



CHAPTER V

RESULTS AND DISCUSSIONS

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

1. Synergistic effect of tin and lithium for propane dehydrogenation : In this part, the effect of tin and lithium loading, operating temperature and hydrogen/hydrocarbon ratio on the performance of platinum catalysts in regard to the amount of coke deposition and subsequent deactivation were studied

2. Determination of coke deposition on metal active site of catalyst by metal active site regeneration method. : In this part, the amounts of metal active sites covered by irreversible, reversible coke and the percentage coverage of Pt/Al₂O₃, Pt-Sn/Al₂O₃ and Pt-Sn-Na/Al₂O₃ catalysts were studied.

SYNERGISTIC EFFECT OF TIN AND LITHIUM FOR PROPANE DEHYDROGENATION

The catalysts prepared in this research were used at temperatures between 500 °C - 650 °C, atmospheric pressure and time on stream 1 hour.

1. Effect of platinum loading

Typical time on stream curves of the performance of the catalysts are given in figure 5.1. Increasing the Pt loading on the catalyst increases the yield per pass (YPP). This coincides with the increase in the formation of unsaturated intermediate hydrocarbons produced by the increase in Pt (73).

Figure 5.2 shows the TPO patterns of the coked catalysts. The oxidation of all coked catalysts occurred in the temperature range 50-700 °C. All of the patterns show two oxidation temperature zone, one at about 110 °C and the other at about 454 °C. The first combustion peak is produced by the burning of coke on the metal with an increase in temperature, the coke deposits on the support which is near the metal is burnt by the oxygen spill-over from Pt. The second combustion peak is due to the combustion of the coke on the rest of the metal and support (73). Since with increasing Pt, coke increases, the area of the TPO patterns also increases, as shown by the patterns of different Pt loading, there were : 1.00 wt % Pt/Al₂O₃ > 0.75 wt % Pt/Al₂O₃ > 0.60 wt % Pt/Al₂O₃ > 0.30 wt % Pt/Al₂O₃.

2. Effect of various promoters

Tin and lithium were the two promoters studied in this part. coke formation took place after the reaction at 500 °C, atmospheric pressure, H₂/HC = 0 and time on stream at 3 hr.

Figure 5.3 shows catalyst performance in the form of yield per pass versus time on stream at constant temperature 500 °C. The results are :

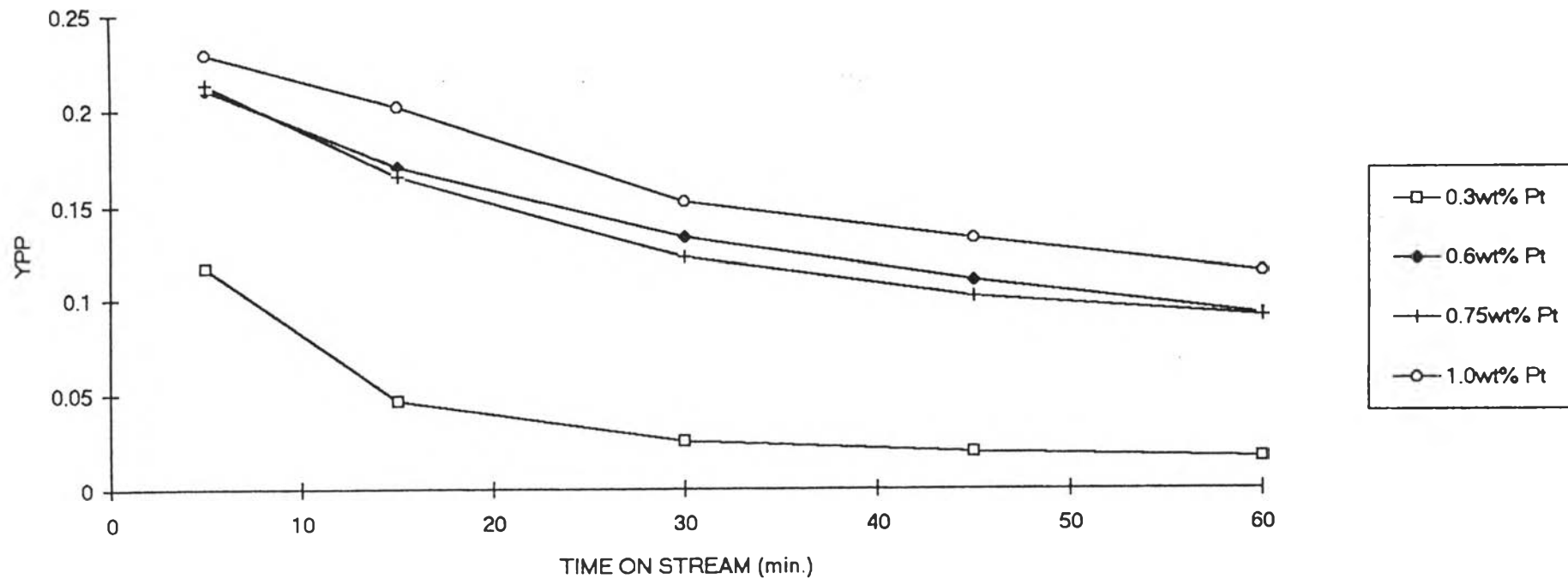


Figure 5.1 Effect of platinum loading in propane dehydrogenation. at temperature = 500 °C, GHSV = 22, 525 hr⁻¹, weight of catalyst = 0.1 gram and feed = 20 % propane in N₂ gas.

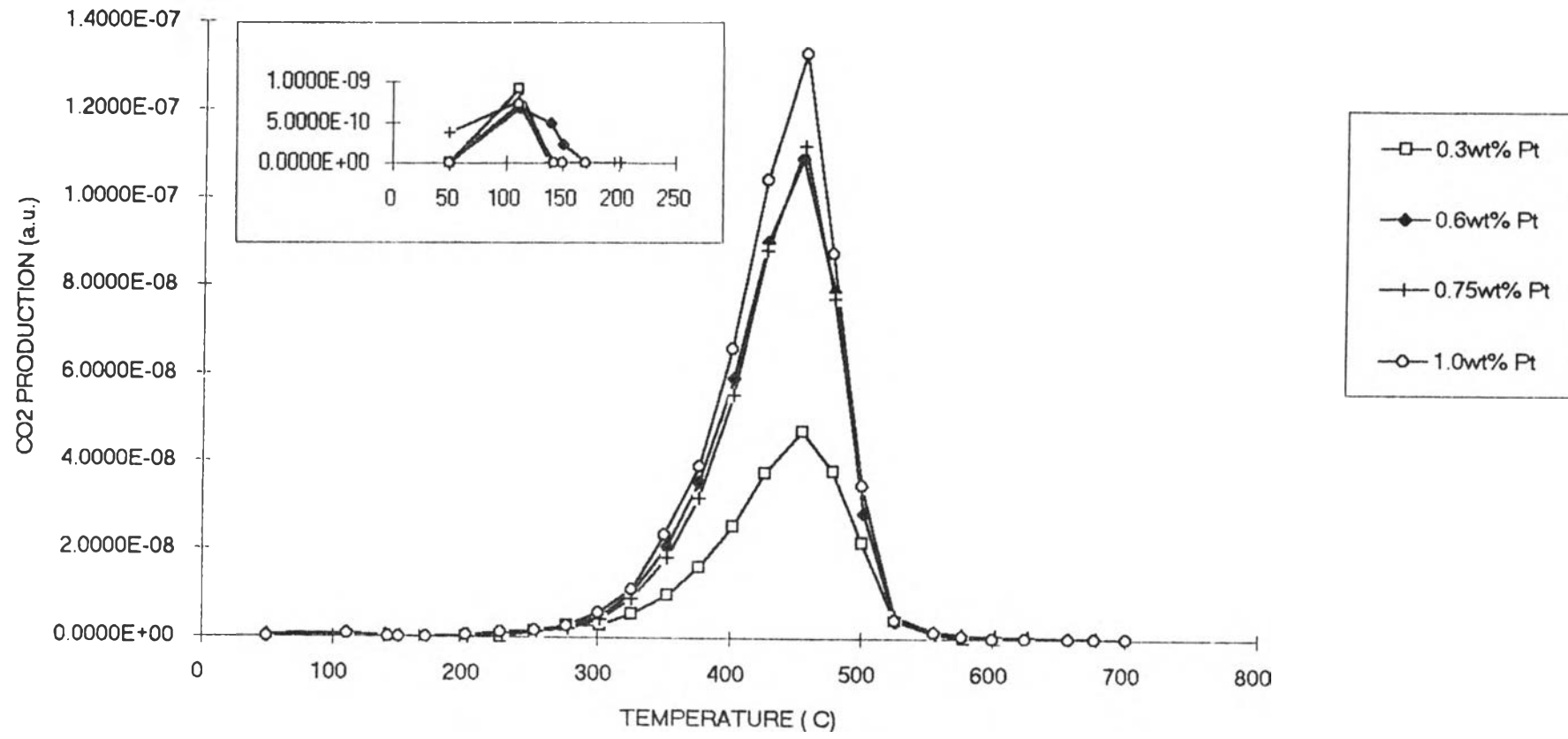


Figure 5.2 Temperature programmed oxidation of various coked catalyst for different platinum loading at 500 °C and H₂/HC = 0 .

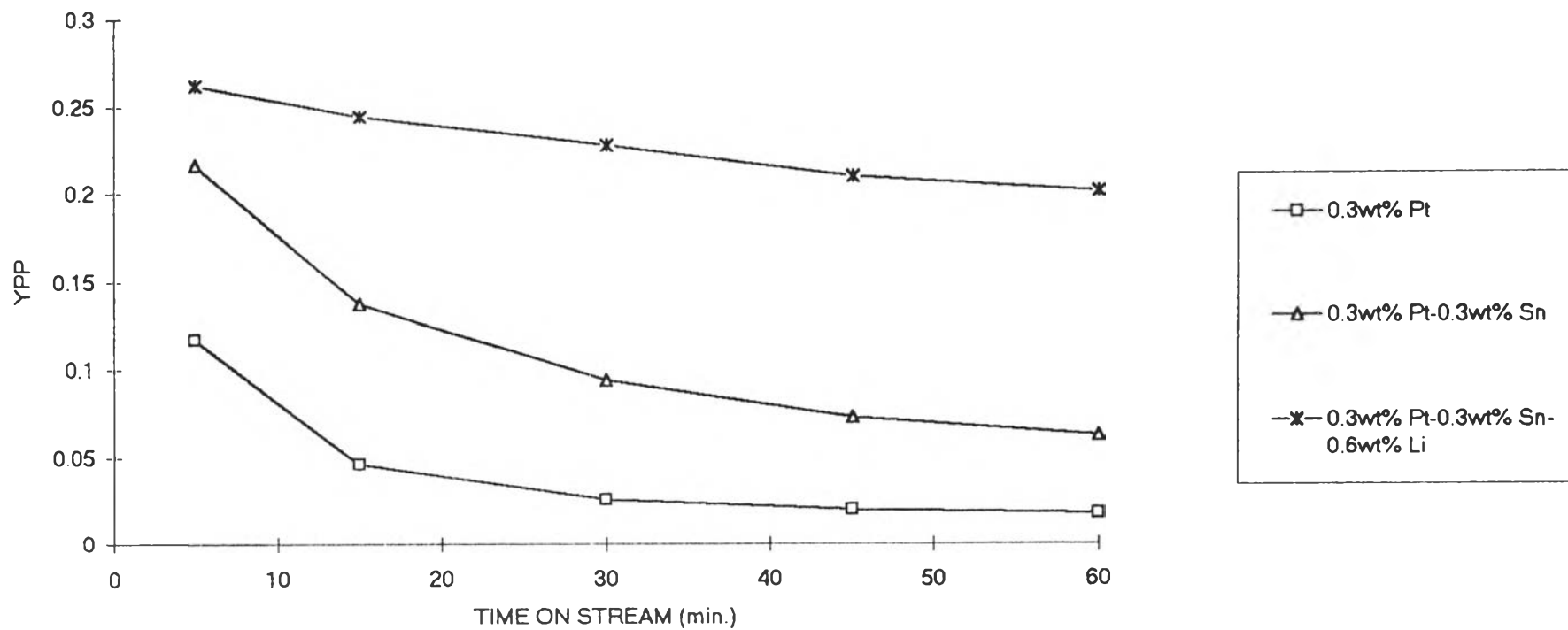
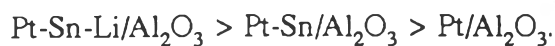


Figure 5.3 Comparative performance due to Sn and Li loading on Pt/Al₂O₃ catalyst at temperature = 500 °C, GHSV = 22525 hr⁻¹, weight of catalyst 0.1 gram and feed = 20% propane in N₂ gas.



