

## CHAPTER V

### THE EXPERIMENTAL RESULTS AND DISCUSSIONS

In this chapter, the experimental results are analysed. The location, combustion temperature and behaviour of reversible coke are presented in section 5.1. The effects of hydrogen / hydrocarbon mole ratio are reported in section 5.2. Section 5.3 demonstrates the effects of variation of reaction temperature. Finally, section 5.4 presents the estimated kinetic parameters of the coke combustion process.

In this research, the dehydrogenation reaction of propane to propylene in a micro reactor is chosen for the preparation of coked catalysts. One type of dehydrogenation catalyst which used was Pt/Al<sub>2</sub>O<sub>3</sub>. The coke catalyst was characterized by Temperature - Programmed Oxidation (TPO.) technique.

#### **5.1 The Deposit Location, Combustion Temperature and Behaviour of Reversible Coke.**

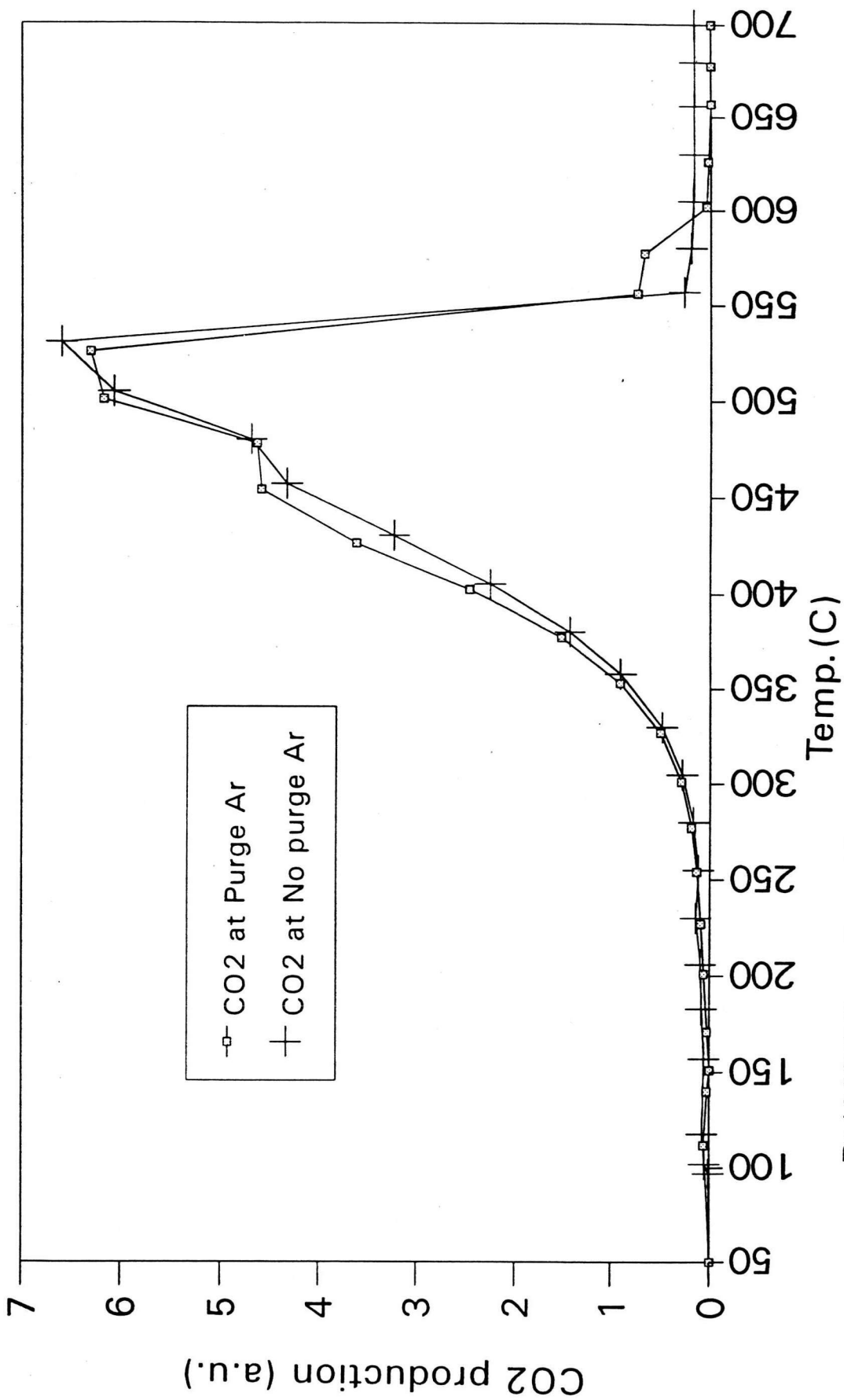
The Temperature - Programmed Oxidation technique can give information of the total amount of coke by measuring the amounts of

carbondioxide produced. The amounts of reversible coke and irreversible coke are categorized by the peak area of low and high oxidation temperatures, respectively. Typical Temperature - Programmed Oxidation results are illustrated in figure 5.1.

The result clearly shows three oxidation zones, the first peak locates at about 110 °C which is in the region of low oxidation temperature zone. This peak represents the amounts of reversible coke or coke precursor. The second is at about 450 °C and the last is at about 550 °C. Both peaks, which locate in high combustion temperature region, represents the irreversible coke deposit on metal sites and support respectively.

To verify the combustion temperature of the reversible coke (1<sup>st</sup> peak), two cool down methods were performed. In the first method, which was used before by Somsak (1992), the catalyst was allowed to cool down immediately when the reaction gas was switched to argon. In the second method, after switching to argon, the catalyst temperature was still maintained at the reaction temperature for at least 2 hours, before being allowed to cool down, to remove the reactant which might still remain on the catalyst surface.

Comparison between Temperature-Programmed Oxidation results, obtained from both experiment, does not demonstrate any discordant, especially the location and magnitude of the first peak which still located at around 110°C.



Pt/Al<sub>2</sub>O<sub>3</sub> at Rxn. Temp. = 600 C, H/C = 0, Time = 40 min.

Figure 5.1. Effect of Argon purging before/after reaction finished.

