

## **CHAPTER V**

### **RESULTS AND DISCUSSION**

The results and discussion in this chapter are divided into five major parts including the study of the intermediates on catalysts, characterization of the intermediates species, physical properties of catalysts, morphology and the proposed mechanism of the formation and removal of the intermediates, respectively.

#### **5.1 The study of the intermediates on catalysts**

##### **5.1.1 The Effect of Type of Hydrocarbons on the Intermediates**

The amount and nature of the intermediates on the spent catalyst were characterized using the temperature programmed oxidation (TPO) technique. The study the effect of hydrocarbon was conducted with two hydrocarbon species of propene and toluene over HY, HMOR, H-ZSM-5, Cu-ZSM-5 catalysts. The reaction temperature was 400 °C for 20 min. The oxidizing gas was 1000ppm NO+1%O<sub>2</sub>/He. The results are attributed to the amount of carbon on catalysts and the amount of nitrogen of the oxidizing gas that calculate from the area underneath as listed in table 5.1. As show in table 5.1, the amounts of the intermediates on catalyst was depended on type of hydrocarbon. These results can be implied that the intermediates formation reaction is affected by type of hydrocarbon. It can observe that the amount of the intermediates on all catalysts by propene was less than the amount of the intermediates on all catalysts by toluene.

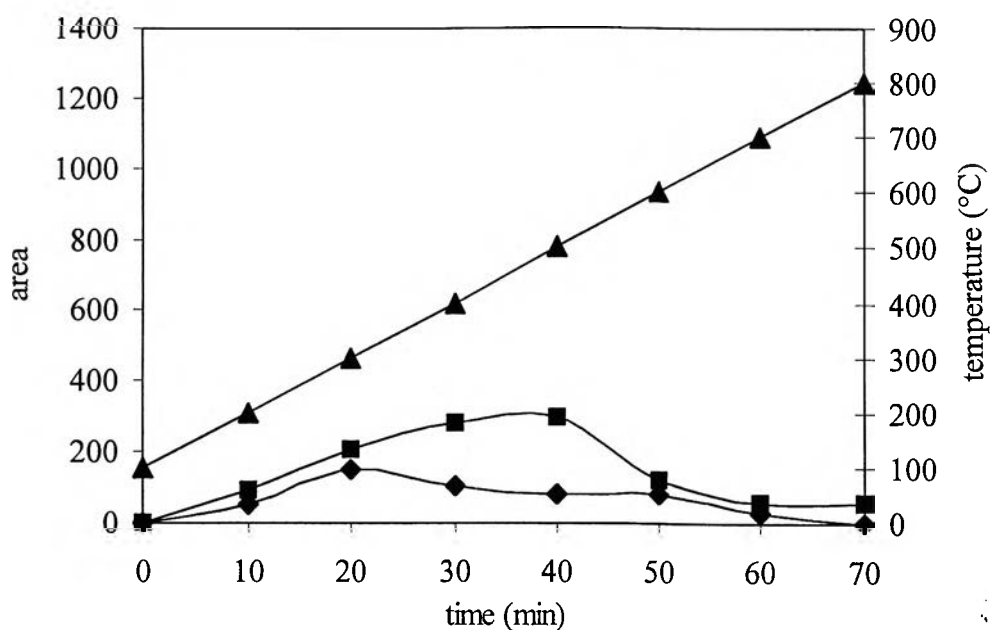
With propene and toluene as the reductants, figures 5.1-5.8 show that the peak areas and the shapes of the TPO profiles were different. The CO<sub>2</sub> and N<sub>2</sub> area often increased initially with increasing temperature until it reaches a maximum, and is then followed by a decrease. For the intermediates formed by using propene on these catalysts, the peaks with maximum temperature are at 475, 730, 480 and 400 °C on HY, HMOR, H-ZSM-5 and Cu-ZSM-5, respectively. In the case of toluene, the peak of these catalysts was recorded at higher temperature on every catalyst, except Cu-

ZSM-5. The peak with maximum temperature is at 680, 780, 670 and 400 °C on HY, HMOR, H-ZSM-5 and Cu-ZSM-5, respectively. This suggests that the nature of the intermediates is different for propene and toluene.

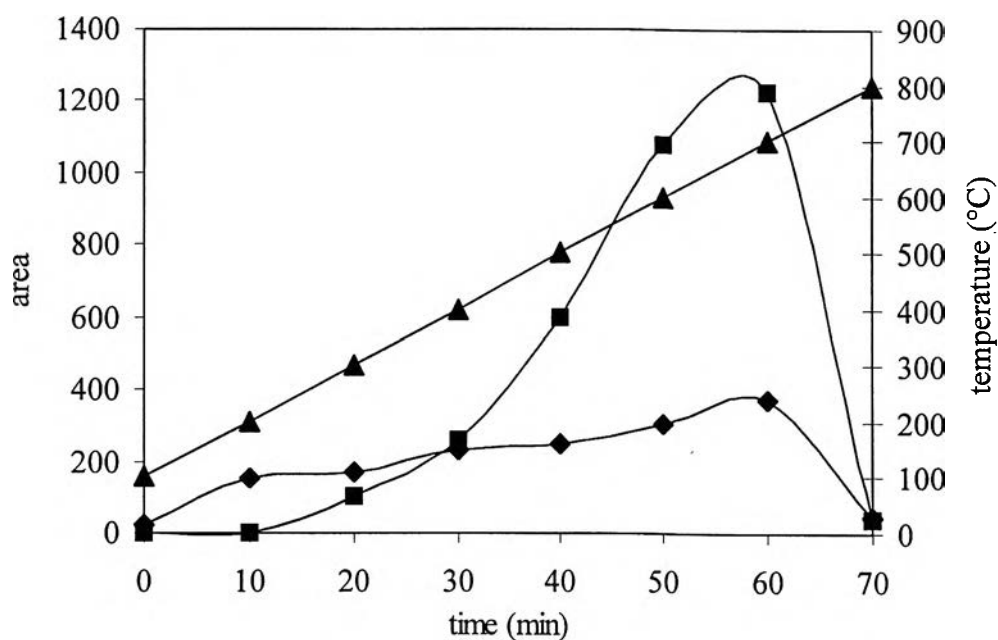
**Table 5.1** The amount of carbon on the catalysts and the amount of nitrogen from the oxidizing gas with various hydrocarbons and catalysts

reactant	catalyst	the amount of carbon on catalyst (%wt)	the amount of nitrogen from the oxidizing gas mixture (%wt)	ratio of nitrogen from the oxidizing gas per carbon on catalyst (wt ratio)
C <sub>3</sub> H <sub>6</sub>	HY	0.21	0.08	0.38
toluene	HY	0.62	0.21	0.34
C <sub>3</sub> H <sub>6</sub>	HMOR	0.93	0.19	0.20
toluene	HMOR	1.21	0.19	0.16
C <sub>3</sub> H <sub>6</sub>	H-ZSM-5	0.33	0.28	0.84
toluene	H-ZSM-5	0.40	0.32	0.80
C <sub>3</sub> H <sub>6</sub>	Cu-ZSM-5	0.47	0.18	0.38
toluene	Cu-ZSM-5	2.12	0.74	0.35

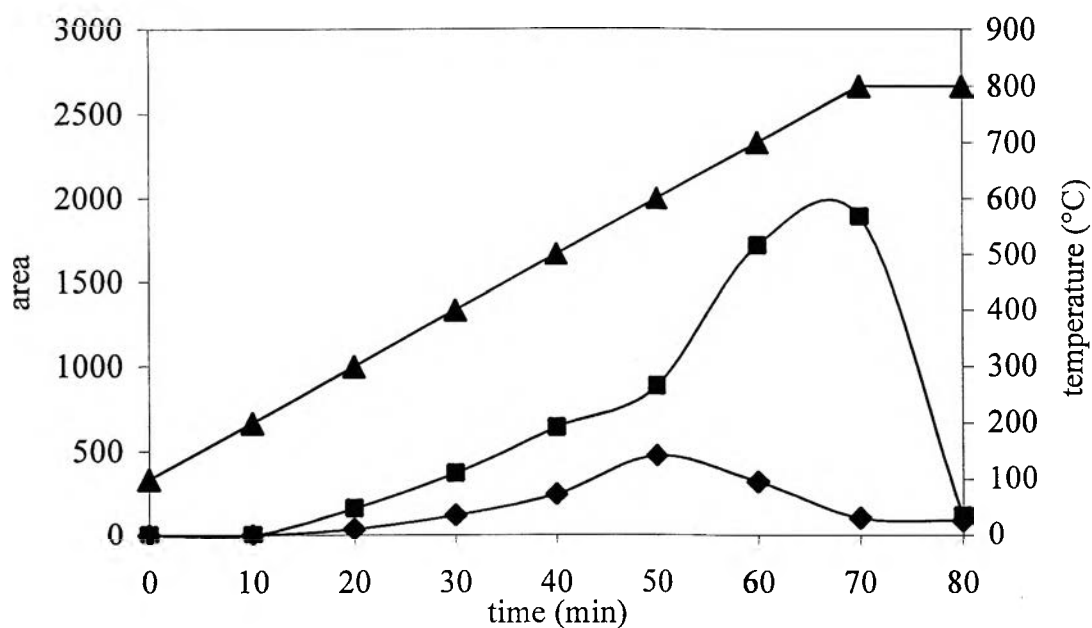
Mostly, the intermediates formed with toluene are “harder” than the intermediates formed with propene. In the case of Cu-ZSM-5 catalyst, the maximum of CO<sub>2</sub> area is observed at the same temperature. It may be the structure of the intermediates that occur from propene and toluene was the like structure. This nature of the intermediate on these catalysts corresponding with literature of Chen *et al.* (1999), which observed that the intermediates are different for n-C<sub>4</sub>H<sub>10</sub> and i-C<sub>4</sub>H<sub>10</sub>, then it can be suggested that the nature of intermediates depend on type of hydrocarbons.