Deactivation of the catalysts can be explained by the mechanism of propane dehydrogenation reaction. Based on Pt/Al₂O₃ catalyst, the addition of Sn to Pt/Al₂O₃ catalyst enhances the performance of catalysts because of the changes in electronic properties of Pt crystallites caused by the incorporation of metallic Sn to form a solid solution with Pt in electron-rich platinum sites (74). When propane is adsorbed on the electron-rich platinum site, the stronger Pt-H interaction induces the C-H bond to be weaker and more easily broken to form propylene products compared to the unpromoted Pt catalyst.

Lithium addition to Pt-Sn/Al₂O₃ increases the performance of the catalyst because the alkaline lithium would act as an electron donor to Pt (75), thus inducing the hydrogen spill-over.

In comparison to the Pt/Al₂O₃ catalyst, as shown in figure 5.4 the Pt-Sn/Al₂O₃ catalyst has the higher total amounts of coke deposition. This can be explained that the higher dehydrogenating activity of Pt-Sn/Al₂O₃ causes the higher coke precursors. In case of the Pt-Sn-Li/Al₂O₃, the total amounts of coke deposition is lower. This might be resulted from the increased hydrogen spill-over effect caused by lithium component that removed coke precursor, the other factor is lithium reduced the acidity of support. Barbier et al (77) showed that the nature of support plays a large part in the rate of coke formation of supported metallic catalysts, the amount of total coke deposits are more important as the acidity of the support is higher.

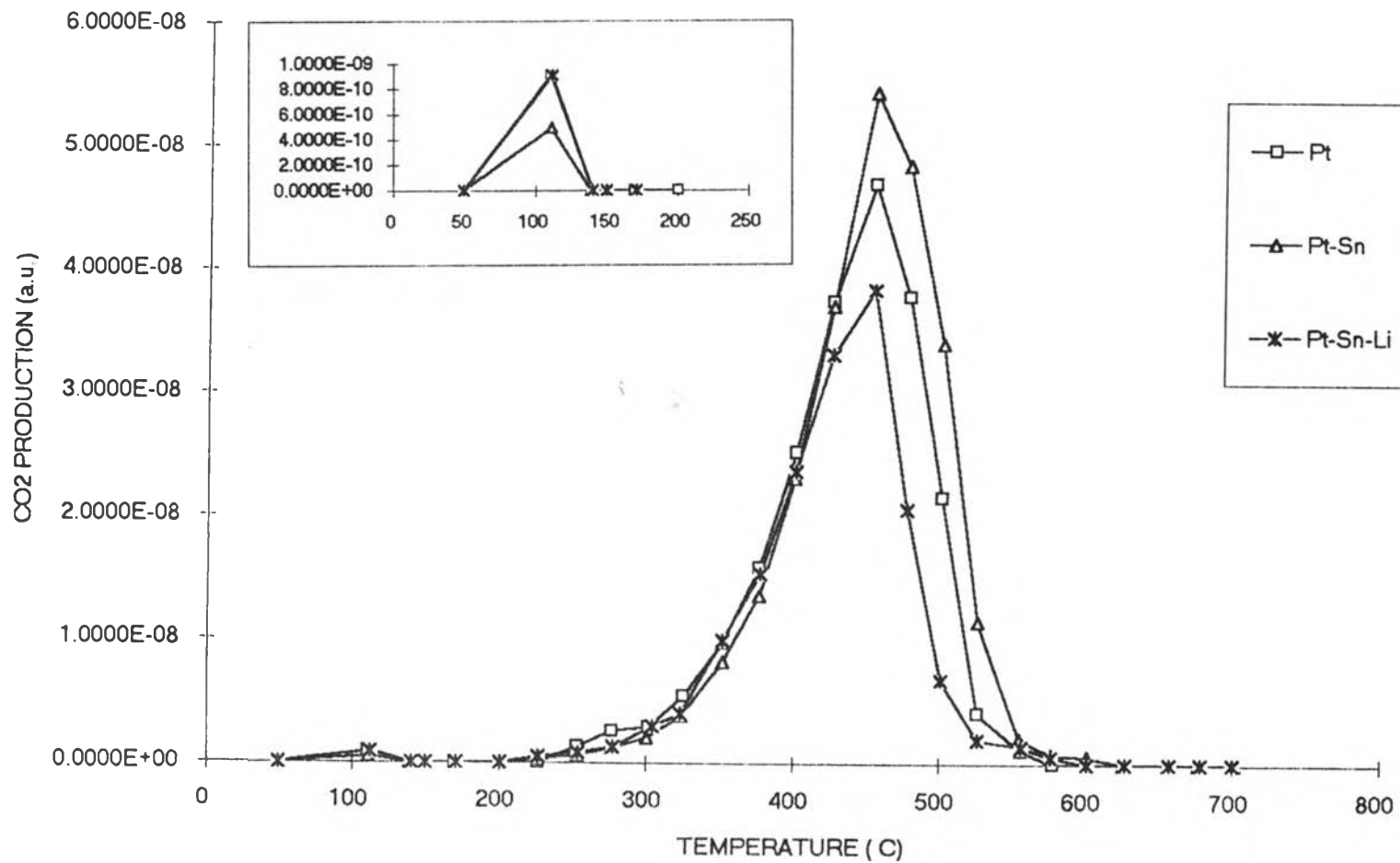


Figure 5.4 Temperature programmed oxidation of various coked catalysts for different promoters at 500 °C and $H_2/HC = 0$.

3. Effect of tin loading on platinum catalyst at different temperature

Figure 5.5 shows the catalyst performance measured at $t = 5$ min. The results show that every Sn/Pt ratio, the yield per pass increases when temperature increases except at 600°C up and Sn/Pt ratio is more than 1, the yield per pass decreases. The reason may be that the increasing of tin loading decreases the adsorption properties but for higher Sn/Pt ratio, with increasing temperature the adsorption passes through a minimum in contrast to a steady increase on the tin free Pt/ Al_2O_3 . This behavior can be explained by an ensemble effect of Pt-Sn cluster by a smaller ensemble size of Pt atoms occurs (18).

Figure 5.6 shows the TPO patterns of coked catalysts at different tin loading on platinum catalyst. All of the patterns show two oxidation temperature zone, one at about 110°C and the other about 454°C . The amounts of irreversible coke deposits increases with a increasing of tin loading until 0.60 wt % Sn, the amounts of irreversible coke decreases. The effect may be due to the formation of small ensemble on the metal surface that do not favour coke formation (78). However, it can also be noted that Pt-Sn cluster is efficient for gasifying carbonaceous residues (79) and coke may be reduced by the enhanced gasification.

4. Effect of lithium loading on platinum-tin catalyst at different temperature

Figure 5.7 shows the catalyst performance measured at $t = 5$ min. The result shows that the addition of lithium to the Pt-Sn/ Al_2O_3 catalyst enhances the catalyst performance and at 600°C , every Li/Pt ratio, the catalyst performance is maximum. The possible reason may be at the temperature beyond

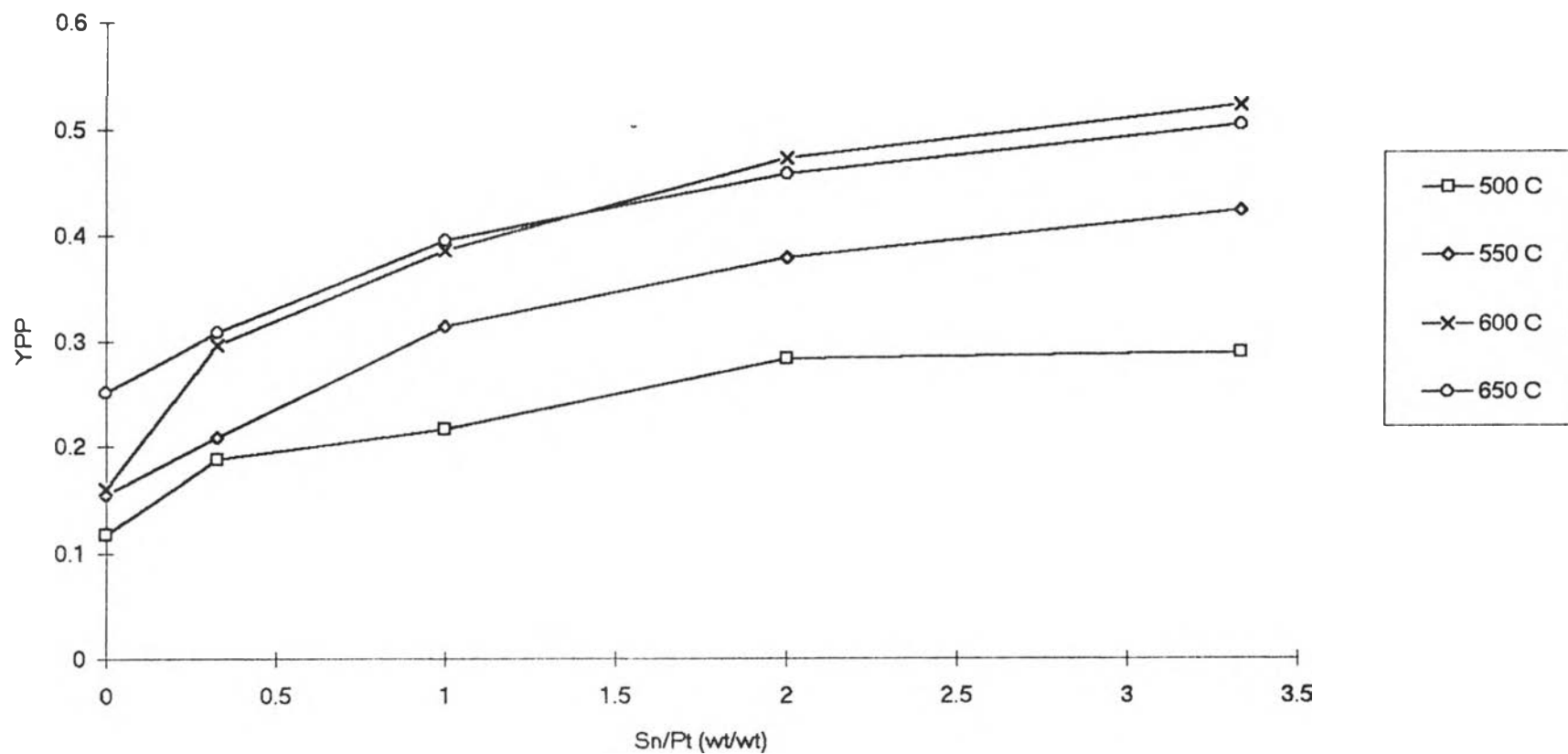


Figure 5.5 Comparative performance due to Sn loading on Pt/Al₂O₃ catalyst at different temperature 500-650 °C, GHSV = 22525 hr⁻¹ weight of catalyst 0.1 gram and feed = 20% propane in N₂ gas.