This result confirm that the first peak should be resulted from the burning of coke precursor rather than the reactant adsorbed on the dehydrogenation catalyst. Good agreement was obtained between location and temperature of this coke in this study, as well as in the previous work (Somsak,1992). But disagreement was obviously from the work of Liu which presented the location of this coke at a temperature around 300 °C which is similar to that indicated by Barbier (1987).

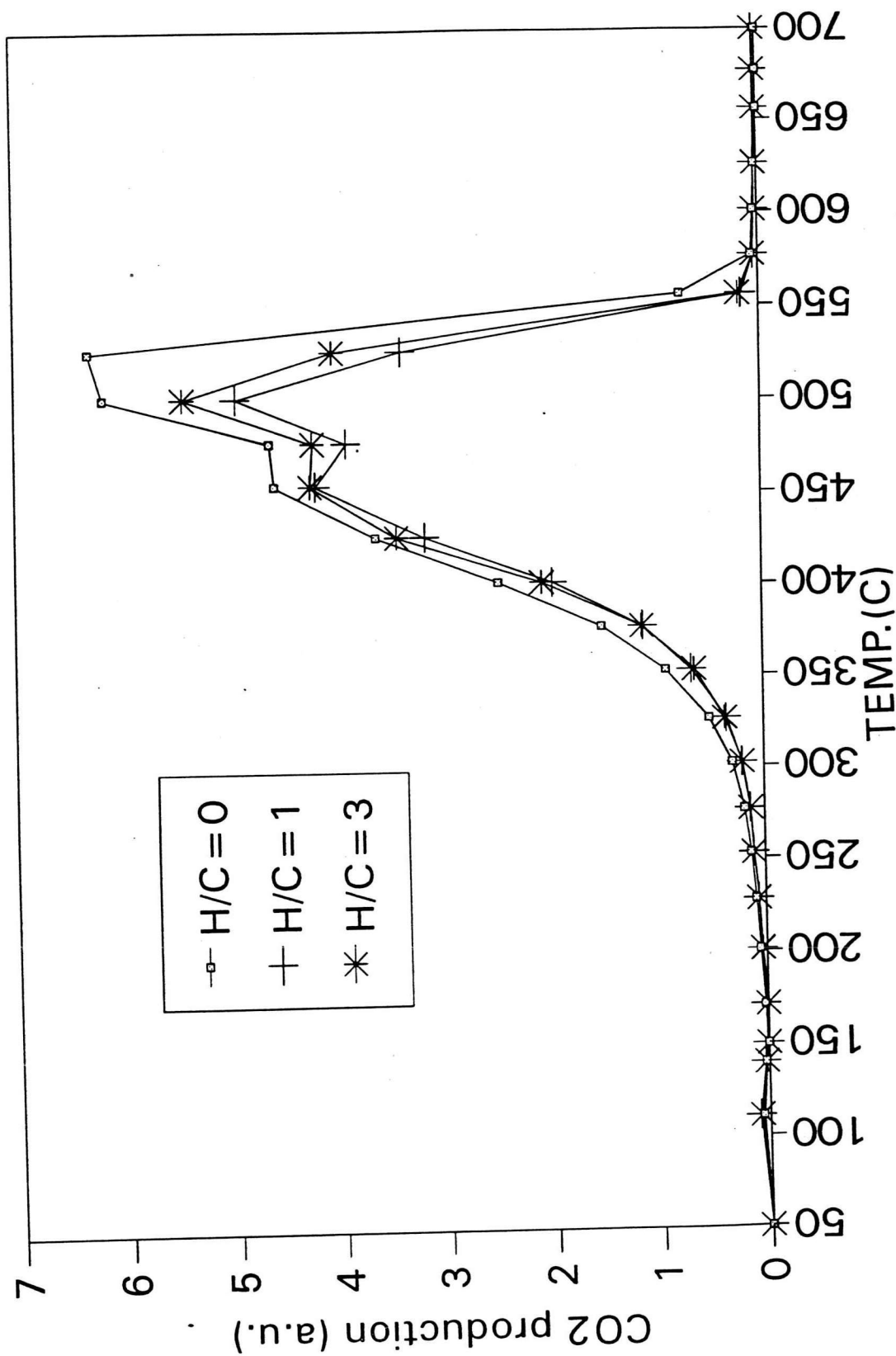
From the above results, the difference in the combustion temperature of the first peak might be because the coke in the later work (Liu & Barbier) was prepared from reforming reaction and/ or catalyst preparation method.

## 5.2 Effect of Hydrogen to Hydrocarbon Mole Ratio.

In this section, the influence of hydrogen to hydrocarbon (H/HC) mole ratio was studied. Original coked catalysts were prepared at H/HC mole ratio of 0,1 and 3. TPO method was used to determine the location and composition of the cokes deposit on the catalysts. TPO data of coke burning at different H/HC mole ratio are compared to each other in figure 5.2.

Figure 5.2, compares three experimental results obtained from H/HC mole ratio equal to 0,1 and 3. The influence of the hydrogen to hydrocarbon mole ratio can be deduced. The three curves differs in only area below curves which represent the amount of each coke. However, all have the same TPO pattern of each coke that typify location and the coke composition. As it can be seen, the shift in peak locations are not observable.

In addition, these results indicate that kinetic parameters evaluated from a coke form at a H/HC mole ratio should be able to be used with cokes form at different H/HC mole ratio and the locations and coke compositions are not affected by changing H/HC mole ratio condition.



Pt/Al<sub>2</sub>O<sub>3</sub> at Rxn. Temp. = 600 C, Time = 40 min.