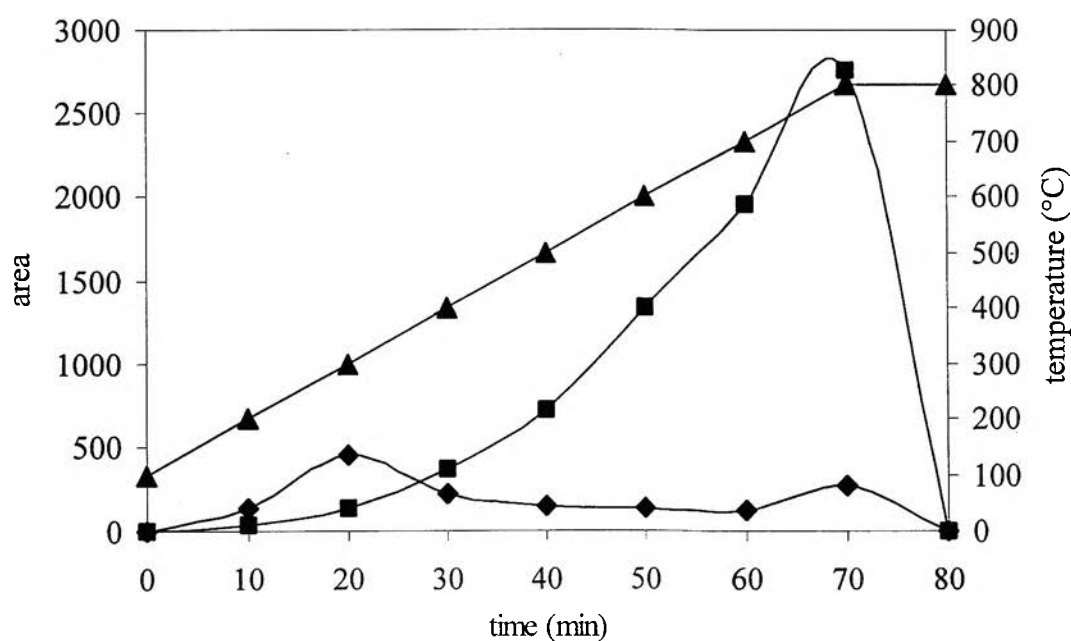
**Figure 5.1** TPO pattern of HY catalyst after adsorption by propene propene (3% mole C) and balance He, GHSV  $\approx 20000 \text{ h}^{-1}$ , TPO by 1000ppm NO+1%O<sub>2</sub>/He, reaction temperature 400°C for 20 min; ■ area CO<sub>2</sub>, ◆ area N<sub>2</sub>, ▲ temperature



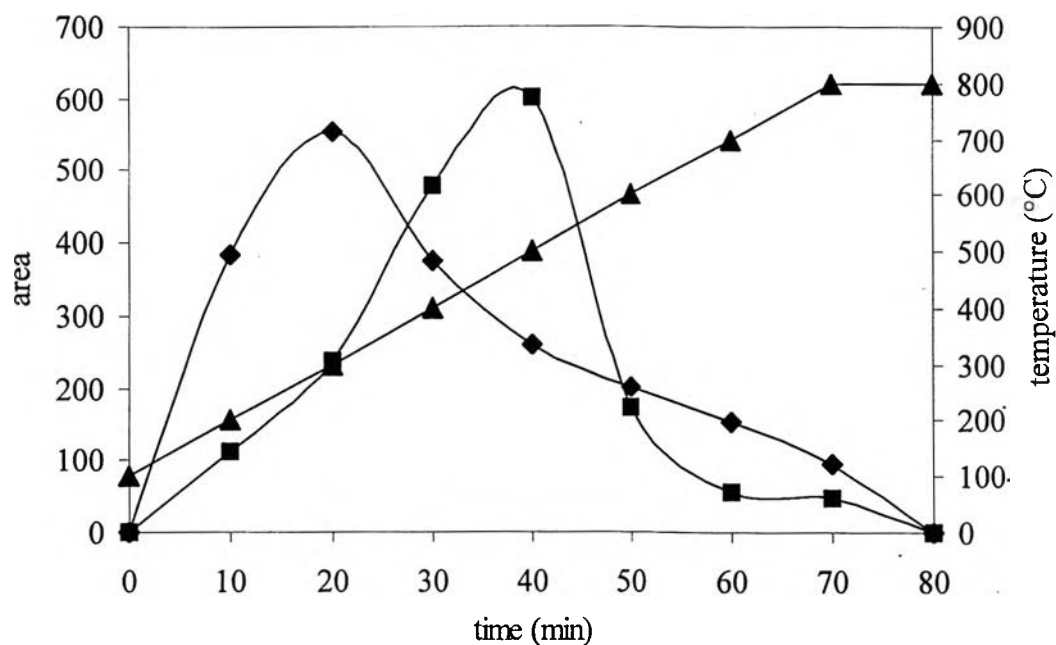
**Figure 5.2** TPO pattern of HY catalyst after adsorption by toluene toluene (3% mole C) and balance He, GHSV  $\approx 20000 \text{ h}^{-1}$ , TPO by 1000ppm NO+1%O<sub>2</sub>/He, reaction temperature 400°C for 20 min; ■ area CO<sub>2</sub>, ◆ area N<sub>2</sub>, ▲ temperature



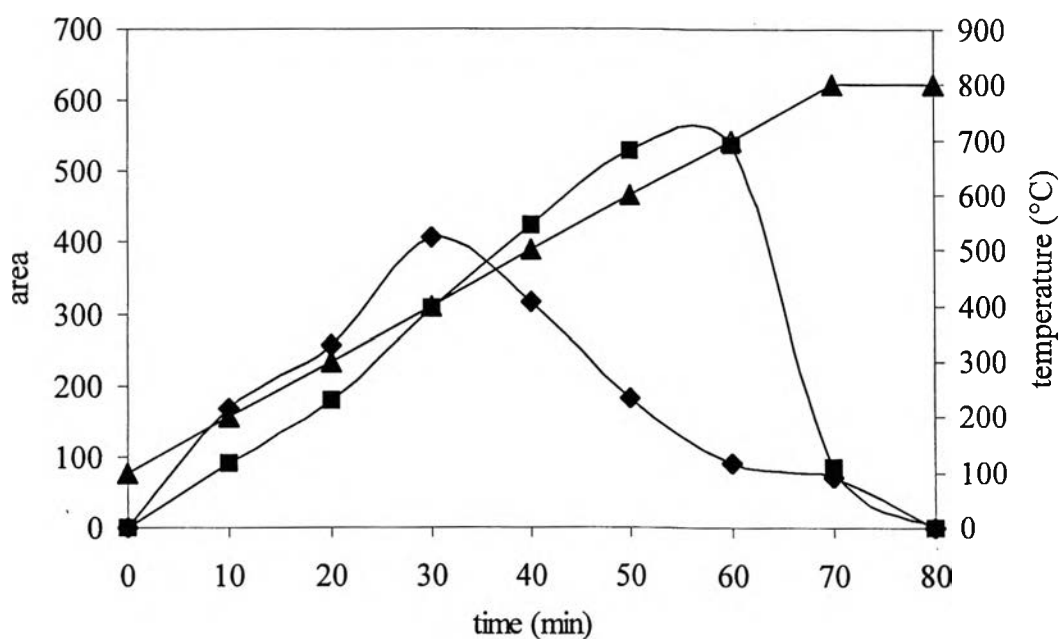
**Figure 5.3** TPO pattern of HMOR catalyst after adsorption by propene propene (3% mole C) and balance He, GHSV  $\approx 20000 \text{ h}^{-1}$ , TPO by 1000ppm NO+1%O<sub>2</sub>/He, reaction temperature 400°C for 20 min; ■ area CO<sub>2</sub>, ◆ area N<sub>2</sub>, ▲ temperature



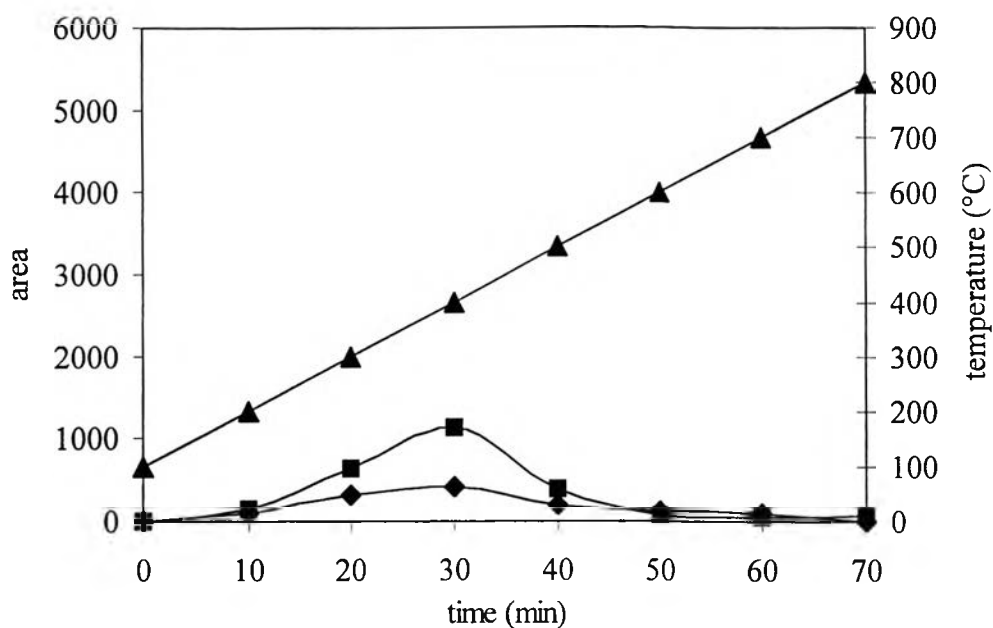
**Figure 5.4** TPO pattern of HMOR catalyst after adsorption by toluene toluene (3% mole C) and balance He, GHSV  $\approx 20000 \text{ h}^{-1}$ , TPO by 1000ppm NO+1%O<sub>2</sub>/He, reaction temperature 400°C for 20 min; ■ area CO<sub>2</sub>, ◆ area N<sub>2</sub>, ▲ temperature