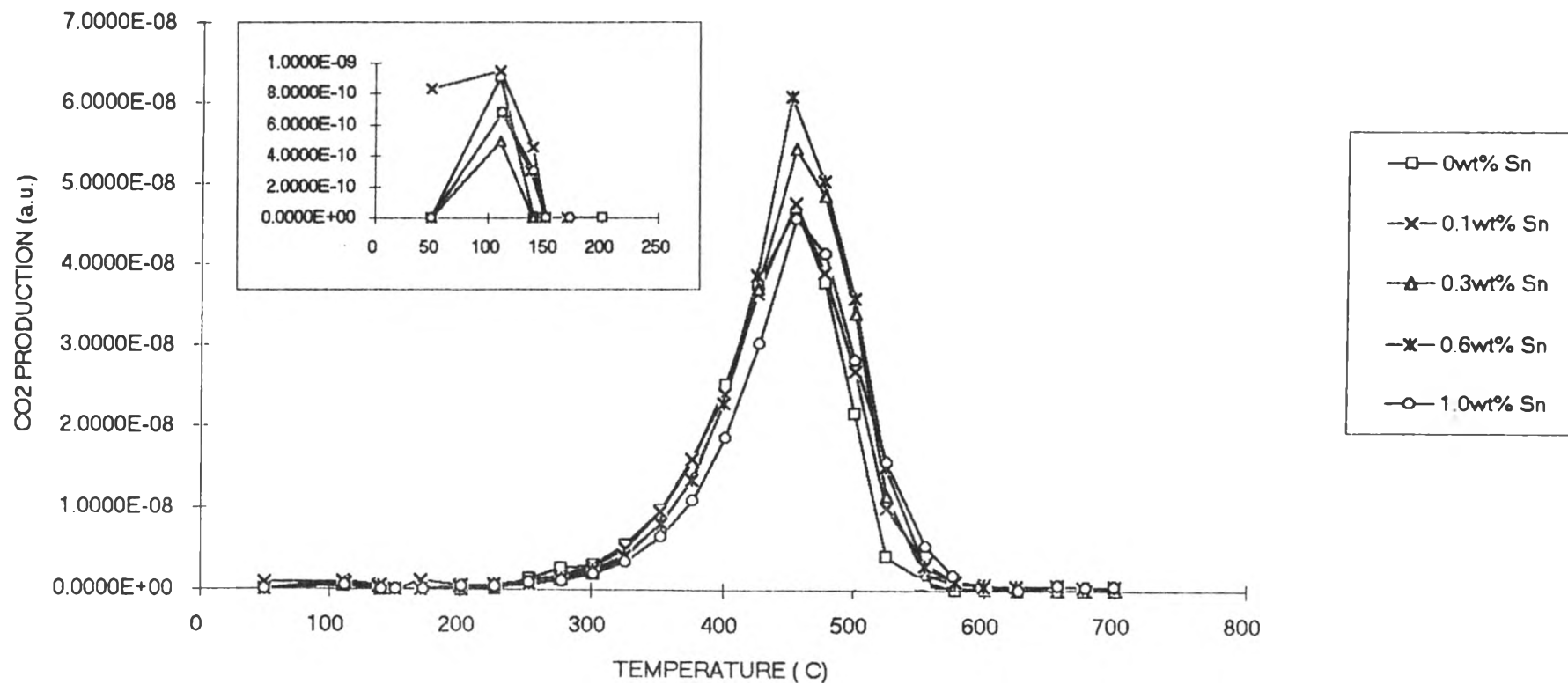


Figure 5.6 Temperature programmed oxidation of various coked catalyst for different tin loading on platinum catalyst at 500 °C and H₂/HC = 0 .

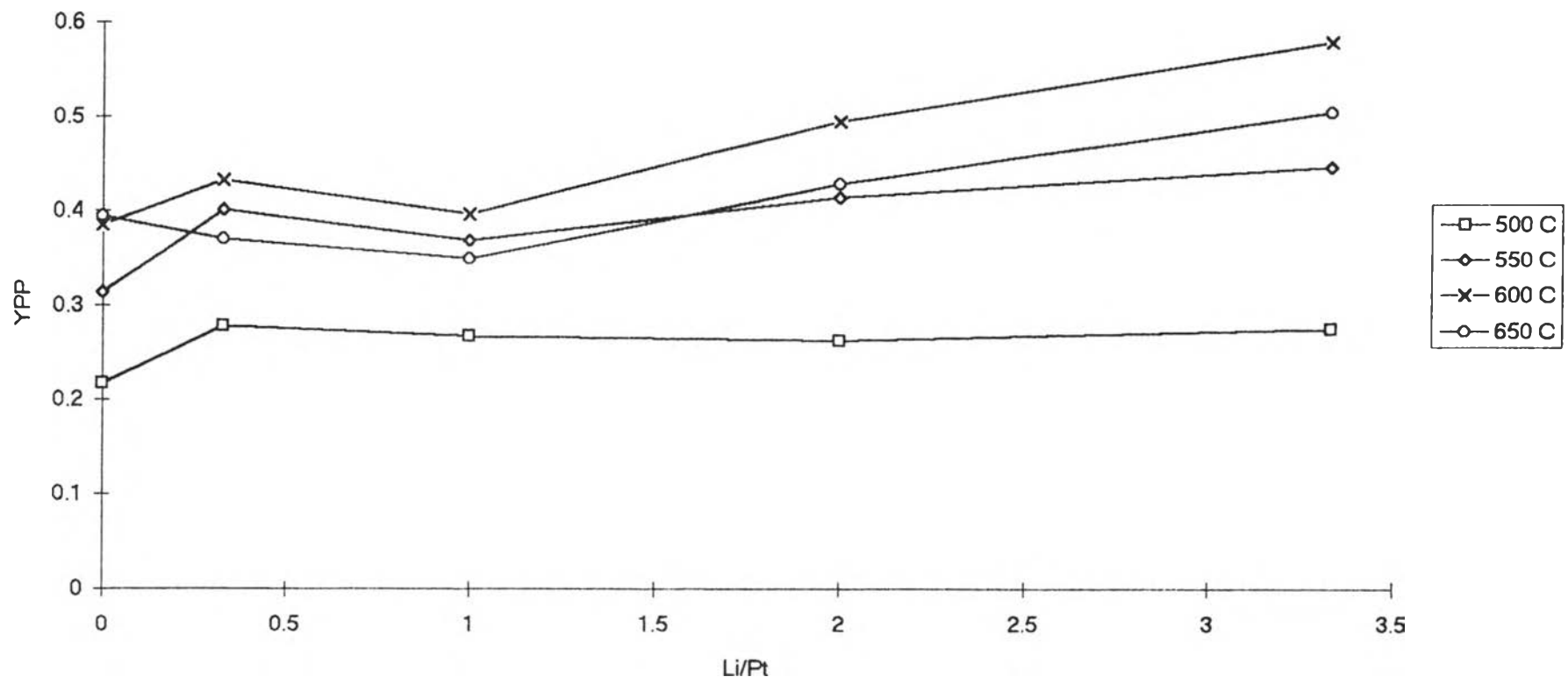


Figure 5.7 Comparative performance due to Li loading on Pt-Sn/Al₂O₃ catalyst at different temperature at temperature 500-650 °C, GHSV = 22525 hr⁻¹, weight of catalyst 0.1 gram and feed = 20% propane in N₂ gas.

600°C the alloy formation may be taken place and the synergistic effect of Li gradually decrease.

Figure 5.8 shows the TPO patterns of coked catalyst at different lithium loading on platinum - tin catalyst. All of the patterns show two oxidation temperature zone, one at about 110°C and the other about 454°C. The amounts of irreversible coke deposition decreases as the lithium loading increases. It concluded that the lithium reduces coke precursor all ranges of the experiment.

5. Effect of hydrogen to hydrocarbon on catalyst performance

For equilibrium limits dehydrogenation reaction, it would be the best to operate at the lowest possible hydrogen pressure. It is clear from figure 5.9 that all Li loading on Pt-Sn/Al₂O₃ catalysts give a better performance with H₂/HC =0 than with H₂/HC =2 and for H₂/HC=2 the catalyst with Li/Pt= 2 gives the maximum performance. This may be related to an optimum ability of lithium to donate electrons under the condition of hydrogen pressure.

6. Comparison of the metal active site among various studied catalysts

The metal active site of catalyst were measured by the CO adsorption, the results are shown in Table 5.1. The metal active site of promoted catalyst is less than of non-promoted catalyst, the possible reason is Pt and promotor form solid solution to be larger crystallite.

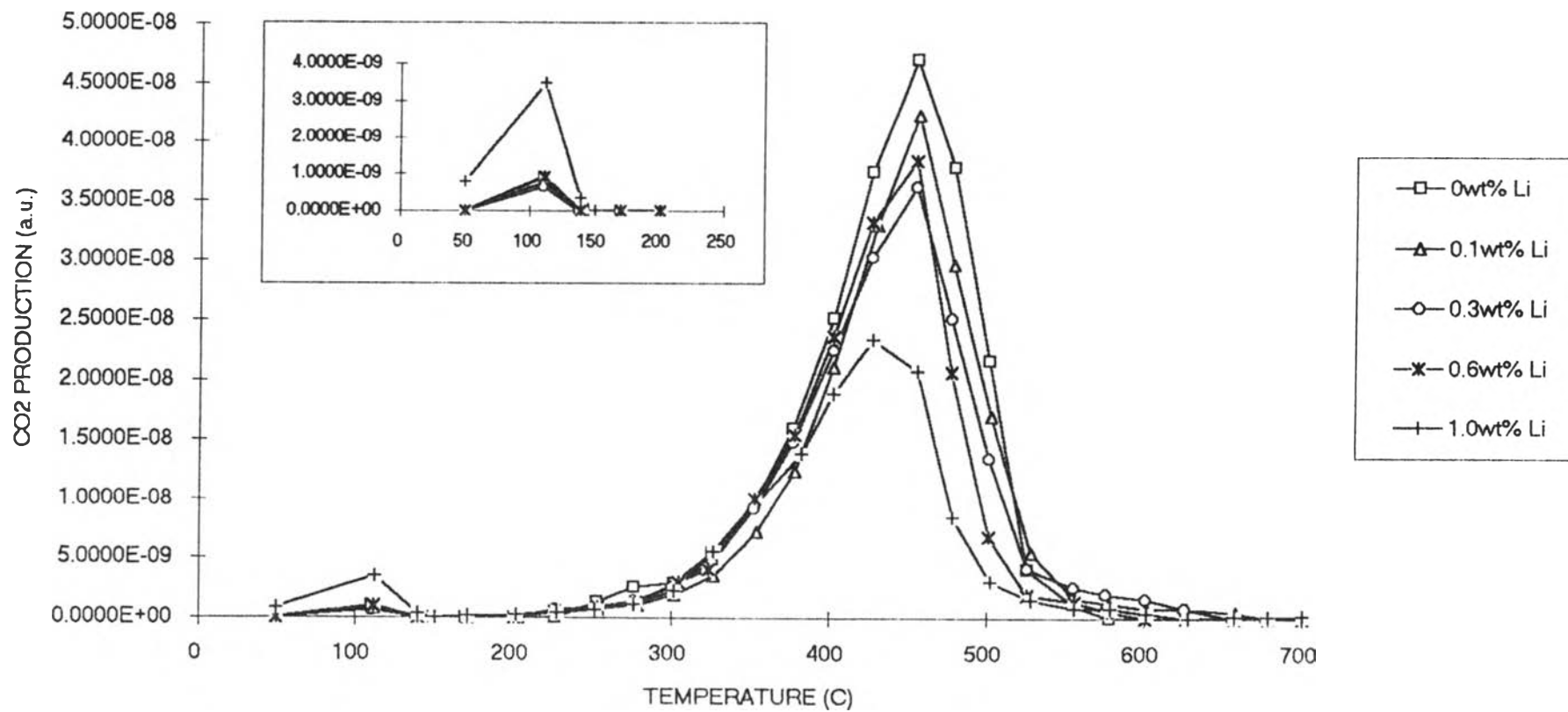


Figure 5.8 Temperature programmed oxidation of various coked catalyst for different lithium loading on platinum-tin catalyst at 500 °C and $H_2/HC = 0$.