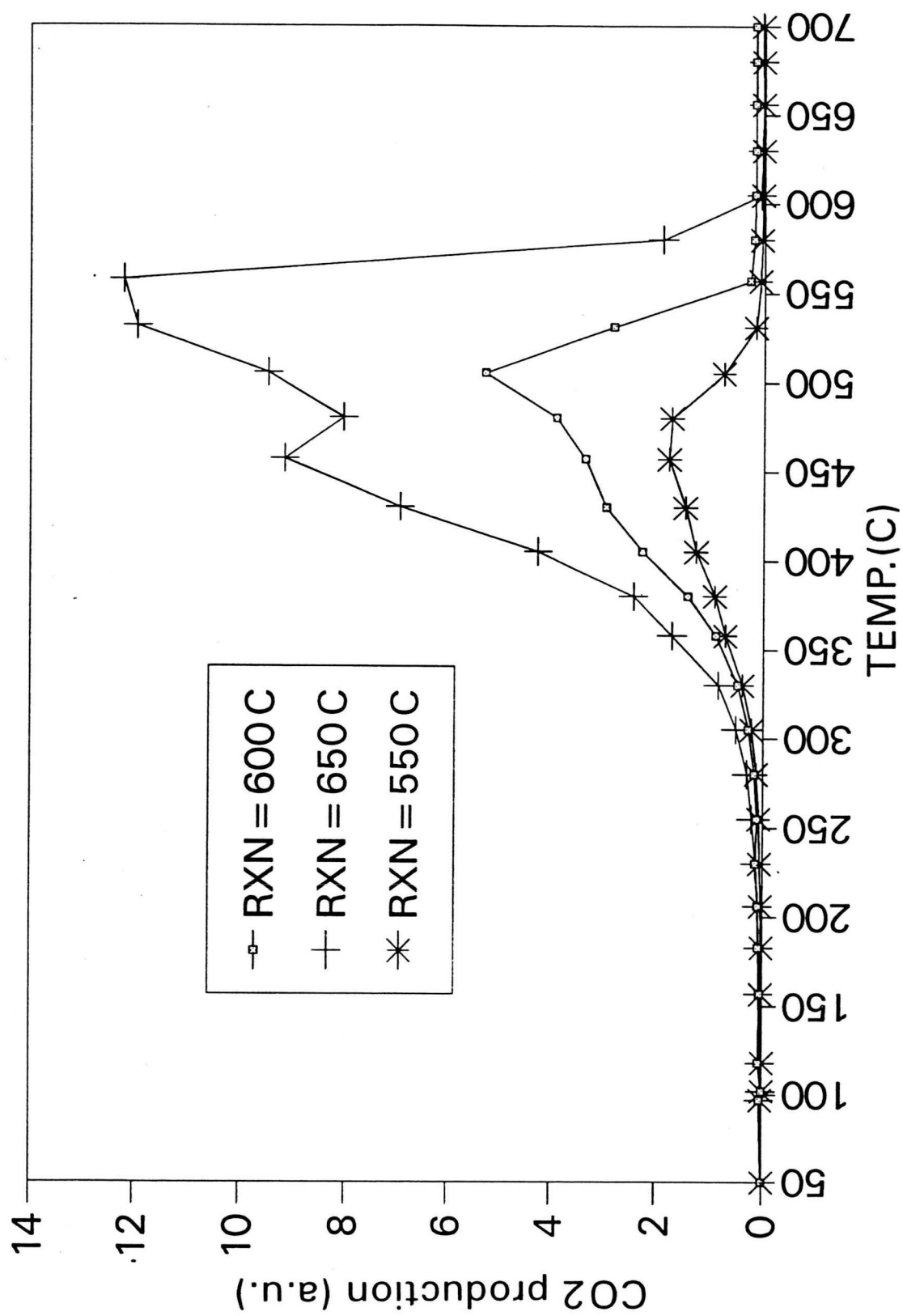
Figure 5.2 Influence of H<sub>2</sub>/HC mole ratio on Temperature-Programmed Oxidation.

### 5.3 The Effect of Variation in Reaction Temperature.

In this part of the experiment, the effect of dehydrogenation reaction temperature was studied. Original coked catalysts were prepared at different reaction temperatures between 550 °C to 650 °C and analysed by Temperature- Programmed Oxidation method.

Temperature - Programmed Oxidation results of coke formed from different reaction temperatures are shown in figure 5.3. The numerical values of these results are reported in appendix D.

Figure 5.3 allows a comparison to be made among different Temperature - Programmed Oxidation (TPO.) of the original coked catalyst when the coke formation condition were 550, 600 and 650 °C. It can be observed that the Temperature - Programmed Oxidation pattern of each coke is similar, the only difference the amount of coke. On the other hand, the changing in dehydrogenation reaction temperature should not have a significant effect on coke composition in this temperature interval. This is because if the cokes on the catalysts have changed their compositions, it should be able to see different Temperature - Programmed Oxidation pattern (i.e. a significant shift in peak location)



Pt/Al<sub>2</sub>O<sub>3</sub> at H/C = 0, Time = 40 min.

Figure 5.3 Influence of dehydrogenation reaction temperature on Temperature-Programmed Oxidation.



The results indicate that kinetic parameters evaluated from a coke form at a reaction temperature should be able to be used with cokes form at different reaction temperatures.

#### 5.4 Kinetic Parameters.

The purpose of this thesis is not to study the detail of mechanism coked combustion. Therefore, kinetic parameter evaluation were successfully calculated with a linear combination of power - law kinetic expressions by:

$$- dC/dt = k P_{O_2}^m C^n$$

where  $P_{O_2}$  = partial pressure of oxygen  
 $C$  = amount of coke  
 $m, n$  = order of reaction with respect to oxygen partial pressure and the amount of coke respectively.

TPO results discussed in sections 5.1, 5.2 and 5.3, show the similar curves of coke burning, especially coke type 2 and 3. The results clearly indicate that the behaviour of the TPO peak exhibits a slow increase in the early stages of combustion, followed by a fast drop in the later stages.

Querini, C.A. and Fund S.C., 1994 described the effect of reaction of carbon on the simulated TPO spectra of a single carbon peak that this characteristic of combustion should be the order below 1. They reported that peak shape and temperature of maximum peak depended on coke reaction order. In addition, the paper also shows that the curve was close to

symmetrical for the first order reaction. Decreasing the order below 1 accentuates the asymmetric character of the peak, i.e. a fast decrease in the reaction rate on the high temperature side of the peak.

In this research, coked catalysts were prepared at various reaction temperature (550, 600 and 650 °C). Coked catalyst burning at different fixed temperature were chosen to evaluate reaction order. From this process one can observe that the amount of carbon dioxide production at low temperature is less than that at high temperature, therefore, it can be concluded that only coke 2 was burnt at low temperature while both coke 2 and coke 3 can burnt completely at high temperature. Then, experiment data were plotted by varying order of reaction. (between 0.5-2.0) Slope of the graph is  $kP_{O_2}^m$

where  $kP_{O_2}^m$  is defined as:

$$kP_{O_2}^m = k_0P_{O_2}^m e^{(-E_a/RT)}$$

Therefore;  $\ln(kP_{O_2}^m) = \ln(k_0P_{O_2}^m) - (E_a/R)/T$  The amount of remained coke was plotted versus time.