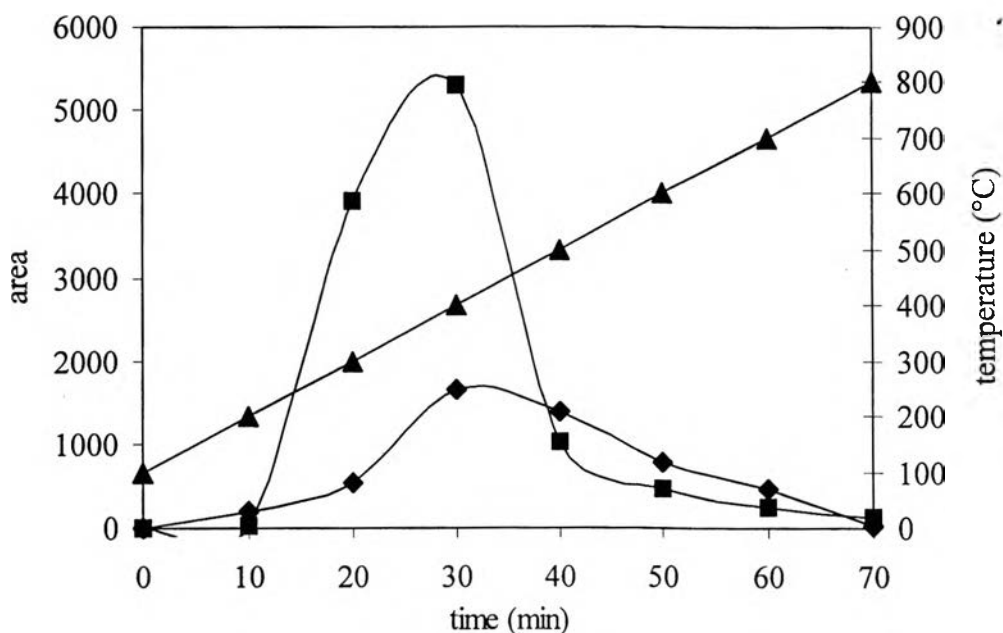
**Figure 5.5** TPO pattern of H-ZSM-5 catalyst after adsorption by propene propene (3% mole C) and balance He, GHSV  $\approx 20000 \text{ h}^{-1}$ , TPO by 1000ppm NO+1%O<sub>2</sub>/He, reaction temperature 400°C for 20 min; ■ area CO<sub>2</sub>, ◆ area N<sub>2</sub>, ▲ temperature



**Figure 5.6** TPO pattern of H-ZSM-5 catalyst after adsorption by toluene toluene (3% mole C) and balance He, GHSV  $\approx 20000 \text{ h}^{-1}$ , TPO by 1000ppm NO+1%O<sub>2</sub>/He, reaction temperature 400°C for 20 min; ■ area CO<sub>2</sub>, ◆ area N<sub>2</sub>, ▲ temperature



**Figure 5.7** TPO pattern of Cu-ZSM-5 catalyst after adsorption by propene propene (3% mole C) and balance He, GHSV  $\approx 20000 \text{ h}^{-1}$ , TPO by 1000ppm NO+1%O<sub>2</sub>/He, reaction temperature 400°C for 20 min; ■ area CO<sub>2</sub>, ◆ area N<sub>2</sub>, ▲ temperature

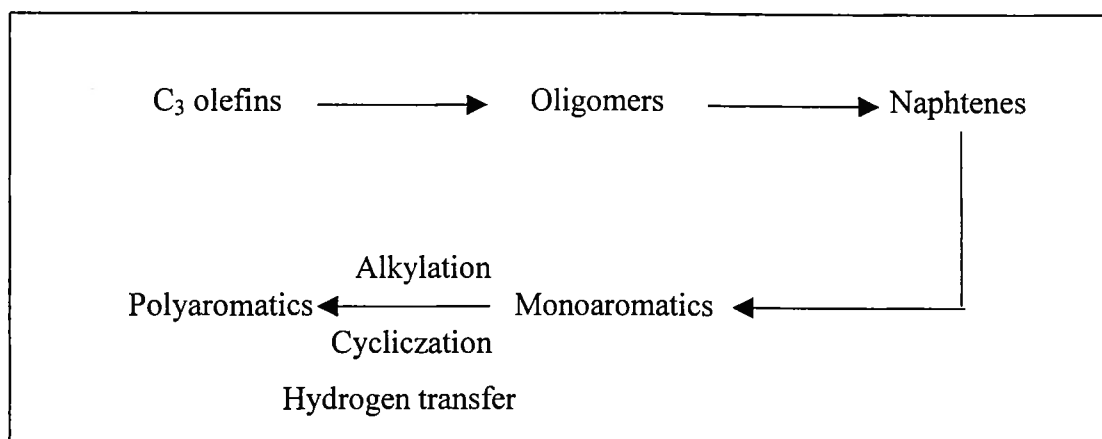


**Figure 5.8** TPO pattern of Cu-ZSM-5 catalyst after adsorption by toluene toluene (3% mole C) and balance He, GHSV  $\approx 20000 \text{ h}^{-1}$ , TPO by 1000ppm NO+1%O<sub>2</sub>/He, reaction temperature 400°C for 20 min; ■ area CO<sub>2</sub>, ◆ area N<sub>2</sub>, ▲ temperature

The maximum of  $N_2$  area is about the same of  $CO_2$  area for propene and toluene but it is lower than  $CO_2$  area. This show that propene is a less effective reductant of the reduction of NO.

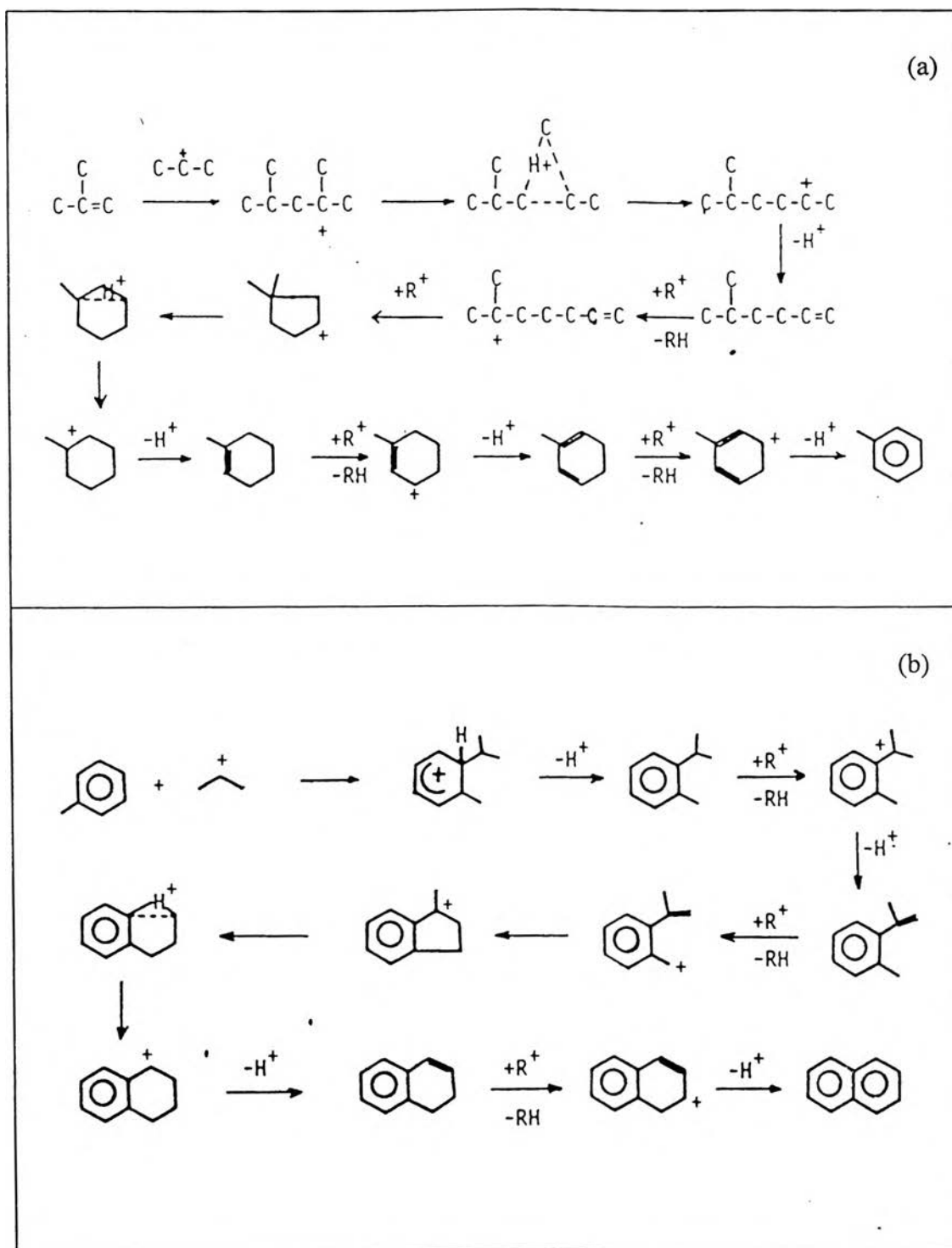
From figures 5.9-5.10, it can suggest that the formation of the intermediates by toluene should be higher than propene because the structure of toluene was look like to the polyaromatic compound than propene. In the same way, the intermediates produced from toluene can remove from the surface of catalyst slower than propene owing to the structure of intermediates from toluene is more complicate than the structure of the intermediates from propene.