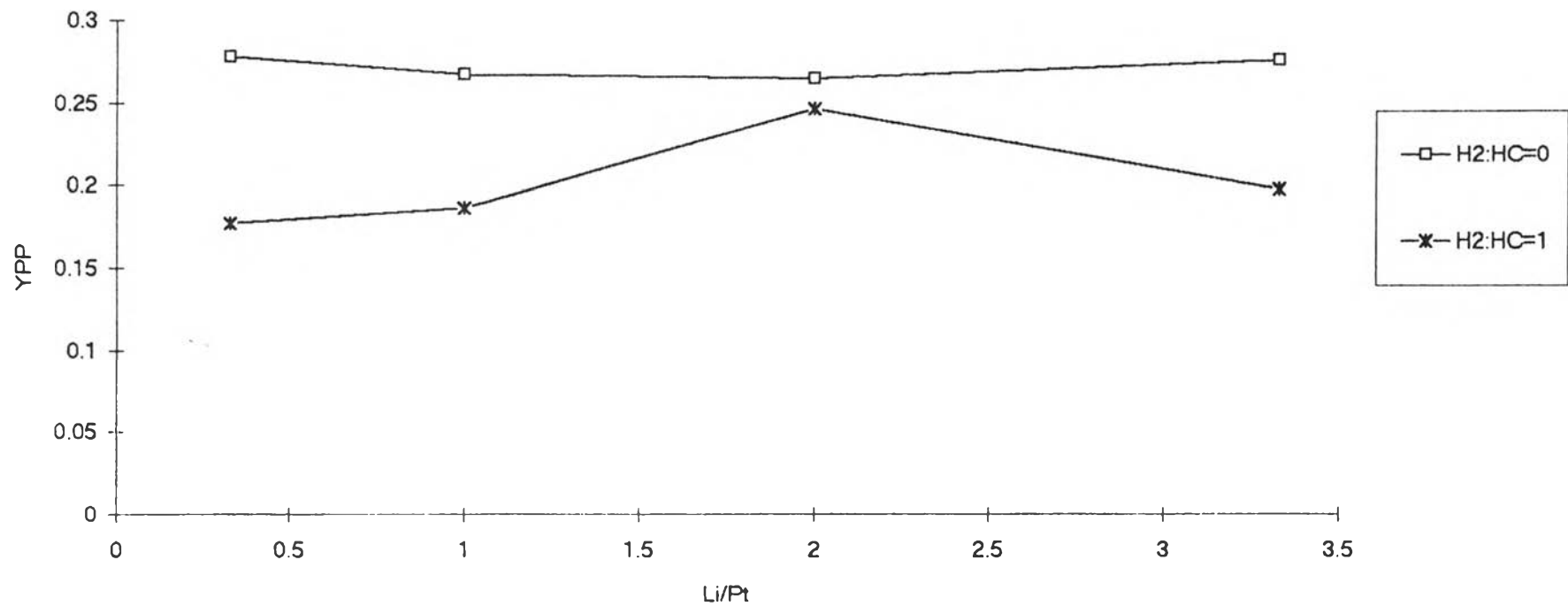


Figure 5.9 Comparative performance of Pt-Sn-Li/Al₂O₃ catalyst at different hydrogen/hydrocarbon ratio and temperature 500 °C GHSV = 22525 hr⁻¹ weight of catalyst 0.1 : gm and H₂/HC = 0 , 2.

TABLE 5.1 The metal active site of catalysts measured by CO adsorption.

Catalyst	Metal active site (molecule of CO/gram of catalyst)
0.30 % Pt/ Al_2O_3	1.63×10^{18}
0.30 % Pt - 0.30 % Sn/ Al_2O_3	0.73×10^{18}
0.30 % Pt - 0.30 % Sn-0.6% Li/ Al_2O_3	1.17×10^{18}

Table 5.2 shows the metal active site of catalyst is decreased at higher reduced temperature. The possible reason is alloy formation between Pt and promoters take place at a higher loading of promotor.

7. Comparison of the electrical conductivity among various studied catalysts

The electrical conductivities of catalysts are shown in table 5.3, the results shows that the electrical conductivity of promoted catalyst is higher than of un-promoted catalyst. It corresponds to the electron transfer phenomenon from promoters to platinum catalyst.

From the experimental results, the synergistic effects of promoters to platinum catalyst are not linear. They depended upon the role or status of promoters at each catalyst composition. Three possible functions of promoters on Pt/ Al_2O_3 catalyst were : (see figure 5.10).

Table 5.2 The active metal site of catalysts in the high reduced temperature.

Catalyst	Reduced temp °C	Active metal site (molecule of CO/gram of catalyst)
0.30%Pt-0.60% Sn/Al ₂ O ₃	600	1.79 X 10 ¹⁸
0.30%Pt-0.60% Sn/Al ₂ O ₃	650	1.62 X 10 ¹⁸
0.30%Pt-1.00% Sn/Al ₂ O ₃	600	1.39 X 10 ¹⁸
0.30%Pt-1.00% Sn/Al ₂ O ₃	650	1.15 X 10 ¹⁸
0.30% Pt-0.30%Sn-0.60% Li/Al ₂ O ₃	600	1.35 X 10 ¹⁸
0.30%Pt-0.30%Sn-0.60% Li/Al ₂ O ₃	650	1.12 X 10 ¹⁸

Table 5.3 The electrical conductivity of various catalyst.

Catalyst	Electrical Conductivity (Ohm ⁻¹ cm ⁻¹)
0.30%Pt/Al ₂ O ₃	3.25 X 10 ⁻⁵
0.30%Pt-0.30%Sn/Al ₂ O ₃	9.43 X 10 ⁻⁵
0.30%Pt-0.30%Sn-0.60% Li/Al ₂ O ₃	20.30 X 10 ⁻⁵

1. Function as textural promoter, promoter had only physical effect to catalyst.

2. Function as structural promoter which chemical composition was changed, the promoter may produce lattice defect and changed the electronic structure of a catalyst.

Both function enhanced the catalyst performance, promoter could sometimes be identified by comparing the metal active site of a catalyst in the presence and absence of the promoter. Another method of identification was by the effective activation energy. This was unchanged by a textural promoter but may be markedly affected by a structural promoter.

3. Function as metal alloy. In this case the catalyst may lose the performance.

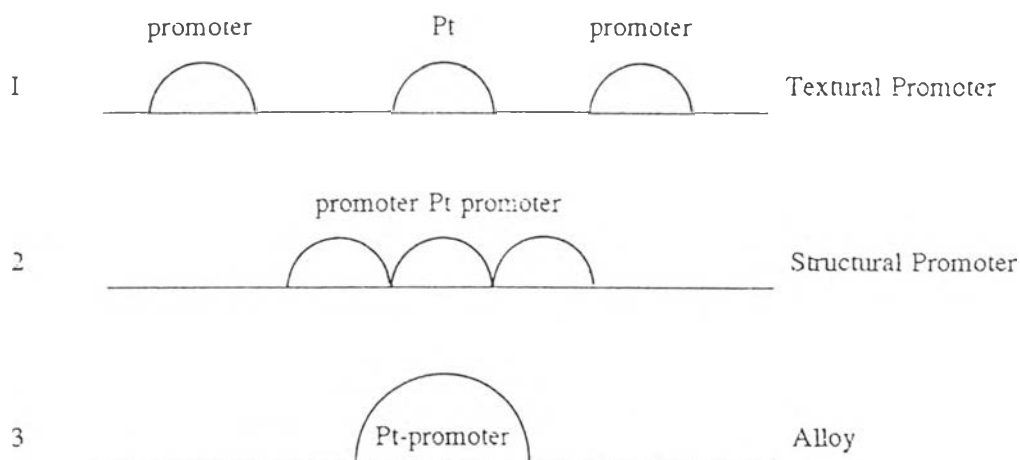


Figure 5.10 The function of promoter on platinum catalyst for propane dehydrogenation reaction.

DETERMINATION OF IRREVERSIBLE COKE DEPOSITION ON METAL ACTIVE SITE OF CATALYST BY METAL ACTIVE SITE REGENERATION METHOD

The Pt/Al₂O₃, Pt-Sn/Al₂O₃ and Pt-Sn-Na/Al₂O₃ catalysts were chosen to study in this part. The coked catalysts were regenerated by 1% O₂ in He gas mixture at 250 °C to oxidize the reversible coke and at 500 °C to oxidize the irreversible coke deposited on metal active site.

1. Effect of various promoters

Jaikaew B (80) studied the effect of alkaline added on platinum-tin catalyst, the result showed that the performance of sodium is higher than lithium, therefore sodium and tin were selected to studied in this part, coke formation took place after the reaction at 500 °C, atmospheric pressure, H₂/HC = 0 and time on stream at 3 hr.

Figure 5.11 shows the TPO pattern of these catalysts, the amounts of total coke deposit on catalyst can be arranged in the following order : Pt-Sn/Al₂O₃ > Pt/Al₂O₃ > Pt-Sn-Na/Al₂O₃. The reason is the same as section 2 of the first part of this chapter.

Figure 5.12 shows the total coke, reversible coke and irreversible coke on the metal site of the catalyst with H₂/HC =0, the result can be ordered as follows.

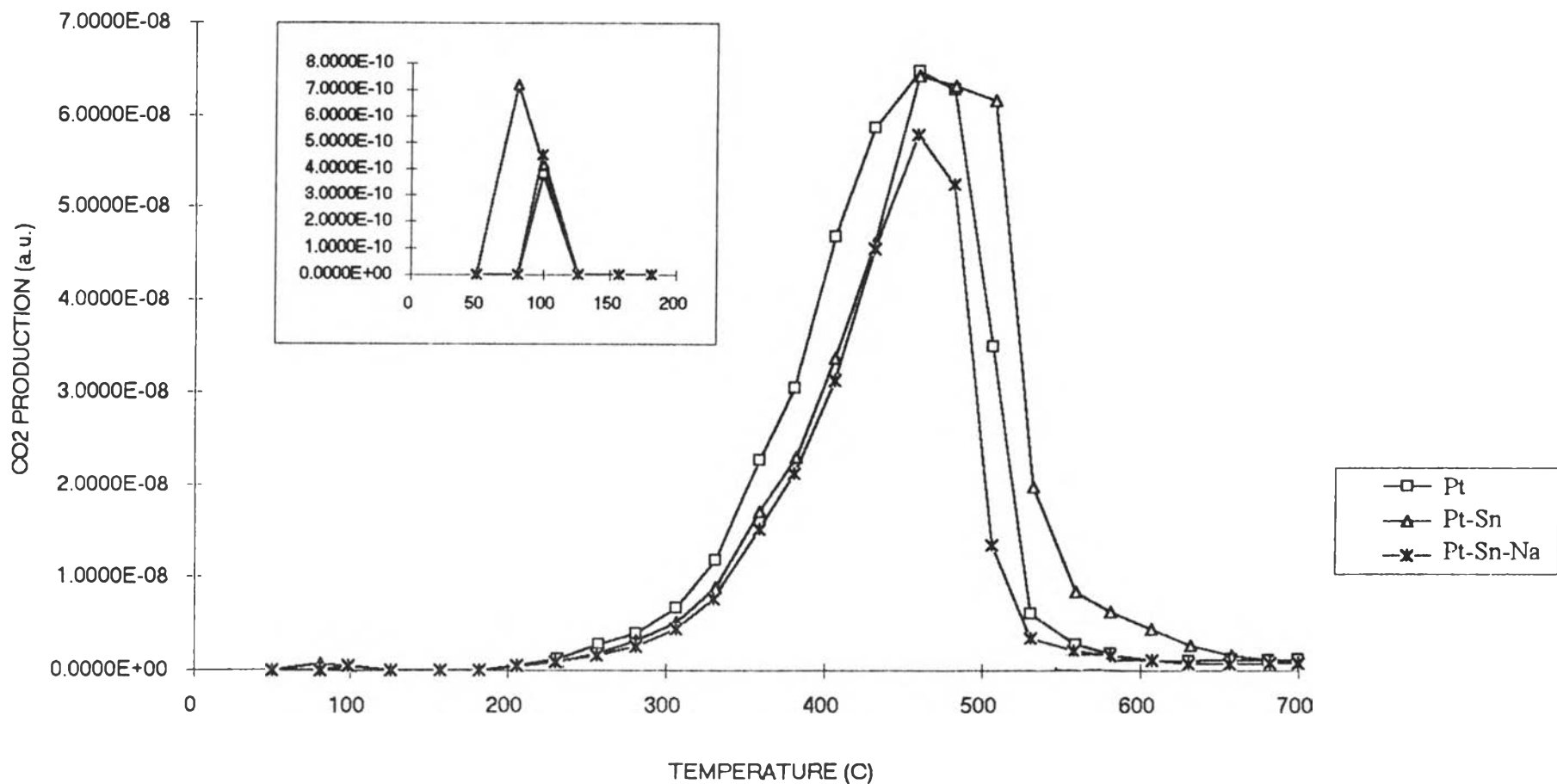


Figure 5.11 Temperature programmed oxidation of various coked catalyst for different promoters at 500 °C and H₂/HC = 0 .