In this study, the kinetic parameters of coke combustion, as well as the order of the reaction with respect to amount of coke, was calculated from the data obtained from burning coked catalysts at different fixed temperature. Typical experimental result is shown one example in figure 5.4. The combustion was calculated by the following expression:

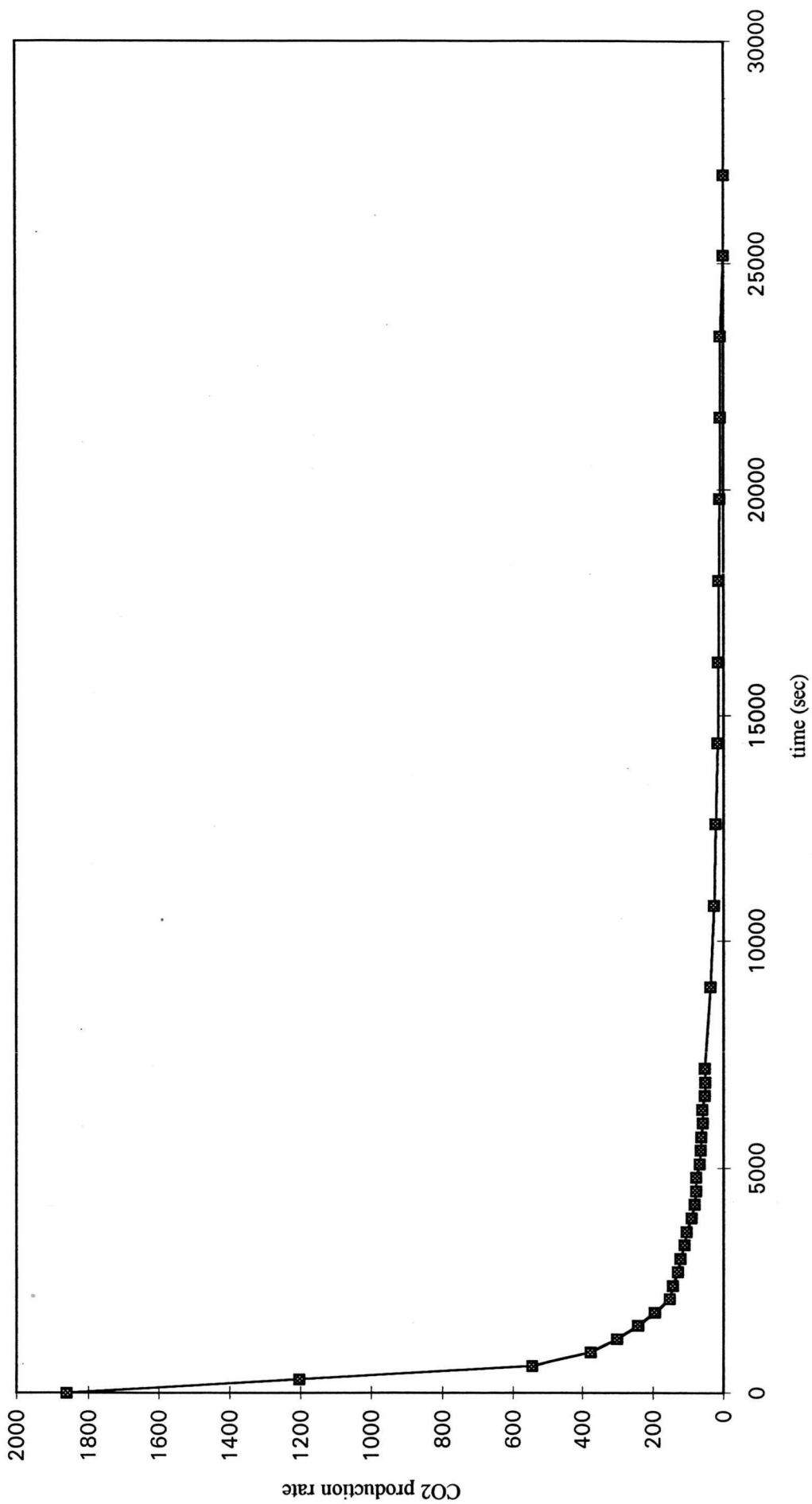


Figure 5.4 CO<sub>2</sub> production rate versus time of a coked catalyst burnt at 400 °C (constant temperature) for dehydrogenation reaction temperature (550 °C).

$$\text{when } n \neq 1; \quad -dC/dt = k'C^n \quad \text{-----(1)}$$

$$C^{(1-n)} = (n-1)k't + C_0^{(n-1)}$$

$$\text{when } n=1; \quad -dC/dt = k't \quad \text{-----(2)}$$

$$C = C_0 e^{-k't}$$

where  $c$  is concentration of coke

$n$  is order of reaction with respect to coke concentration.

$k'$  is constant.

The results indicate that the order of the combustion rate with respect to concentration of coke should be around 0.5. Typical plot between  $C^{0.5}$  versus time of the result shown in figure 5.4 are illustrated in figure 5.5.

The results from the curves of coked burning at different fixed temperature. The plotted between  $\ln(\text{slope})$  and  $1/T$  shows a straight line, whose slope is  $(-Ea/R)$  and x-axis intercept is  $\ln(k_0 P_{O_2}^m)$ , which shows in figure 5.6 and 5.7 respectively. This research did not vary oxygen partial pressure. Therefore, the reaction order with respect to oxygen partial pressure can not be evaluated. Table 5.1 shows data of determine kinetic parameters obtained from coked catalyst burnt at different fixed temperature. Although, coke3 can be burnt at a low temperature, this will take a long time. This is because the breaking of the long chain into short chains is very slow.