With all zeolites the intermediate formation occurs probably through the same steps (figure 5.9) [Guisnet et al. (1989)]: oligomerization of the olefin, cyclization of the oligomers, transformation through hydrogen transfer into monoaromatics, alkylation of these monoaromatics then cyclization and hydrogen transfer to give biaromatics, triaromatics etc.



**Figure 5.9** Mode of the intermediates formation of olefin [Guisnet and Magnoux (1989)]

Figure 5.10 (a) gives a possible mode of formation of a monoaromatic from propene. Figure 5.10(b) shows how a supplementary aromatic ring could be formed.



**Figure 5.10** Mechanisms of the intermediates formation. [Guisnet and Magnoux (1989)]. Modes of formation of (a) toluene from propene and (b) naphthalene from toluene.



From the ratio of the amount of nitrogen from oxidizing gas mixture per the amount of carbon on catalyst (the calculation method showed in appendix A), it can observe that these ratios were nearly close in the case of same catalysts although the type of hydrocarbons (propene or toluene) and amounts of carbon on catalyst were different. Then, it can conclude that  $\text{NO}_x$  in the oxidizing gas is oxidized to  $\text{NO}_2$  in the presence of  $\text{O}_2$  and can oxidized the intermediate to  $\text{N}_2$  [Guyon *et al.* (1996)].  $\text{NO}_2$  can remove the intermediate of each catalyst have the same efficiency and not depending on the type of hydrocarbons. Furthermore, it can conclude that the formation of  $\text{NO}_2$  and intermediate occur at the same type of active site.

### 5.1.2 The Effect of Catalysts on the Intermediates

In this section, the reaction experiments were conducted with two hydrocarbon species of propene and toluene over HMOR, HY, H-ZSM-5 and Cu-ZSM-5 catalysts. The reaction temperature was 400 °C for 20 min. The oxidizing gas was 1000ppm  $\text{NO}+1\%\text{O}_2/\text{He}$ .

Compared with the catalysts, it was considerable difference in the TPO results of HY, HMOR, H-ZSM-5 and Cu-ZSM-5 catalysts, exhibited in figures 5.1-5.8. As show in table 5.1, the amounts of carbon on catalyst were depended on type of catalysts. These results can be implied that the intermediates formation reaction is affected by type of catalysts. It can suggest that the different amount of carbon on these catalyst depended on the number of acid site on catalysts. Naturally, the zeolite catalysts had not the same acidity. The density and the strength of their acid sites were different (Table 5.2). Therefore certain differences in the amount of the intermediates could probably be due to the differences in acidity. The lower amount of carbon on catalyst is due for a large part to the lower number of the acid site.

It is noticed that the intermediates on Cu-ZSM-5 catalyst can be easier removed in lower temperature than H-ZSM-5, HY and HMOR, respectively. It may owe the structure of intermediates formed on  $\text{NO}_x$  reduction reaction of each catalyst were different. For Cu-ZSM-5, The ability of coke to reduce nitrogen oxide was

significantly enhanced by the presence of oxygen. The crucial role of oxygen appeared to be to induce the generation of an adsorbed state of  $\text{NO}_x$  on the exchanged-Cu site. [Ansell *et al.*(1993)]. Thus,  $\text{NO}_2$  from the reduction of NO in the presence  $\text{O}_2$ , was existed at lower temperature that can remove the intermediate on Cu-ZSM-5 catalyst at the lower temperature than other catalysts.

**Table 5.2** The acid site of the zeolite catalysts [Guisnet and Magnoux (1989)]

catalyst	Total number of acid site ( $10^{20} \text{ g}^{-1}$ )
HY	2.5
HMOR	10.8
H-ZSM-5	2.2

Considering the ratio of nitrogen from the oxidizing gas per carbon on catalyst comparing between HY, HMOR, H-ZSM-5 and Cu-ZSM-5 catalysts, the results show that these ratio of H-ZSM-5 catalyst is higher than the ratios of Cu-ZSM-5, HY and HMOR catalysts. This can imply that H-ZSM-5 catalyst is active in NO reduction in the intermediates removal reaction step more than Cu-ZSM-5 and HMOR catalysts. But Cu-ZSM-5 and HMOR catalysts are active in intermediates forming reaction step more than HY and H-ZSM-5 catalyst due to the higher amount of formed intermediates on Cu-ZSM-5 and HMOR catalysts. Then, it can conclude that Cu-form of ZSM-5 is active in the first main step involving intermediates formation and H-form of ZSM-5 catalyst is active in the second main step involving intermediates removal. This phenomenon can be the explanation of the Cu-ZSM-5 catalyst nature that the increase of Cu content enhances activity of NO conversion up to limit value, excess amount of copper appears to suppress activity for  $\text{NO}_x$  removal of catalysts [Goryashenko *et al.*(1998)]. As discuss is above that Cu cation is more active for intermediates formation and H cation is more active for intermediates removal, then it can be explained that the suppression of  $\text{NO}_x$  reduction reaction when copper was over loading may be due to the decrease of H cation which active for intermediates removal reaction. And the optimum copper content may be the optimum point

between the amount of copper cation which active for intermediates formation and the amount of H cation which active for intermediates removal.

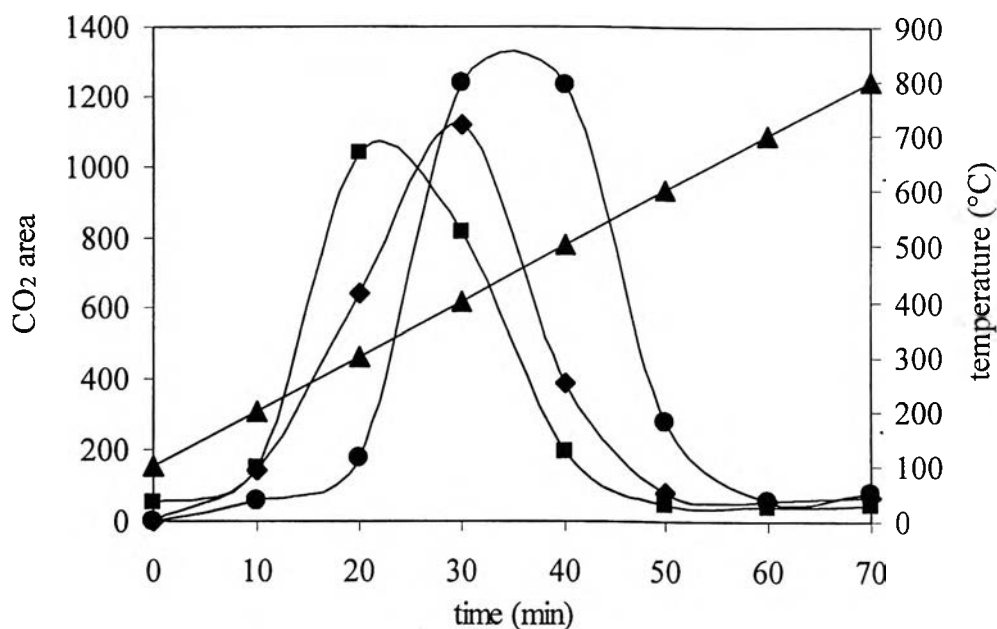
### 5.1.3 The Effect of the Reaction Time on the Intermediates

The experiments were carried on the  $C_3H_6$  over Cu-ZSM-5 at  $400^\circ C$  with various reaction times (5, 20 and 60 minutes). The oxidizing gas was 1000ppm  $NO+1\%O_2/He$ . The effect of time on the amount of carbon on catalyst and nitrogen from the oxidizing gas were demonstrated in table 5.3, figures 5.11 and 5.12, respectively. It was seen that they had the same trend. Initially, the amounts of carbon, nitrogen and ratio of nitrogen from the oxidizing gas per carbon on catalyst increase rapidly and then they increase slowly after 20 min. These may result from the intermediates formation. In the first period, the intermediates were sharply appeared since the catalyst surface was still clean. Hence, the gas reactants can easily reach the active site to form intermediates. In contrast to the longer time, active sites of the catalyst surface were covered by the intermediates, thereby, decreasing intermediates formation.

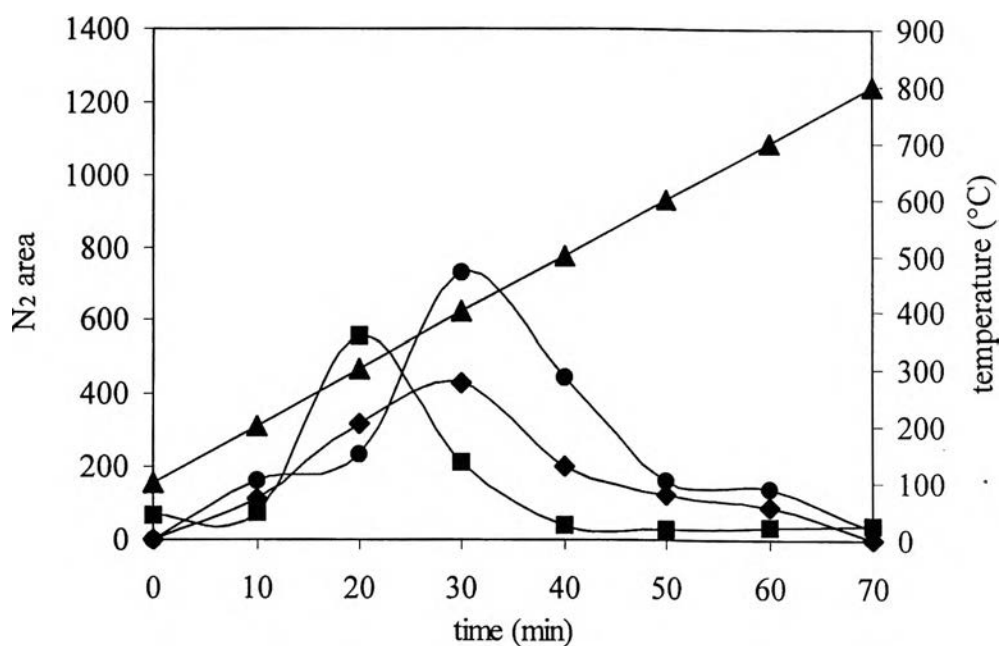
**Table 5.3** The amount of carbon, nitrogen and ratio of nitrogen from the oxidizing gas per carbon on Cu-ZSM-5 catalyst by propene at  $400^\circ C$  with various times

time (min)	the amount of carbon on catalyst (%wt)	the amount of nitrogen from the oxidizing gas mixture (%wt)	ratio of nitrogen from the oxidizing gas per carbon on catalyst (wt ratio)
5	0.45	0.15	0.34
20	0.47	0.18	0.38
60	0.59	0.27	0.48