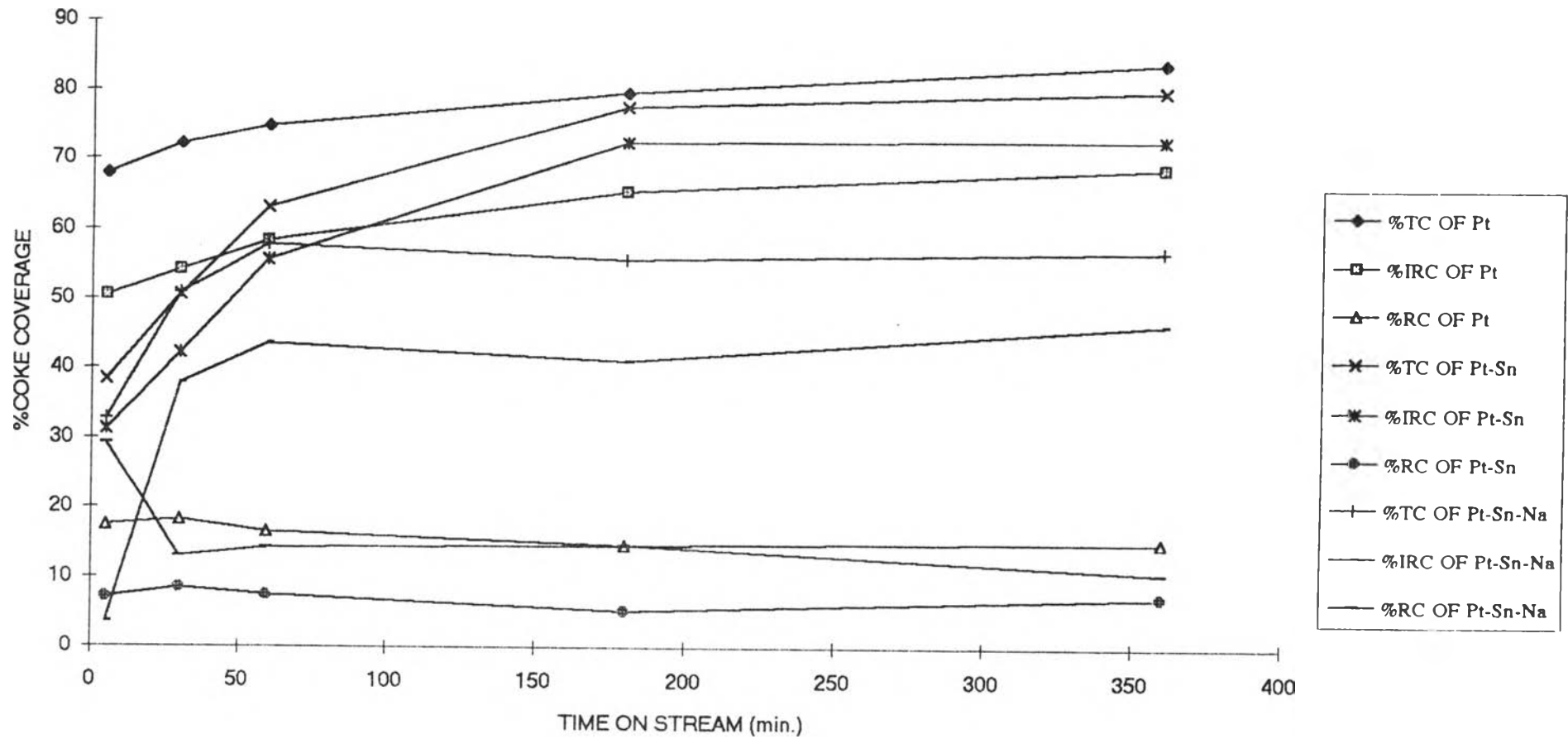


Figure 5.12 Total coke, reversible coke and irreversible coke on the metal site of various coke catalyst.

Total coke on metal site : $\text{Pt}/\text{Al}_2\text{O}_3 > \text{Pt-Sn}/\text{Al}_2\text{O}_3 > \text{Pt-Sn-Na}/\text{Al}_2\text{O}_3$.
 Irreversible coke on metal site : $\text{Pt-Sn}/\text{Al}_2\text{O}_3 > \text{Pt}/\text{Al}_2\text{O}_3 > \text{Pt-Sn-Na}/\text{Al}_2\text{O}_3$.
 Reversible coke on metal site : $\text{Pt}/\text{Al}_2\text{O}_3 > \text{Pt-Sn-Na}/\text{Al}_2\text{O}_3 > \text{Pt-Sn}/\text{Al}_2\text{O}_3$.

In comparison to the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst, the $\text{Pt-Sn}/\text{Al}_2\text{O}_3$ catalyst have lower total coke deposits on the metal site. This can be explained by the proposed drain-off mechanism. It is suggested that coke precursors are adsorbed less strongly. Consequently they are more mobile and can more easily migrate to the alumina where they are finally deposits as coke. For $\text{Pt-Sn-Na}/\text{Al}_2\text{O}_3$, total coke deposits on the metal site is the least due to more coke precursor is eliminated by hydrogen spill-over.

Although the total coke deposits on the metal site of $\text{Pt-Sn}/\text{Al}_2\text{O}_3$ catalyst is lower, main coke is irreversible coke since $\text{Pt-Sn}/\text{Al}_2\text{O}_3$ catalyst has a high dehydrogenation activity in converting coke to be more irreversible, therefore, the irreversible coke deposited on $\text{Pt-Sn}/\text{Al}_2\text{O}_3$ catalyst is higher than on $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. For $\text{Pt-Sn-Na}/\text{Al}_2\text{O}_3$, the irreversible coke deposited on the metal site was the least due to more coke precursor is eliminated by hydrogen spill over.

According to the fact that the main coke deposits on $\text{Pt-Sn}/\text{Al}_2\text{O}_3$ catalyst is irreversible coke, therefore the reversible coke on $\text{Pt-Sn}/\text{Al}_2\text{O}_3$ catalyst is lower than on $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. The reversible coke on $\text{Pt-Sn-Na}/\text{Al}_2\text{O}_3$ catalyst is higher than on $\text{Pt-Sn}/\text{Al}_2\text{O}_3$ catalyst, it may be because the hydrogen spill-over caused by sodium component removes coke precursor and keep the nature of coke to be more reversible but the reversible coke is lower than on $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. The possible explanation is the sodium component effect is not enough to compensate the converting coke to be irreversible coke by tin effect.

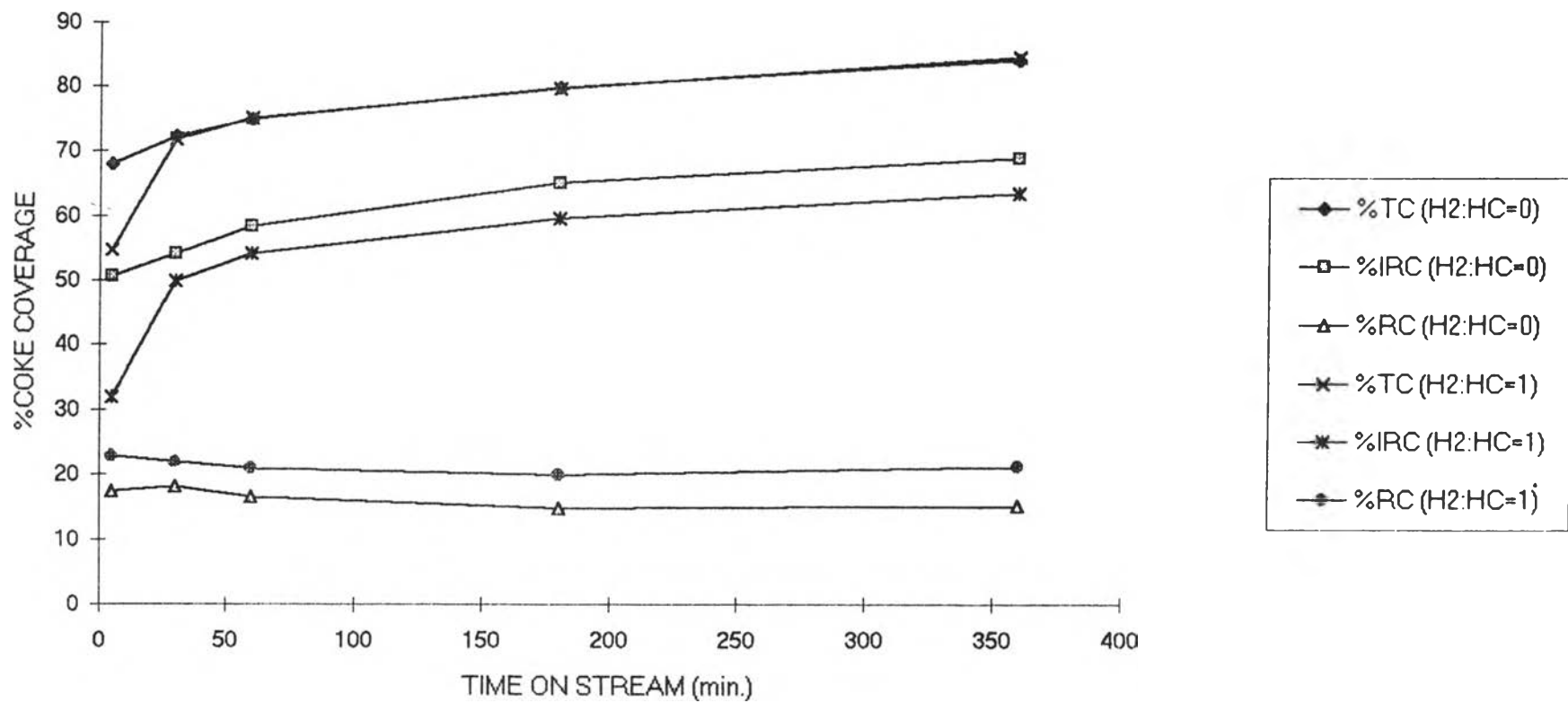


Figure 5.13 Total coke, reversible coke and irreversible coke on the metal site of 0.3% Pt/Al₂O₃ catalyst with different H₂/HC.

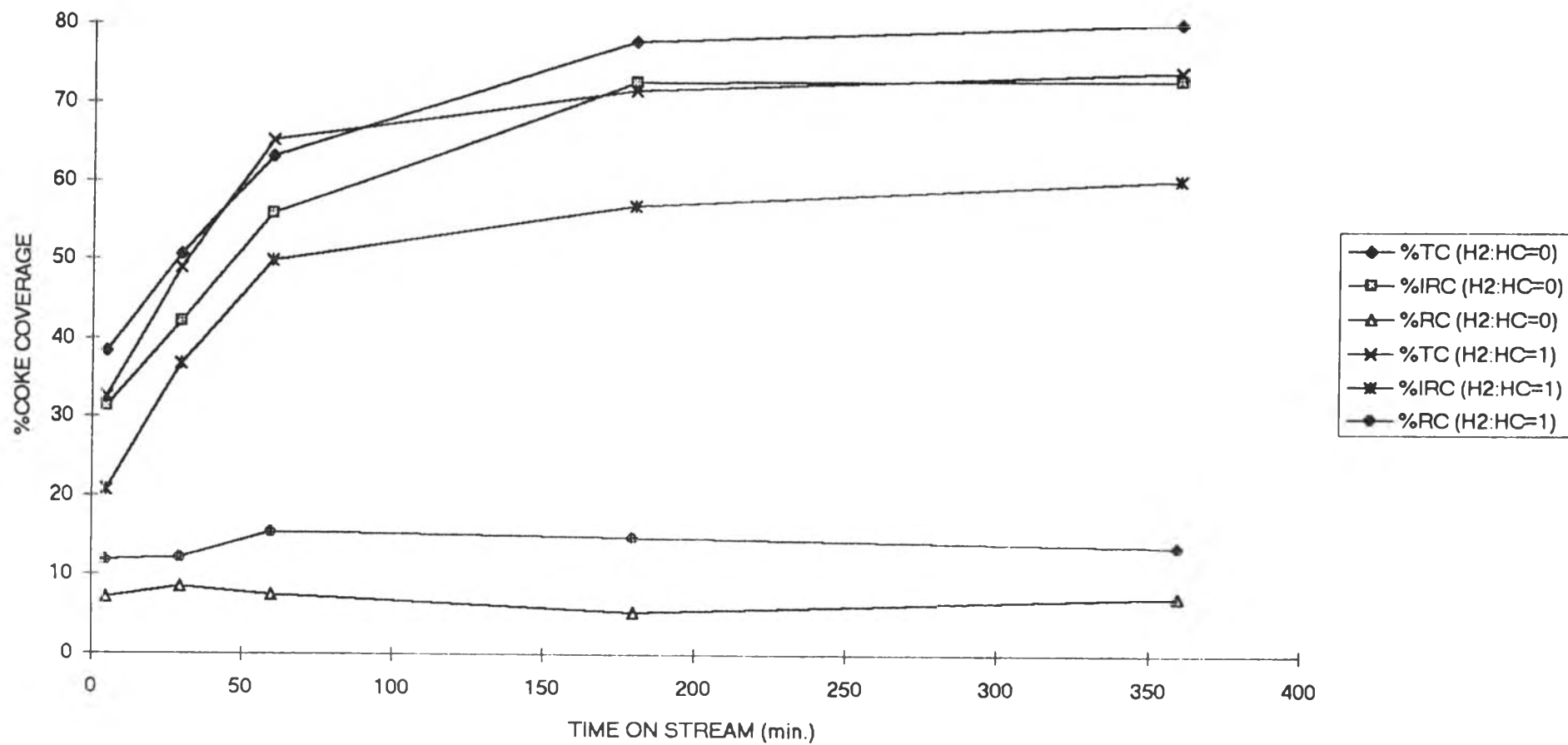


Figure 5.14 Total coke, reversible coke and irreversible coke on the metal site of 0.3 % Pt-0.3 % Sn/Al₂O₃ catalyst with different H₂/HC.