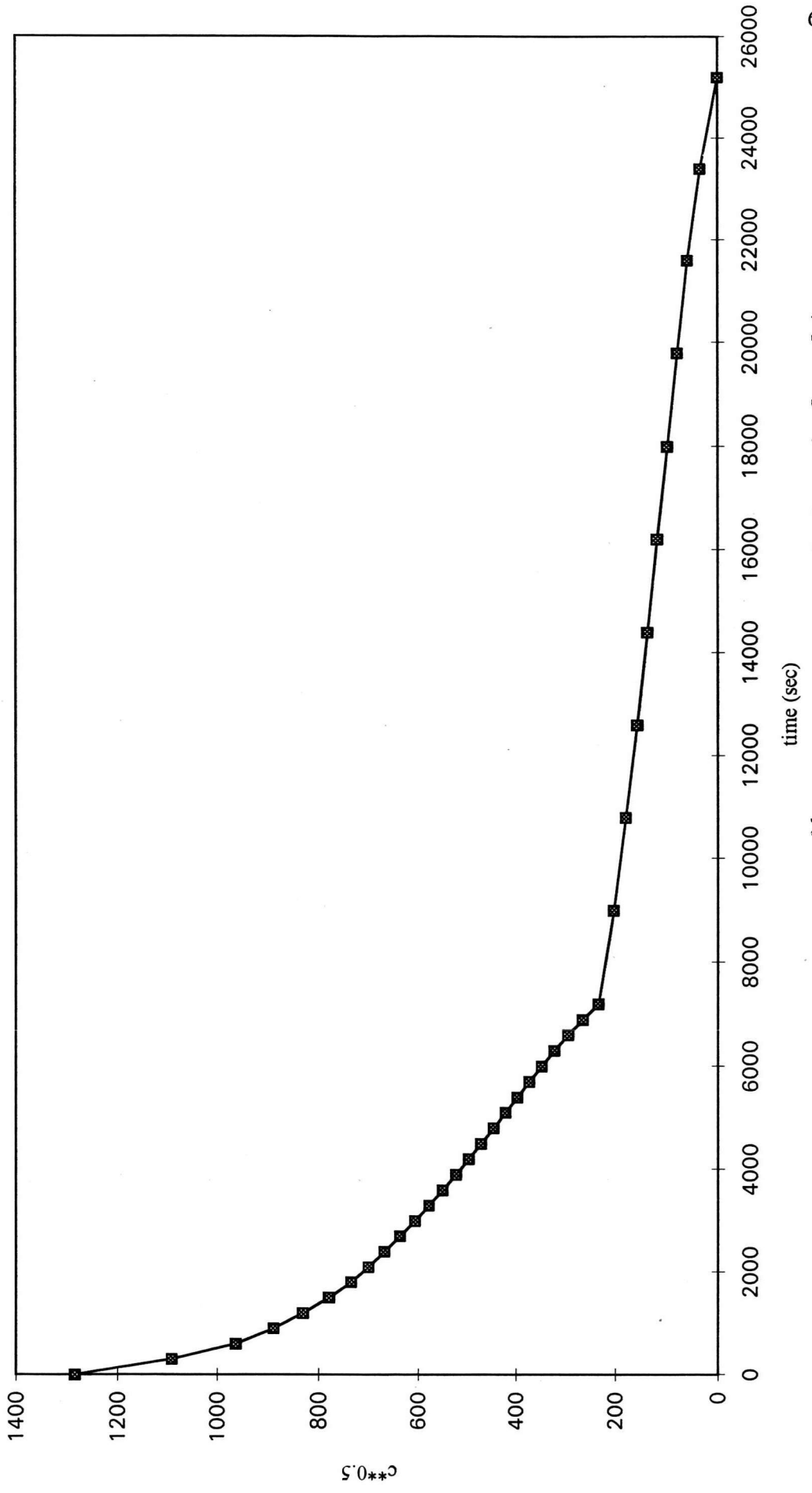


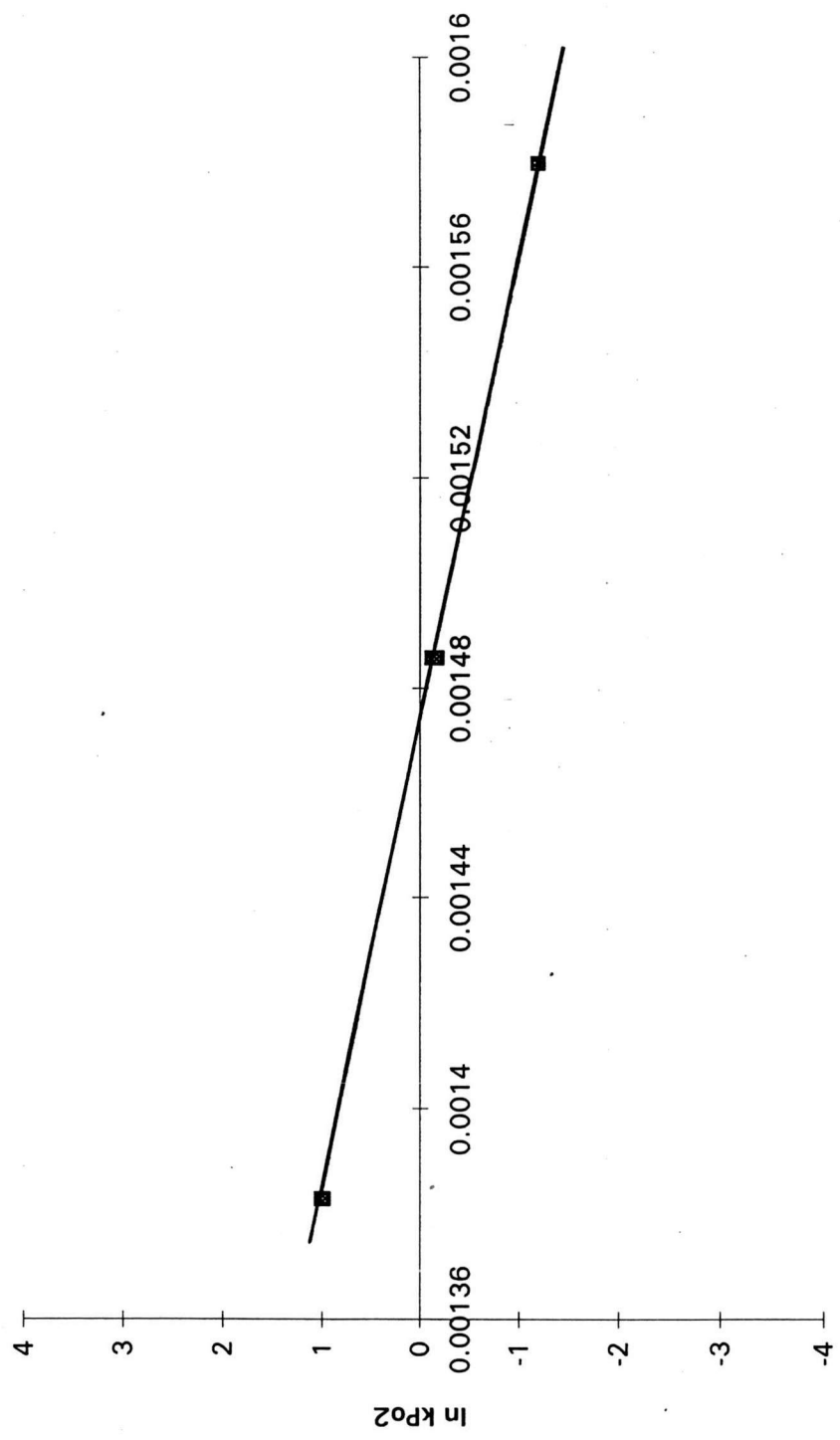
Figure 5.5 Plot between  $C^{0.5}$  versus time of the result shown in figure 5.4.