It can suggest that  $NO_2$  have more potential to remove the intermediates at the increased time. It may be indicate that most of the intermediates formed on the acid site of the catalyst and  $NO_2$  formed on copper ion site. According to

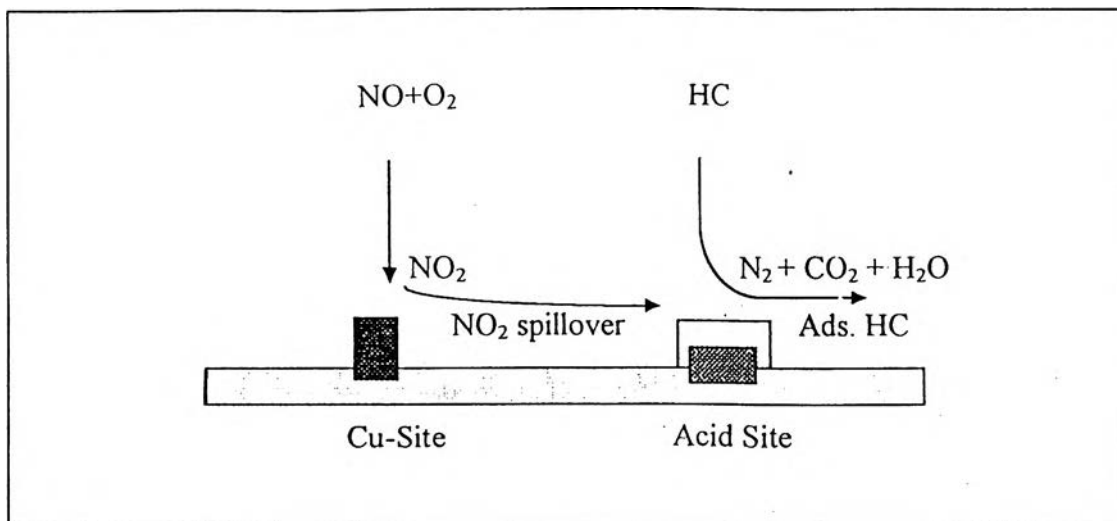


**Figure 5.11** TPO pattern of CO<sub>2</sub> on Cu-ZSM-5 catalyst at various times after adsorption by propene; propene (3% mole C) and balance He, GHSV  $\approx 20000 \text{ h}^{-1}$ , TPO by 1000 ppm NO+1%O<sub>2</sub>/He, reaction temperature 400°C;  
 ■ 5 min, ◆ 20 min, ● 60 min, ▲ temperature



**Figure 5.12** TPO pattern of N<sub>2</sub> on Cu-ZSM-5 catalyst at various times after adsorption by propene; propene (3% mole C) and balance He, GHSV  $\approx 20000 \text{ h}^{-1}$ , TPO by 1000 ppm NO+1%O<sub>2</sub>/He, reaction temperature 400°C;  
 ■ 5 min, ◆ 20 min, ● 60 min, ▲ temperature

Chalermvanapong (1997), The following model has been proposed as shown in figure 5.13.



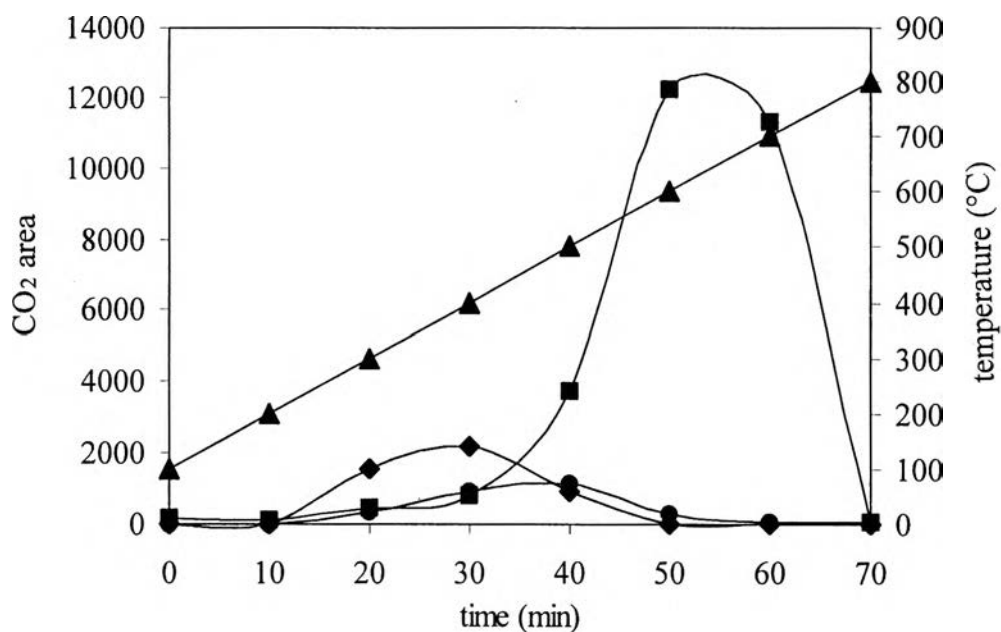
**Figure 5.13** The mechanism model of NO reduction by hydrocarbon on Cu-ZSM-5 [Chalermvanapong (1997)].

This model relates to the well known formation of  $\text{NO}_2$  on Cu-ZSM-5 [Petunchi and Hall (1994), Guyon *et al.* (1996)].  $\text{NO}_2$  is likely produced at Cu sites and spillover to acid site that is not covered by the intermediates and then interacts with adsorbed hydrocarbon on that sites. The acid sites of the zeolite catalyst is proper for the hydrocarbon combustion [Chalermvanapong (1997)]. The intermediates could form on both acid sites and Cu sites but preferred occurred on the acid sites. Then  $\text{NO}_2$  led to a substantial increase on the vacant Cu sites. Therefore, the ratio of the carbon on the intermediates and the nitrogen from the oxidizing gas were increased when the reaction time increased.

#### 5.1.4 The Effect of NO+O<sub>2</sub> on the Intermediates Formation

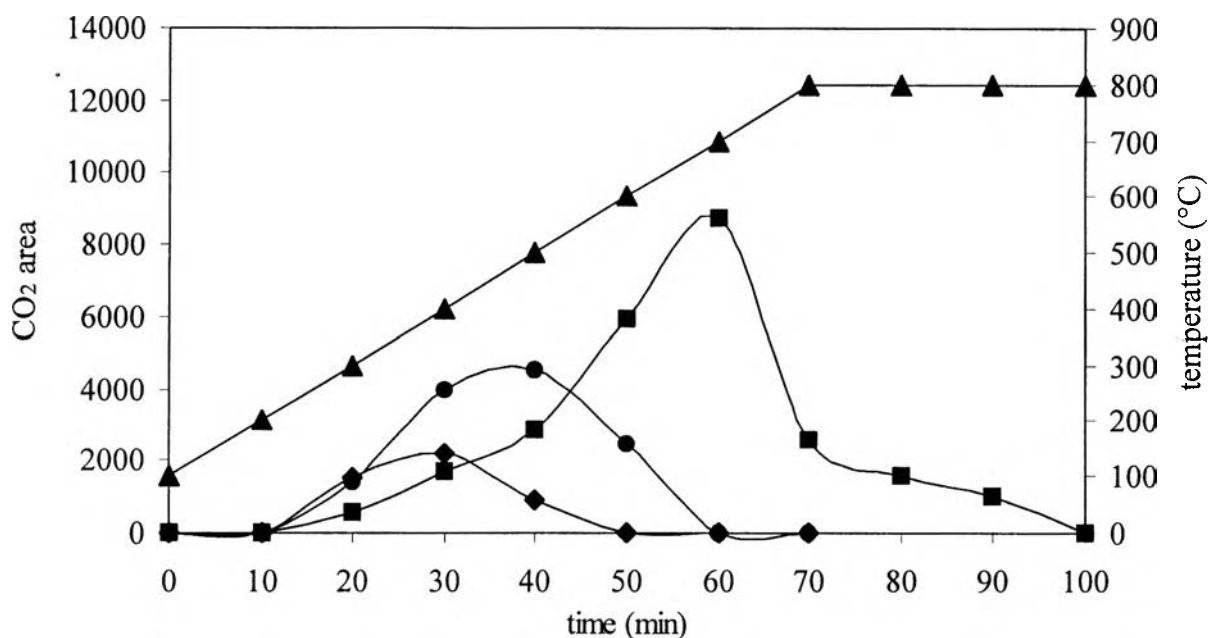
The effect of NO+O<sub>2</sub> on the intermediates formation observed over the catalyst after being reacted with six reactants (C<sub>3</sub>H<sub>6</sub>+NO+O<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>+NO, C<sub>3</sub>H<sub>6</sub>, toluene+NO+O<sub>2</sub>, toluene+NO, toluene) at 400°C on Cu-ZSM-5 catalyst for 20 min. The oxidizing gas was 1%O<sub>2</sub>/He. TPO spectra are illustrated in figures 5.14-5.17, respectively.