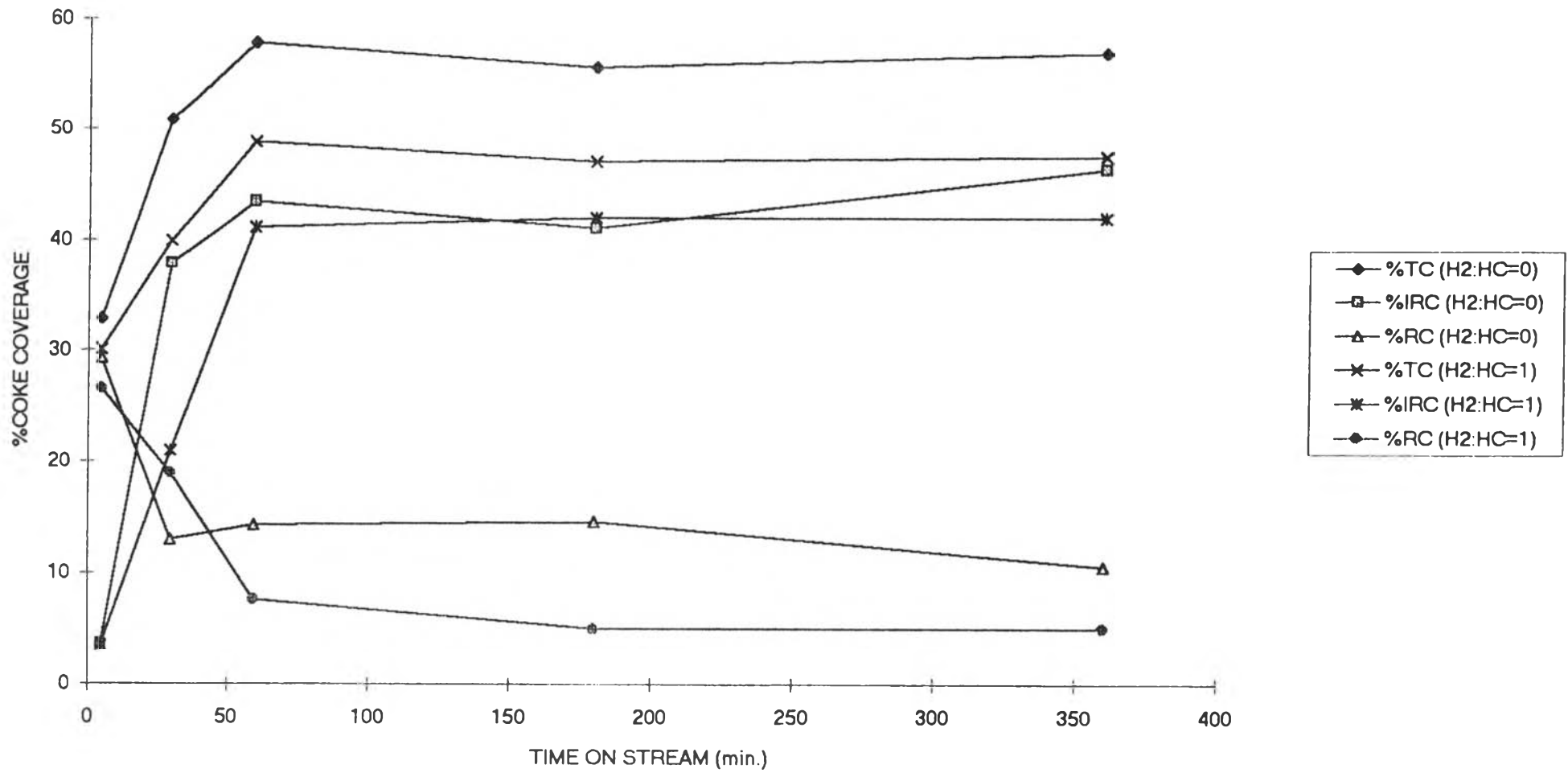


Figure 5.15 Total coke , reversible coke and irreversible coke on the metal site of 0.3 % Pt-0.3 % Sn - 0.6 % Na/Al₂O₃ catalyst with different H₂/HC.

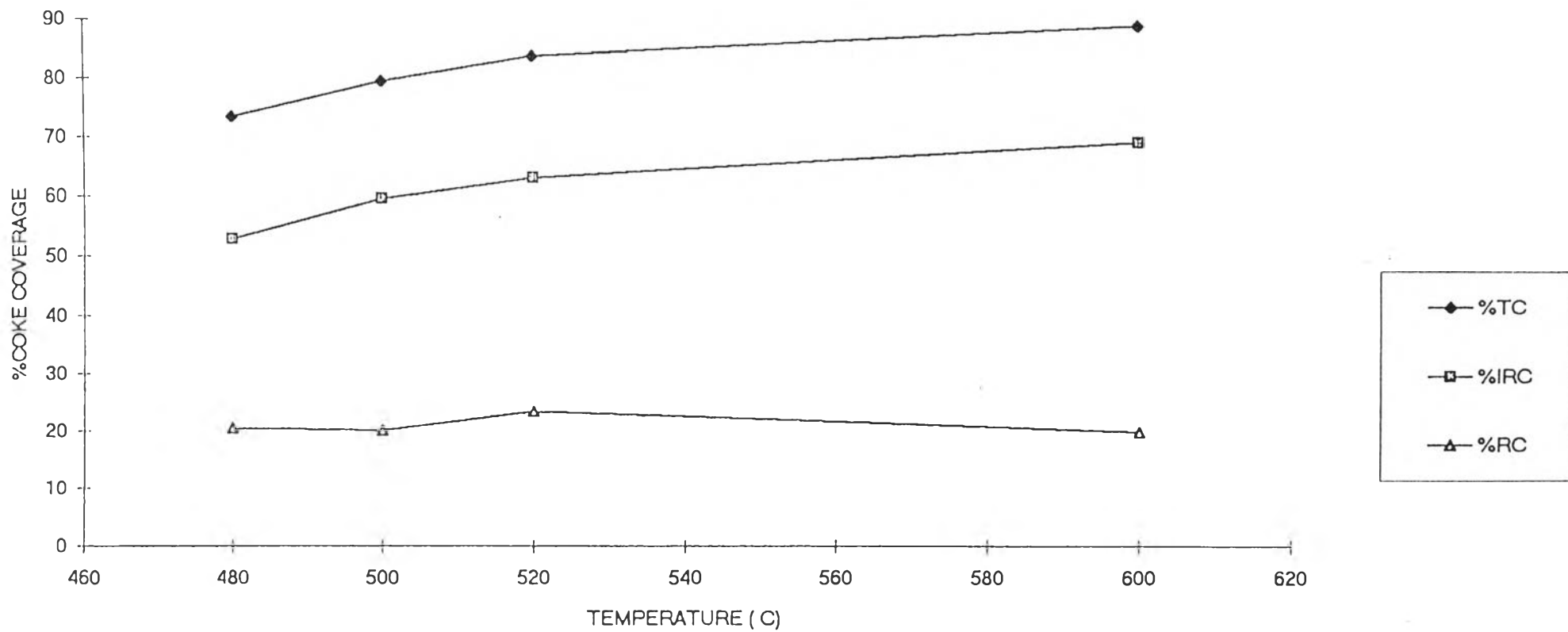


Figure 5.16 Total coke, reversible coke and irreversible coke on metal site of 0.3 % Pt/Al₂O₃ catalyst vary with reaction temperature at H₂/HC =1.

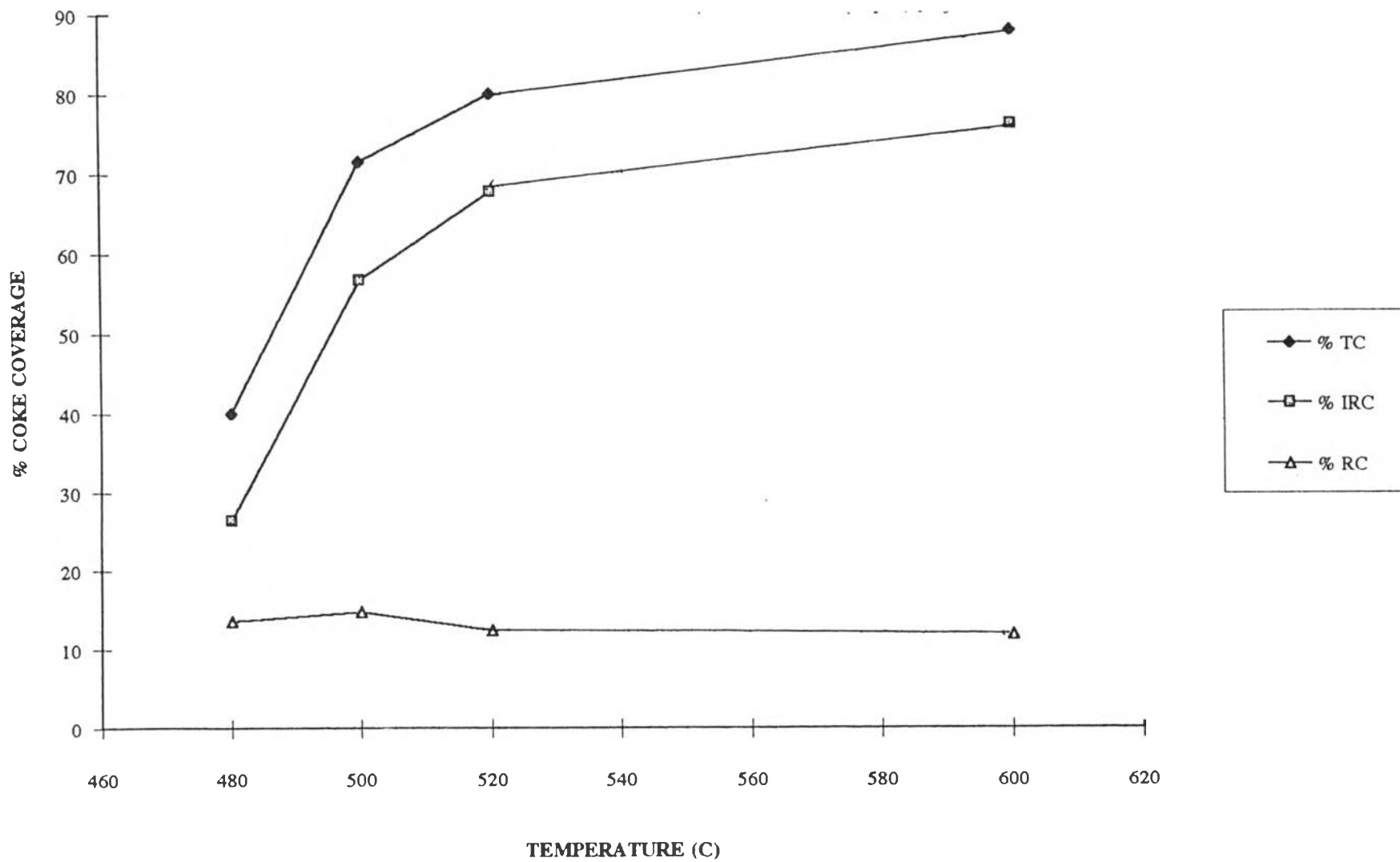


Figure 5.17 Total coke, reversible coke and irreversible coke on metal site of 0.3 % Pt-0.3 % Sn/Al₂O₃ catalyst vary with reaction temperature at H₂/HC =1.