Table 5.1 Data to determine kinetic parameter at fixed temperature.

Coke 2	Reaction Temp. (° C)	Combustion Temp. (° C)	$\ln (kP_{O_2}^m)$
Coke 2	550	360	-1.1896
		400	- 0.1298
		450	1.0043
	600	400	-0.1758
		450	0.9767
Coke 3	600	500	0.9677
		550	1.1397
		575	1.6830
	650	530	1.0515
		560	1.2384
		580	1.3421

The numerical values of kinetic parameters were approximated by integrating equation 1 or 2 and calculating the gradients of curve obtained (figure 5.5). At this moment it can be approximated that the kinetic parameters of the coke on the metal sites (coke 2) and that of the coke on the support (coke 3) are about

	$\ln (k_0 P_{O_2}^m)$ (arbitrary unit)	$E_a/R$ (deg.K)
coke2	16.3	11100
coke3	6.8	4560



$1/T \text{ (K}^{-1}\text{)}$

Figure 5.6 Plot between  $\ln kP_{O_2}^m$  versus  $1/T$  of coke 2



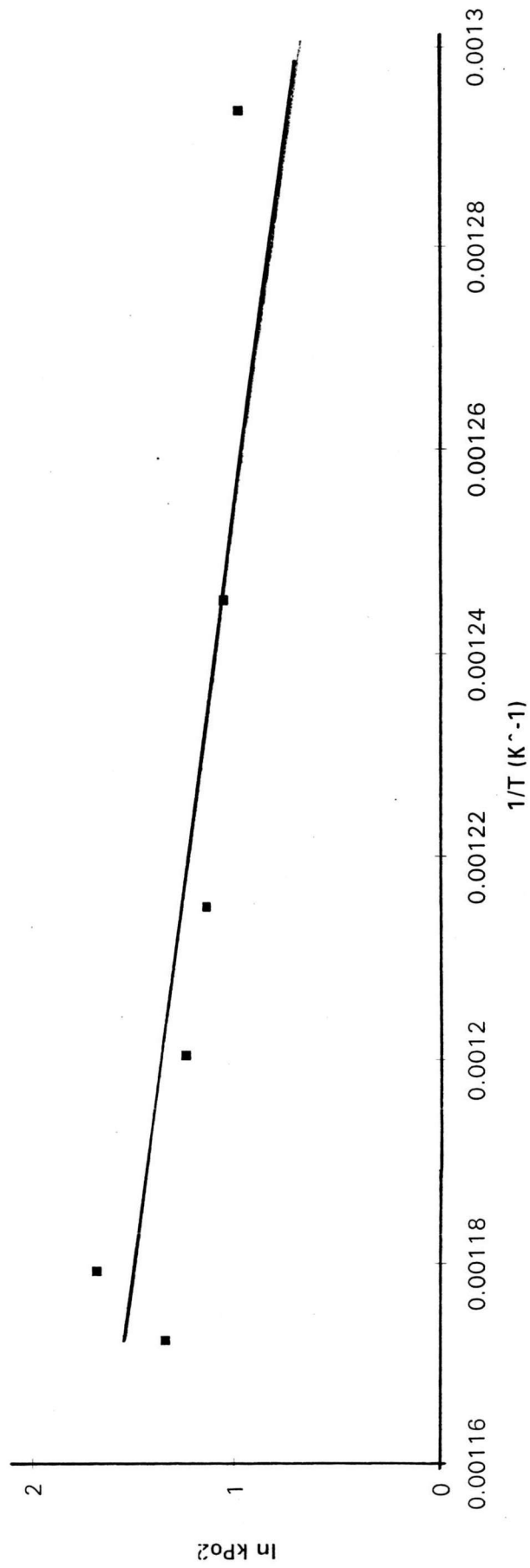


Figure 5.7 Plot between  $\ln kP_{O_2}^m$  versus  $1/T$  of coke 3

The values of the coke precursor (cokel) can not be measured because this coke rapidly burn off at low temperature and its amount is very small.

The simulation results and the experimental results are shown together in figures 5.8, 5.9 and 5.10 respectively. The model equations are solved by using the explicit Euler's method. Simulation shows that in order to predict a TPO curve using the above kinetic parameter. It has to assume that the combustion of coke 3 can begin only after coke 2 has been removed from the metal sites. The data also suggest that the metal sites should involve in the combustion of coke, and the series of combustion should be coke 1, coke 2 followed by coke 3 respectively.

The comparisons show that both peak heights and peak locations obtained from the model of this study agree very well with the experimental data.