Figure 5.14 and 5.15 shows that C<sub>3</sub>H<sub>6</sub>+NO+O<sub>2</sub> formed a significant amount of carbon on the catalyst, whereas the other reactants resulted in a little amount of carbon on the catalyst. Also, the case of toluene+NO+O<sub>2</sub>, the amount of carbon on the catalyst was more than the amount of carbon from toluene+NO and toluene only, respectively. Table 5.4 showed the amount of carbon on Cu-ZSM-5 catalyst with various reactants. However, the amount of carbon on the catalyst from C<sub>3</sub>H<sub>6</sub>+NO+O<sub>2</sub> was higher than C<sub>3</sub>H<sub>6</sub>+NO and C<sub>3</sub>H<sub>6</sub> about 10 times but the amount of carbon on the catalyst from toluene+NO+O<sub>2</sub> was higher than toluene+NO and toluene only about 4 times. It can indicate that C<sub>3</sub>H<sub>6</sub> is more active in HC-SCR of NO on Cu-ZSM-5 catalyst than toluene. This result can imply that the most possible part of intermediates forming step of the HC-SCR of NO is the corporation of the three reactant gas species (NO, C<sub>3</sub>H<sub>6</sub> or toluene, and O<sub>2</sub>). Our results was corresponding with Cowan *et al.* (1995) and Cant *et al.*(1995), they concluded that the rate determining step is the formation of the intermediates. It involved the breaking of a carbon hydrogen bond and detachment of hydrogen from methane by adsorbed nitrogen dioxide to form a methyl species, which reacts further with a nitrogen oxide in one pathway but with oxygen in the other. Additionally, Ditri *et al.* (1993) suggest that the step of the intermediate formation of selective catalytic reduction of nitrogen oxide over Cu-ZSM-5 is the rate determining step result in the large intermediate formation.



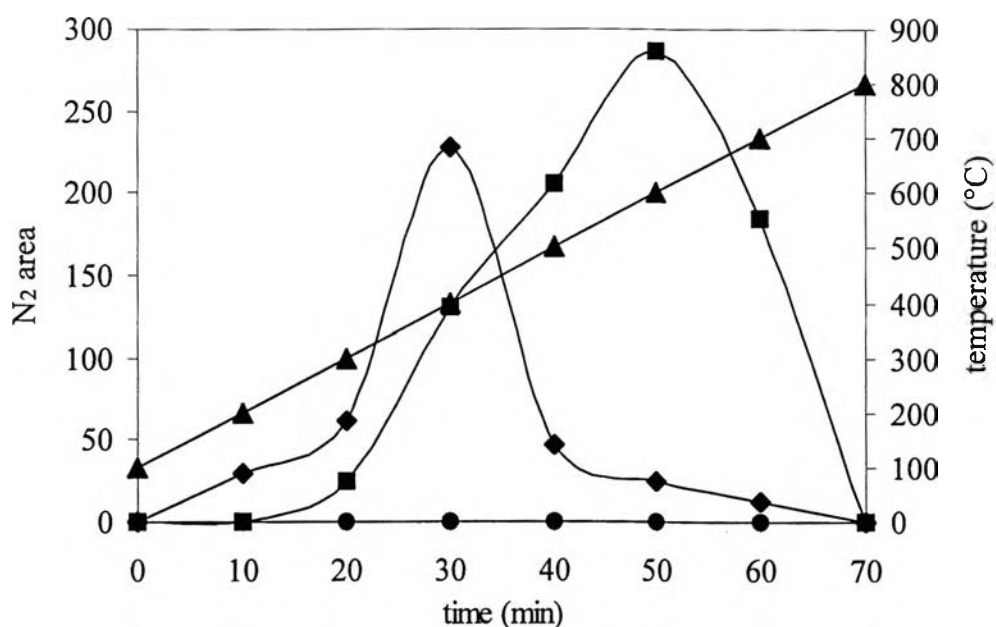
**Figure 5.14** TPO pattern of CO<sub>2</sub> on Cu-ZSM-5 catalyst with various reactants after adsorption by propene ; GHSV  $\approx 20000 \text{ h}^{-1}$ , reaction temperature  $400^\circ\text{C}$  for 20 min;

■ C<sub>3</sub>H<sub>6</sub>+1000NO+10%O<sub>2</sub>/He, ◆ C<sub>3</sub>H<sub>6</sub>+1000NO, ● C<sub>3</sub>H<sub>6</sub>, ▲ temperature

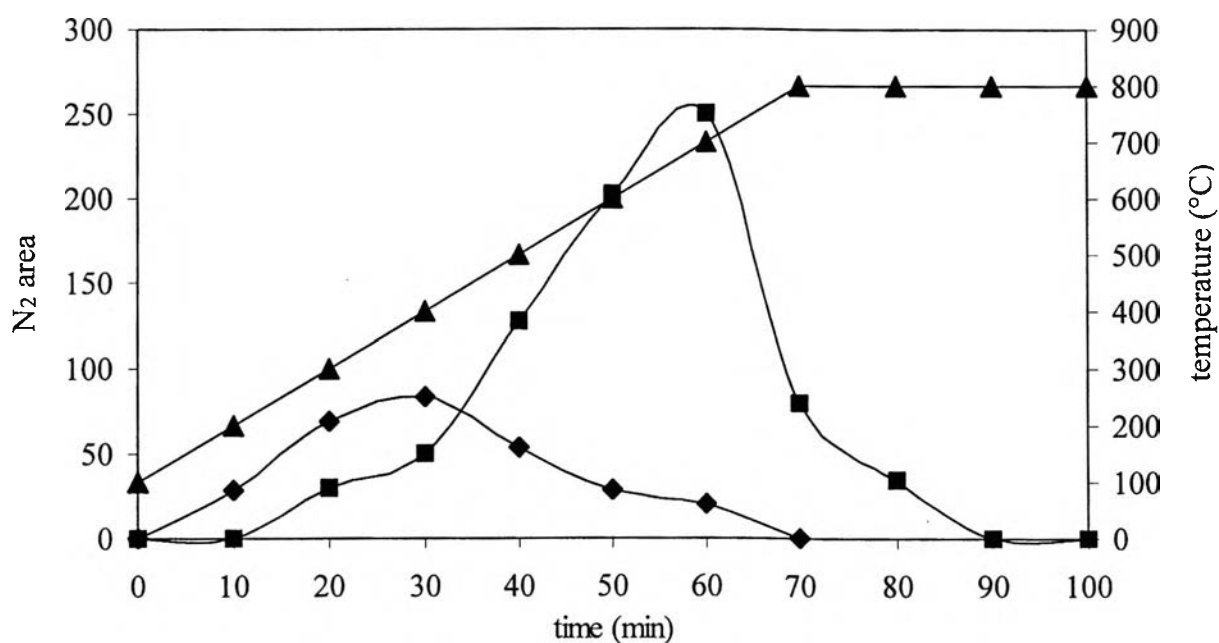


**Figure 5.15** TPO pattern of CO<sub>2</sub> on Cu-ZSM-5 catalyst with various reactants after adsorption by toluene ; GHSV  $\approx 20000 \text{ h}^{-1}$ , reaction temperature  $400^\circ\text{C}$  for 20 min;

■ toluene+1000NO+10%O<sub>2</sub>/He ◆ toluene+1000NO, ● toluene,



**Figure 5.16** TPO pattern of N<sub>2</sub> on Cu-ZSM-5 catalyst with various reactants after adsorption by propene; GHSV  $\approx 20000 \text{ h}^{-1}$ , reaction temperature 400°C for 20 min; ■ C<sub>3</sub>H<sub>6</sub>+1000NO+10%O<sub>2</sub>/He, ◆ C<sub>3</sub>H<sub>6</sub>+1000NO, ▲ temperature



**Figure 5.17** TPO pattern of N<sub>2</sub> on Cu-ZSM-5 catalyst with various reactants after adsorption by toluene GHSV  $\approx 20000 \text{ h}^{-1}$ , reaction temperature 400°C for 20 min; ■ toluene+1000NO+10%O<sub>2</sub>/He, ◆ toluene+1000NO, ▲ temperature



**Table 5.4** The amount of carbon on Cu-ZSM-5 catalyst with various reactants

reactant	the amount of carbon on catalyst (%wt.)	
	C <sub>3</sub> H <sub>6</sub>	Toluene
hydrocarbon	0.52	2.14
hydrocarbon +1000ppm NO	0.87	2.36
hydrocarbon +1000ppm NO+10%O <sub>2</sub> /He	5.53	4.83