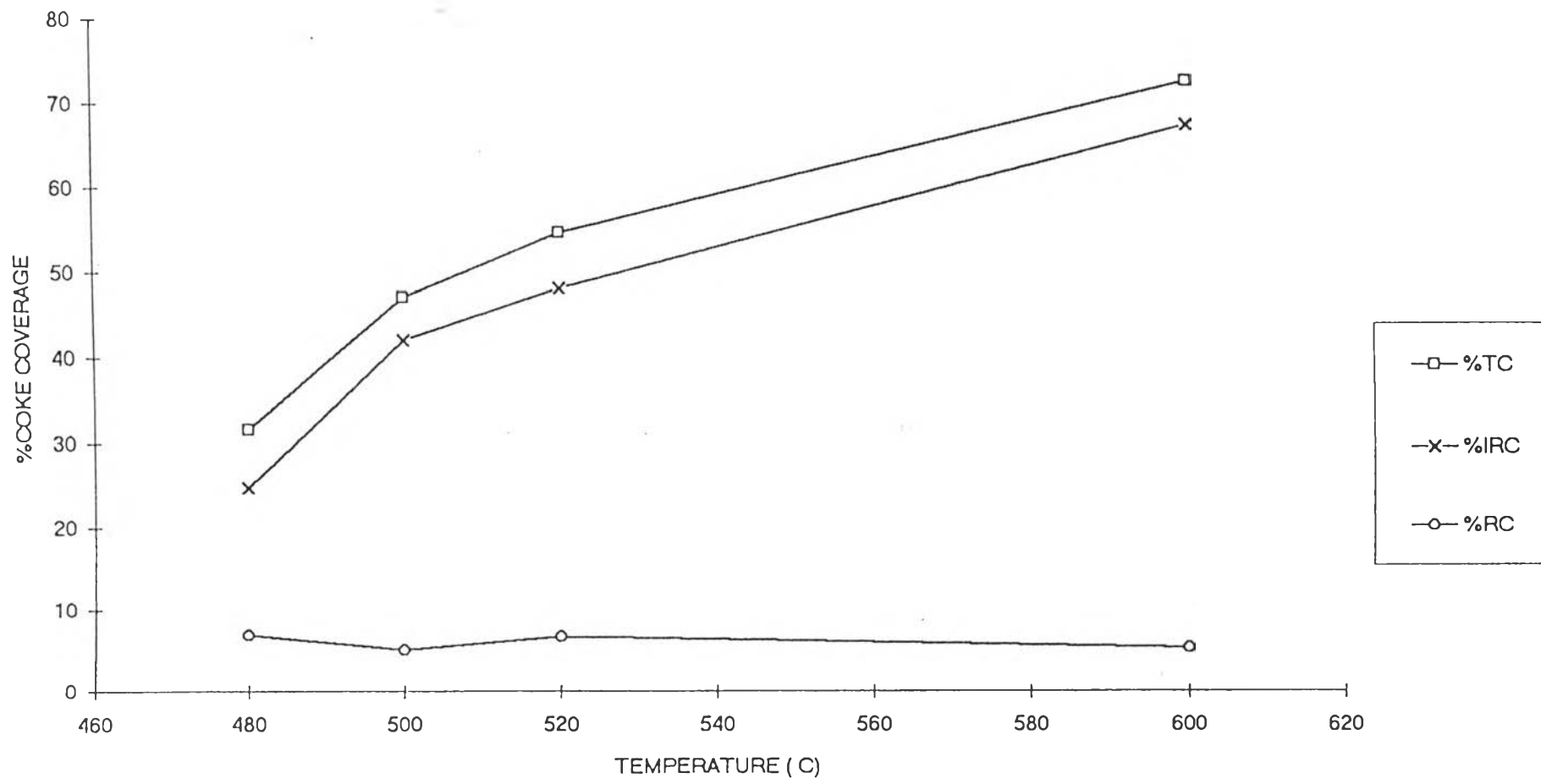


Figure 5.18 Total coke, reversible coke and irreversible coke on metal site of 0.3 % Pt - 0.3 % Sn-0.6 % Na/Al₂O₃ catalyst vary with reaction temperature at H₂/HC =1.

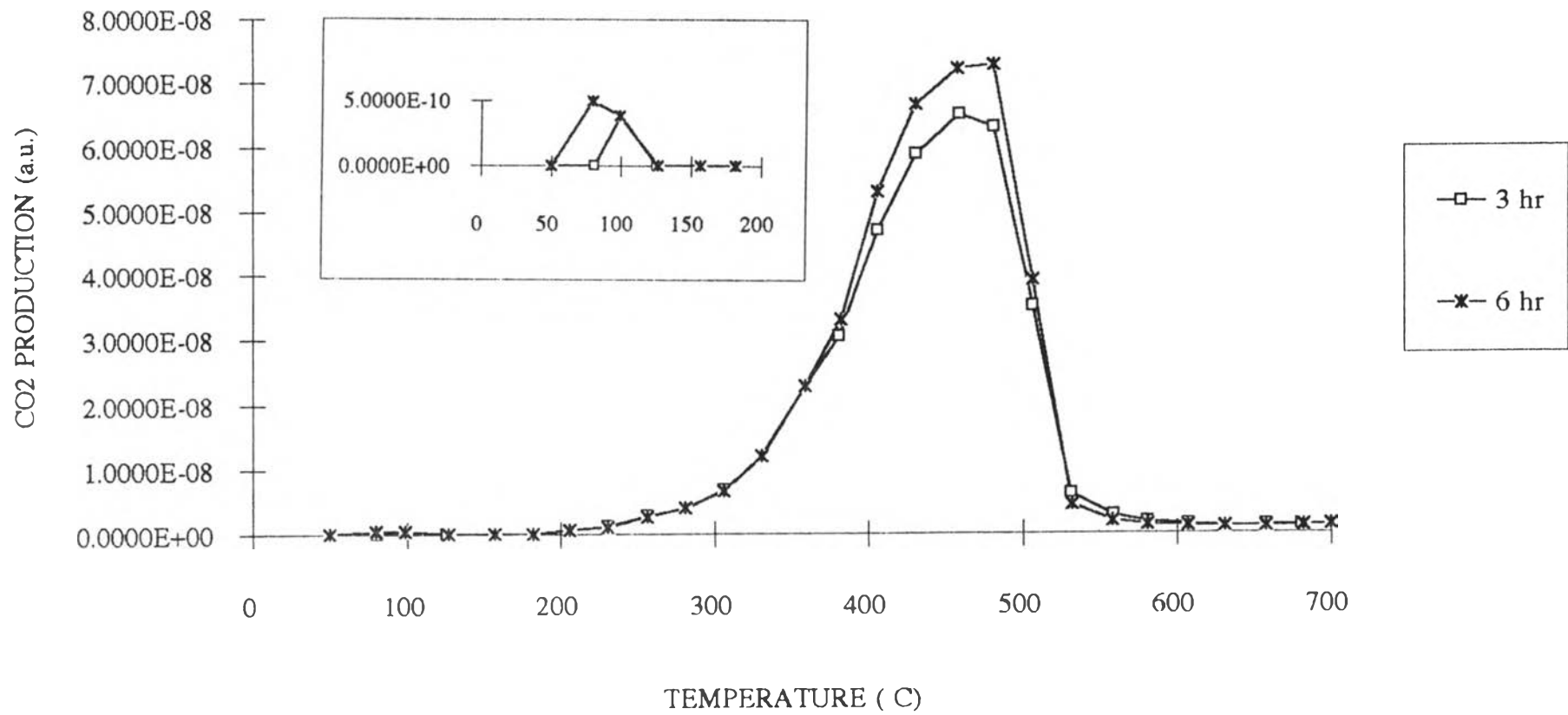


Figure 5.19 Temperature programmed oxidation of coked 0.3 % Pt/Al₂O₃ catalyst at H₂/HC = 1 with different time on stream.

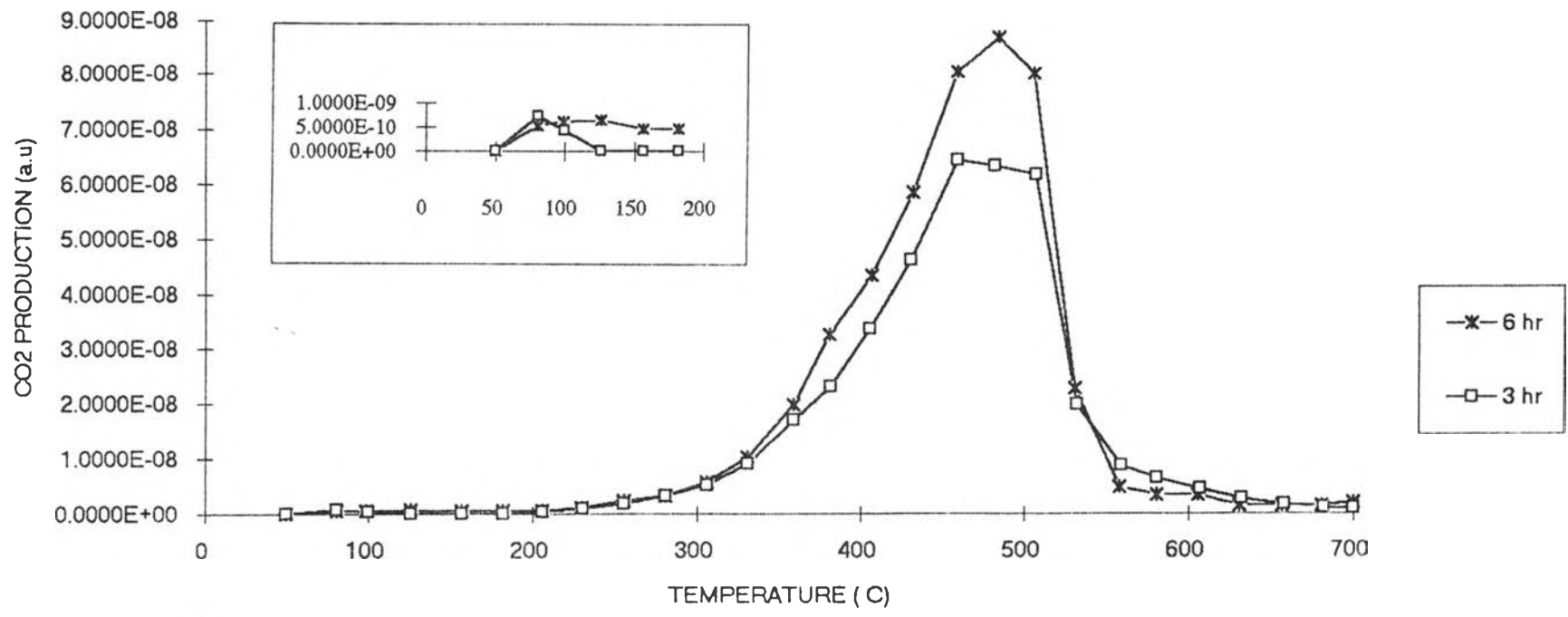


Figure 5.20 Temperature programmed oxidation of coke 0.3 % Pt-0.3 % Sn/Al₂O₃ catalyst at H₂/HC =1 with defferent time on stream.

