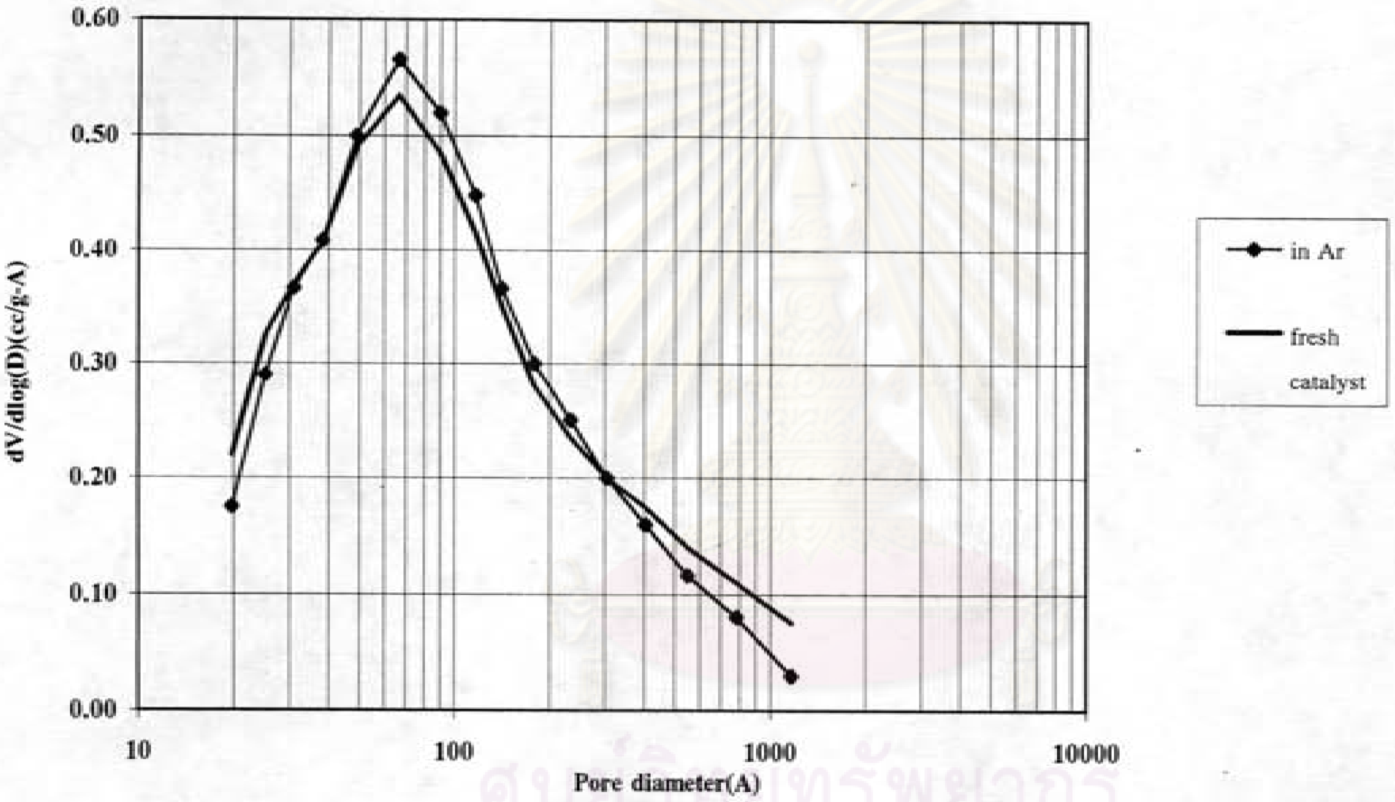

Figure 5.12 Pore size distribution of Pt-Sn/Al_2O_3 catalyst treated at 600°C in Ar for 6 hr.