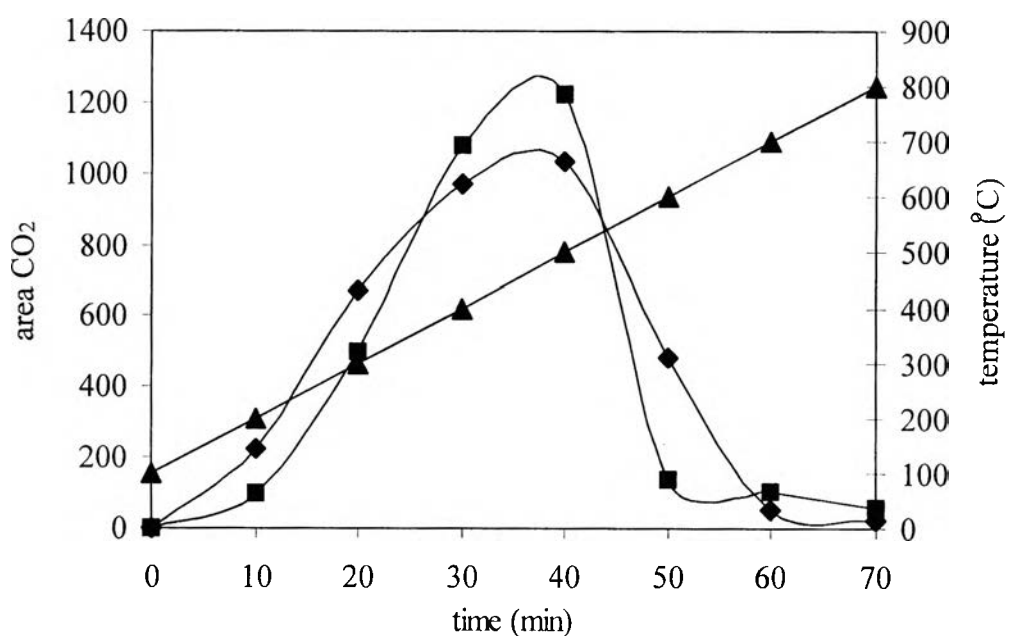
Considering figures 5.16 and 5.17, where N<sub>2</sub> area from reactor outlet of temperature programmed oxidation experiment on Cu-ZSM-5 catalyst after reaction by varying reactants were plotted versus temperatures, it is seen that N<sub>2</sub> would emerge only from the system that consisted of NO+O<sub>2</sub>. This implies that the adsorbed intermediates in selective catalytic reduction (SCR) reaction are formed by the interaction of C<sub>3</sub>H<sub>6</sub> (or toluene), NO and O<sub>2</sub>. The results are correspondent with the literatures. Chang and McCarty (1998) found that co-adsorption of NO and O<sub>2</sub> led to a substantial increase in the amount of NO<sub>x</sub> adsorbed. Similar behavior was reported over Co-ZSM-5 catalyst [Sun *et al.* (1996)] where NO was hardly adsorbed in the reaction temperatures, but the interaction between NO and Co cations was greatly enhanced in the presence of O<sub>2</sub>. In addition, Pinaeva *et al.* (1999) suggested that over Co-ZSM-5, Co ion located at the interface of Co clusters and zeolites were found to react with NO in the presence of O<sub>2</sub> to form anchored NO<sub>2</sub> delta+ species stabilized under reaction conditions. Therefore, it can be proposed that the initial step of the NO-SCR reaction with hydrocarbon reductant in the presence of excess oxygen over Co-ZSM-5 catalyst is the adsorption of NO<sub>y</sub> species formed by the interaction with NO and O<sub>2</sub>. Then NO<sub>y</sub> species will interact with hydrocarbon and form nitrogen-containing intermediates which are the intermediates of the reaction. However, the formation of intermediate species depends mainly on hydrocarbon reductant and affects the reaction activity.

Furthermore, the study of the nature of the intermediate that affected by NO+O<sub>2</sub> on the intermediate formation were conducted after reaction of C<sub>3</sub>H<sub>6</sub>+NO+O<sub>2</sub>

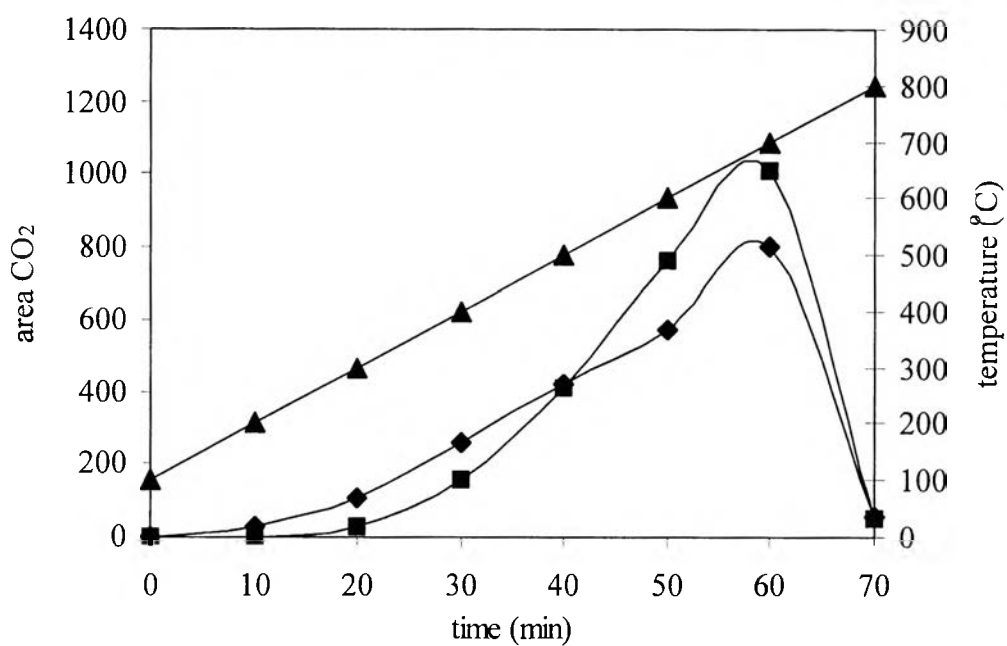
and  $C_3H_6$  on Cu-ZSM-5 and H-ZSM-5 catalyst. From TPO experiment, it found that the time of 2 min for  $C_3H_6+NO+O_2$  and 90 min for  $C_3H_6$  over Cu-ZSM-5 catalyst, the amount of carbon on Cu-ZSM-5 catalyst has the equal amount. (%C ~ 0.4). In the case of H-ZSM-5 catalyst, the time of 3 min for  $C_3H_6+NO+O_2$  and 360 min for  $C_3H_6$ , the amount of carbon on Cu-ZSM-5 catalyst has the equal amount. (%C ~ 0.6). The same amount of carbon on catalysts and the reaction time are shown in table 5.5. The nature of the intermediate from the different reactants on Cu-ZSM-5 and H-ZSM-5 are illustrated in figure 5.18. It found that the nature of the intermediate from  $C_3H_6+NO+O_2$  and  $C_3H_6$  have the same behavior. The maximum peaks of  $CO_2$  area of  $C_3H_6+NO+O_2$  and  $C_3H_6$  on Cu-ZSM-5 and H-ZSM-5 catalysts produced about 480 °C and 700 °C, respectively.

**Table 5.5** The same amount of carbon on Cu-ZSM-5 and H-ZSM-5 catalysts and the reaction time

Catalyst	reactant	the amount of carbon on catalyst (% wt.)	reaction time (min)
Cu-ZSM-5	$C_3H_6$	0.62	90
Cu-ZSM-5	$C_3H_6+NO+O_2$	0.65	2
H-ZSM-5	$C_3H_6$	0.42	360
H-ZSM-5	$C_3H_6+NO+O_2$	0.45	3



(a) Cu-ZSM-5 catalyst



(b) H-ZSM-5 catalyst

**Figure 5.18** TPO patterns of (a) Cu-ZSM-5 and (b) H-ZSM-5 catalyst with various reactants for the same amount of carbon ; ■ C<sub>3</sub>H<sub>6</sub>+NO+O<sub>2</sub>, ◆ C<sub>3</sub>H<sub>6</sub>

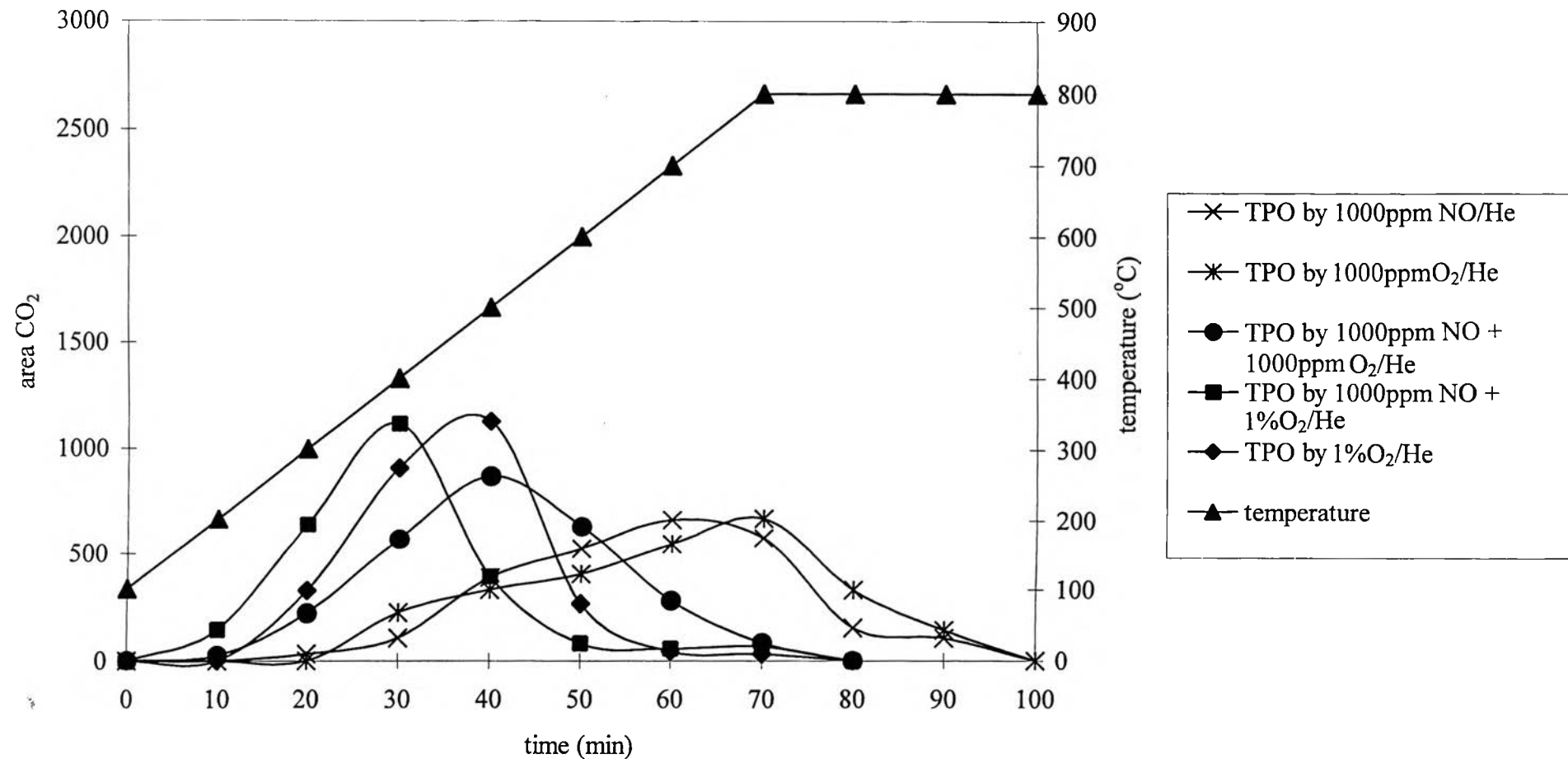
### 5.1.5 The Effect of NO+O<sub>2</sub> on the Intermediates Removal

In order to study the mechanism of intermediates removal in the NO reduction with propene and toluene over Cu-ZSM-5 catalyst, TPO experiments by varying oxidizing gas (O<sub>2</sub> and NO+O<sub>2</sub>) and varying the concentration of O<sub>2</sub> and NO+O<sub>2</sub>. The experiments were conducted on Cu-ZSM-5 catalyst after being reacted by C<sub>3</sub>H<sub>6</sub> at 400°C for 20 min. The results are shown in figure 5.19-5.22. Table 5.6 showed the amount of carbon on Cu-ZSM-5 catalyst with various oxidizing gas.