The TPO curves obtained from simulation show fast decrease and sudden increase when coke 2 is completely removed and coke 3 begins burning. This phenomenon is not observed from experimental results obtained from using the TG system (which continuously measures the weight change). The reason for this should be because the model assumes that coke 2 or each metal sites is completely removal is not simultaneously. However, in reality the

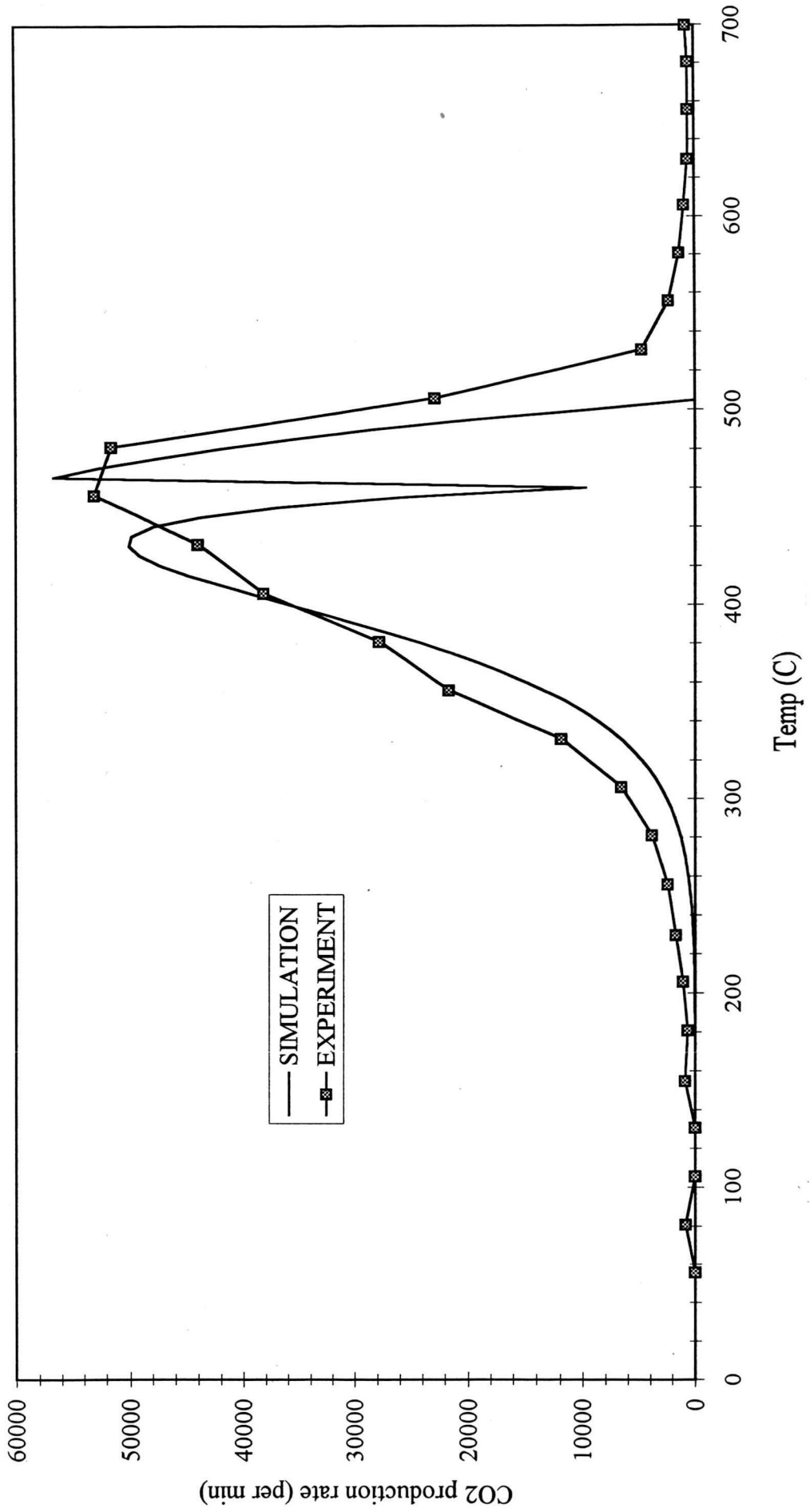


Figure 5.6 Comparison of experimental and simulated results for Temperature-Programmed Oxidation at 550 °C. 8