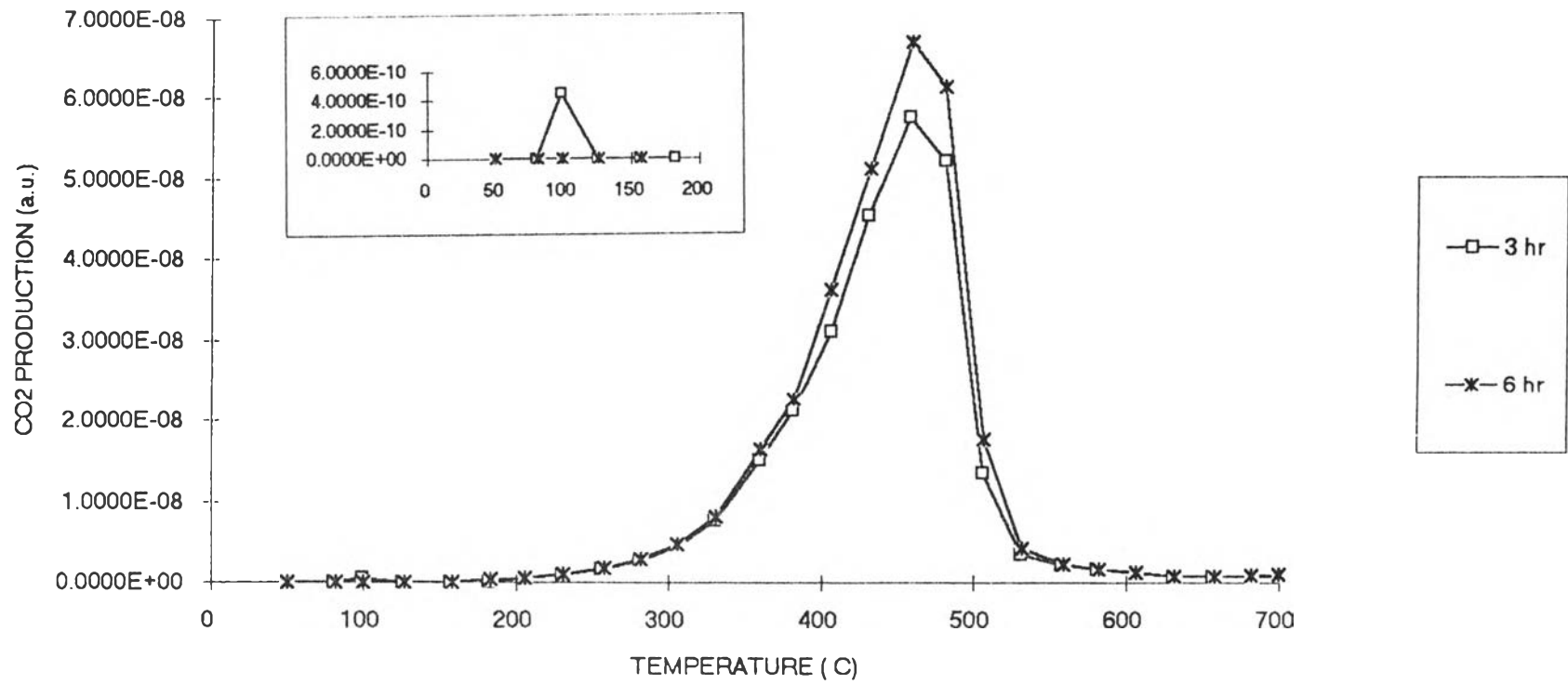


Figure 5.21 Temperature programmed oxidation of coke 0.3 % Pt - 0.3 % Sn-0.3 % Na/Al₂O₃ catalyst at H₂/HC = 1 with different time on stream.

formed very rapidly on the platinum sites, more deposit is formed, a substantial part of the Pt becomes covered by coke. After this first period the “surviving” Pt sites produce coke with a lower but constant rate. All the coke are immediately transferred from Pt to acidic sites of the alumina where the final coke formation takes place. This is in accordance with the conclusion of Barbier et al (14,15) that the carbon coverage of the metal remains constant while coke is deposited on the support.

In addition, the reversible coke for Pt/Al₂O₃ and Pt-Sn/Al₂O₃ at time on stream = 6 hr. is higher than at time on stream = 3 hr. and for Pt-Sn-Na/Al₂O₃ the result is opposite. It gave the comment that reversible coke can grow on acid site of alumina support by coke precursor migrated from metal site and transform to irreversible coke. The other assumptions are both reversible and irreversible coke can migrate to acid site of alumina support.

In a long run of dehydrogenation reaction, dehydrogenation activity is not zero because of the still vacant site due to ensemble effect on the metal site. Proposed model of coke formation is shown in figure 5.22.

STEP 1 : Propane is adsorbed on the metal active site, series of fragmentation and dehydrogenation reactions lead to reversible coke formation on the reversible coke site.

STEP 2 : On the reversible coke site, reversible coke migrates to irreversible coke site where all reversible coke deposits on the irreversible site is transformed to irreversible coke by hydrogen removal.

STEP 3 : Coke precursor, reversible coke and irreversible coke drain - off from the metal site to alumina.

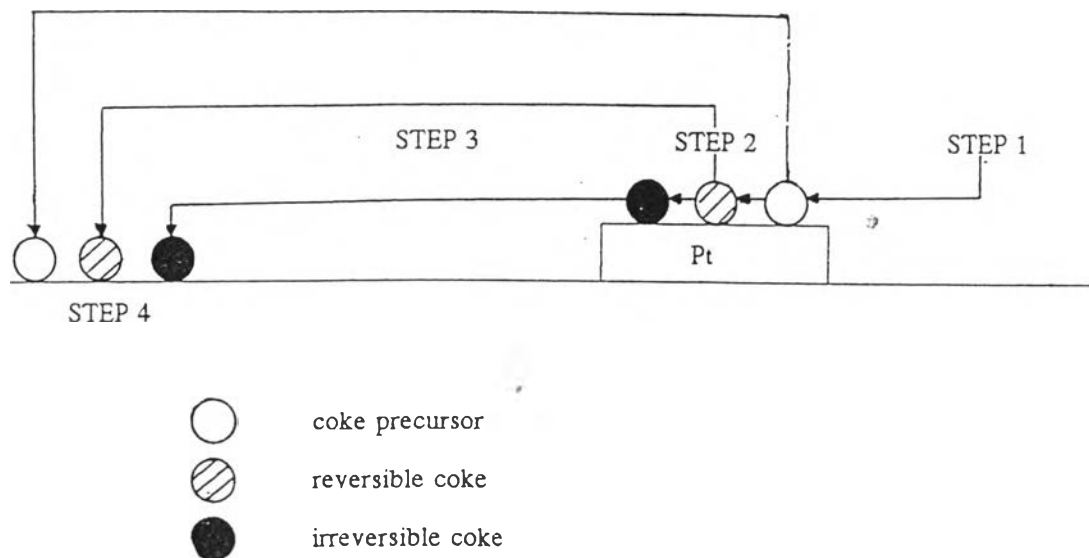


Figure 5.22 Proposed model for coke formation.

STEP 4 : Reversible coke on alumina transforms to irreversible coke by hydrogen removal.

The amount of reversible coke on metal site must be due to :

Rate of reversible coke = Rate of reversible coke formation - rate of reversible deposits on metal active site
 coke transforms to irreversible coke - rate of reversible coke drains-off to acid sites of alumina

The amount of reversible coke on support must be due to :

Rate of reversible coke = Rate of coke precursor drains off and transforms to deposits on acid site of alumina
 reversible coke + rate of reversible coke drains off - rate of reversible coke transforms to irreversible coke on acid site of alumina

The amount of irreversible coke on metal site must be due to :

Rate of irreversible coke deposits on metal active site = Rate of reversible coke transforms to irreversible coke - rate of irreversible coke drains off to acid site of alumina

The amount of irreversible coke on support must be due to :

Rate of irreversible coke deposits on acid site of alumina = Rate of irreversible coke drains off + rate of reversible coke transforms to irreversible coke on acid site of alumina

The regeneration method was divided into 4 parts. The first part gave the total metal site. The second part gave the vacant site, the difference between the first and second part gave the total coke deposited on the metal site. The third part was reversible coke regeneration performed at a temperature of 250 °C, this temperature was set by observing reversible coke formation on the TPO curve at a temperature lower than 250 °C, this part gave the vacant site and reversible coke site, the difference between the first and the third part gave irreversible coke deposited on the metal site. The difference between total coke and irreversible coke was reversible coke deposited on the metal site. For the last part, the criteria for adoption in the experiment was set as the number of metal sites of catalysts after regeneration must be the same as fresh catalyst on the basis that the metal site was not diminished by other factors during dehydrogenation reaction. The temperature of 500 °C was chosen by observing the second peak of the TPO pattern representing irreversible coke around 400-500 °C. The results of metal site after regeneration at 500 °C are shown in Table 5.4.

Proposed model of the metal site regeneration is shown in figure 5.23

Table 5.4 % error of metal site after irreversible coke regeneration at 500 °C. (compared with fresh catalyst)

Catalyst	Conditions			% error
	Temperature	H ₂ /HC	Time on Stream	
0.3 % Pt/Al ₂ O ₃	500 °C.	0	6 hr.	0.09
	500 °C.	1	6 hr.	5.93
	520 °C.	1	3 hr.	1.70
	600 °C.	1	3 hr.	1.78
0.3 % Pt-0.3 % Sn/Al ₂ O ₃	500 °C.	0	6 hr.	4.23
	500 °C.	1	6 hr.	3.29
	520 °C.	1	3 hr.	7.58
	600 °C.	1	3 hr.	2.90
0.3 % Pt-0.3 Sn-0.6% Na/Al ₂ O ₃	500 °C.	0	6 hr.	5.63
	500 °C.	1	6 hr.	9.34
	520 °C.	1	3 hr.	8.03
	600 °C.	1	3 hr.	11.35

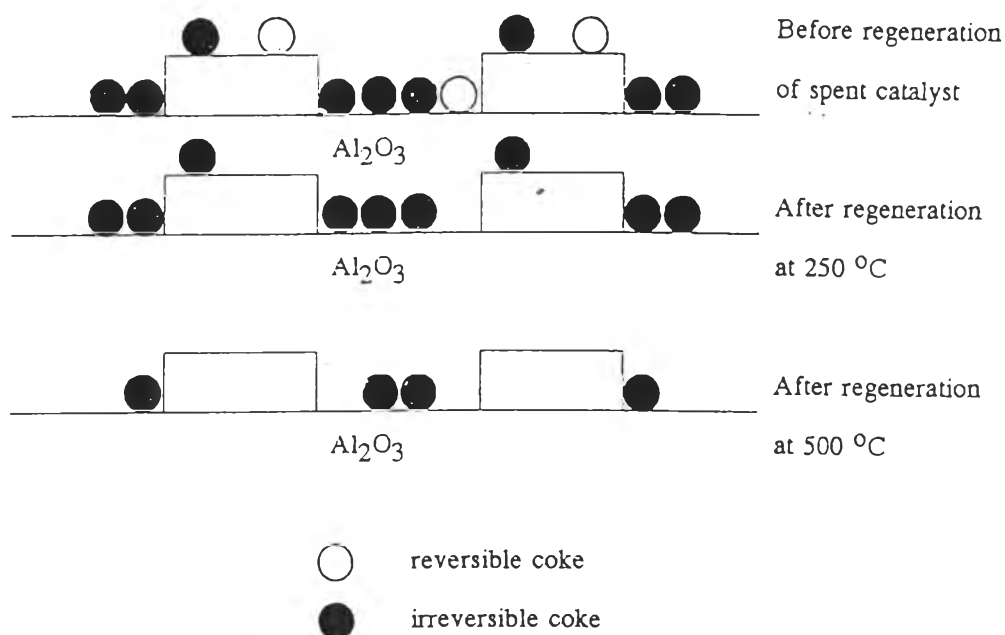


Figure 5.23 Proposed model of regeneration.

The proposed model in figure 5.23 can be explained by the fact that when the dehydrogenation reaction proceeded, there are reversible coke and irreversible coke deposit on both alumina and metal site. After regeneration at 250 °C all reversible coke is removed by gasification with oxygen to form carbon dioxide and leave only the irreversible coke deposits on the metal site and alumina. After regeneration at 500 °C, the irreversible coke deposits on the metal site is eliminated by oxygen, only some irreversible coke still deposits on alumina but it has no effect on the activity of dehydrogenation catalyst.

Compared to the work of J. Biswas et al (17) for determination of coke deposited on metal site. J. Biswas et al used TPO to separate coke deposited on metal from coke deposited on alumina and used TGA for determining reversible coke and irreversible coke but this study used metal site measurement by CO adsorption to determine reversible coke and irreversible coke and used TPO to find reversible coke regeneration temperature. There are two advantages for this

research. First, it is a direct method to determine reversible coke site, irreversible coke site and vacant site. Second, this method can be verified by checking the metal site of spent catalysts after removal all coke deposits on metal that must be the same as fresh catalysts. J. Biswas's method was based on the assumption that there was no reversible coke deposited on alumina but this study shows that reversible coke can be deposited on both metal sites and alumina.

In the experimental data, J. Biswas et al showed that the fraction of irreversible coke deposited on the metal site increased with temperature, But in this study, the difference between total coke and irreversible coke, i.e. reversible coke, deposits on the metal site is constant with temperature range of 480-600 °C and time on stream.