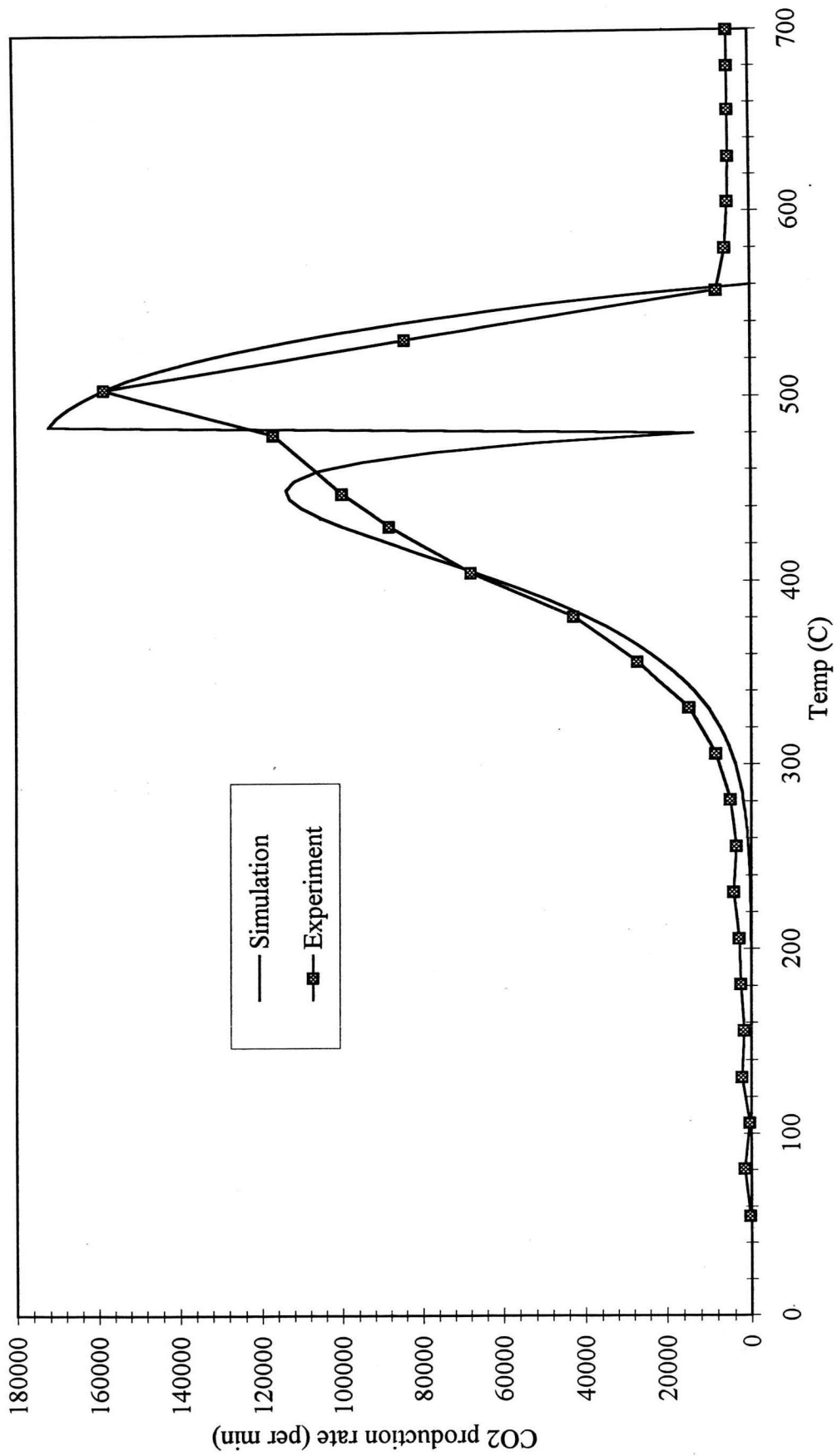


Figure 5.9 Comparison of experimental and simulated results for Temperature-Programmed Oxidation at 600 °C.

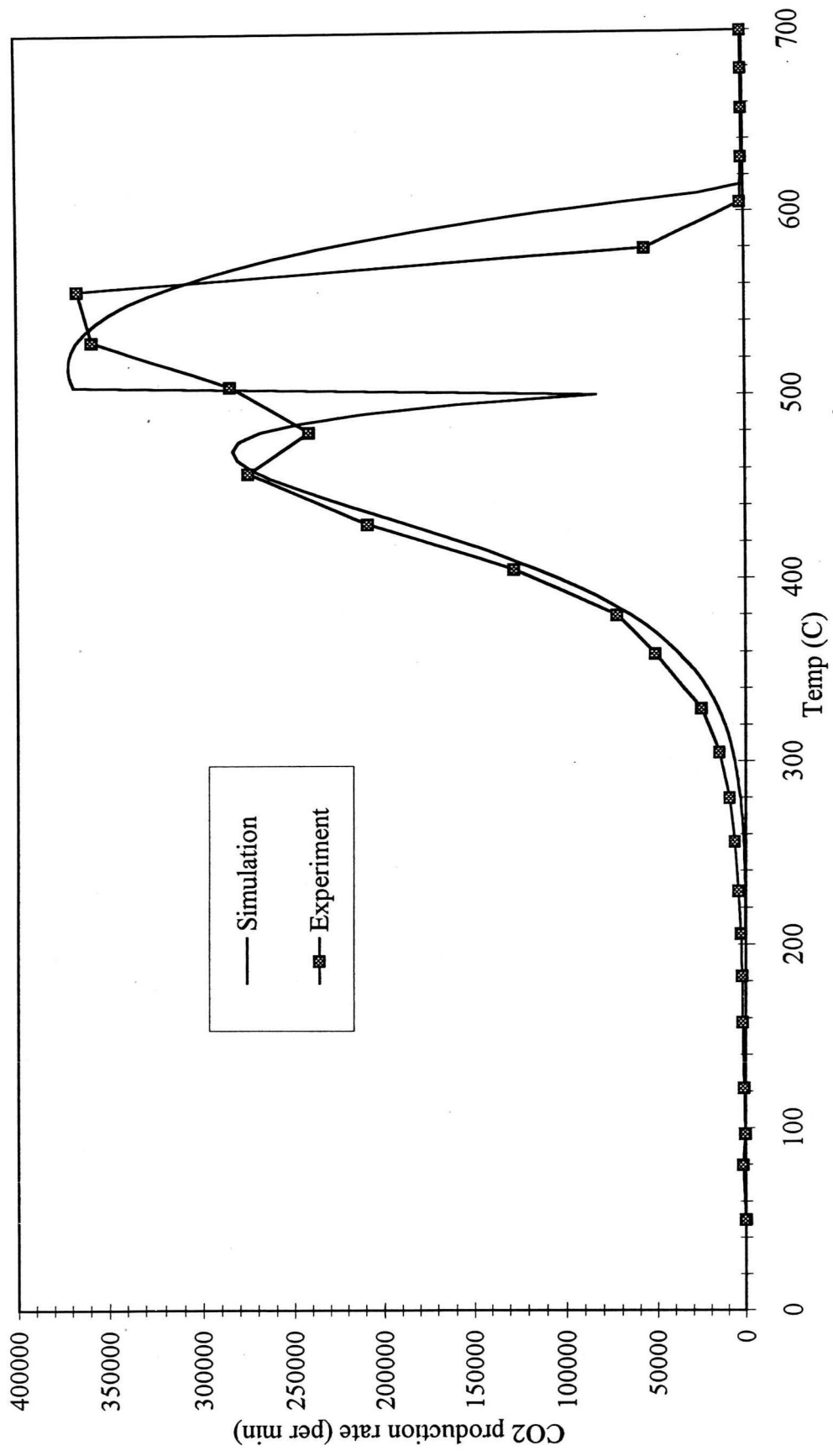


Figure 5.10 Comparison of experimental and simulated results for Temperature-Programmed Oxidation at 650 °C.

removal is not simultaneous but take a period of time and this will cause a smooth continuity between the 2<sup>nd</sup> peak and the 3<sup>rd</sup> peak.

The other data of coked burning were shown in appendix D. However,  $\ln(k_0 P_{O_2}^m)$  value which emerge from this study, includes catalyst activity, i.e. surface area, implicitly. For this reason, it can be concluded that kinetic parameters determined from the same composition catalyst but differ surface area should presented the same  $-E_a/R$  but may be indicate different  $\ln(k_0 P_{O_2}^m)$  value.