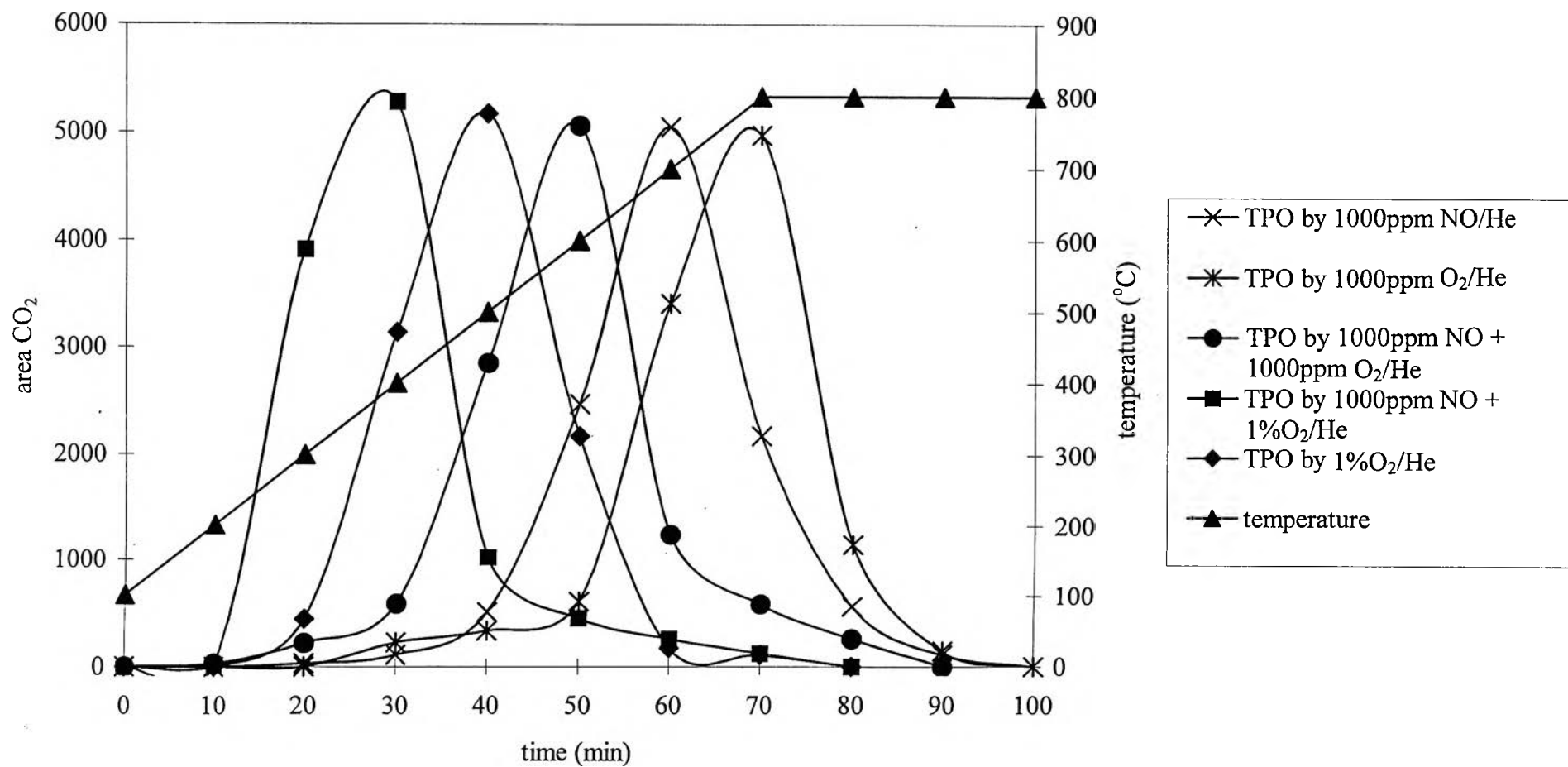
**Table 5.6** The amount of carbon on Cu-ZSM-5 catalyst with various oxidizing gas

The oxidizing gas	the amount of carbon on catalyst (%wt.)	
	C <sub>3</sub> H <sub>6</sub>	toluene
1000ppm NO/He	0.40	2.08
1000ppm O <sub>2</sub> /He	0.45	2.05
1000ppm NO+1000ppm O <sub>2</sub> /He	0.44	2.10
1000ppm NO+1%O <sub>2</sub> /He	0.47	2.12
1%O <sub>2</sub> /He	0.52	2.15

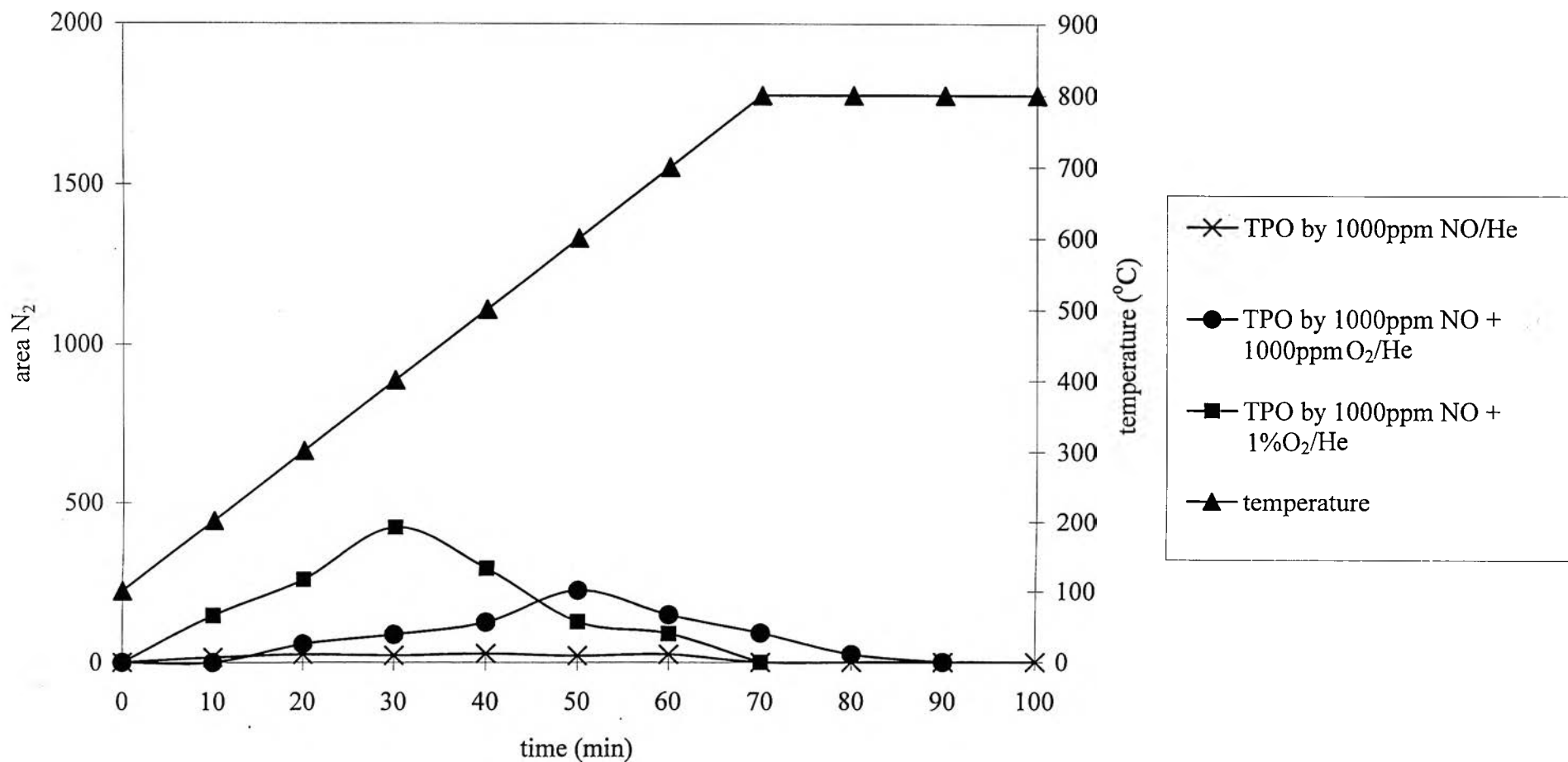
As seen in figures 5.19 and 5.20, the amount of CO<sub>2</sub> that was observed from every oxidizing gas was equal. From the TPO results, the presence of NO+O<sub>2</sub> in the oxidizing gas shown the efficiency for the intermediates removal at the lower temperature region than the oxidizing gas of NO or O<sub>2</sub> only. The oxidizing gas of NO can remove the intermediate at the lower temperature than O<sub>2</sub>. These results imply that the intermediates removal reaction is effectively occurred in the presence of NO+O<sub>2</sub>. Therefore, it can be concluded that the corporation of NO and O<sub>2</sub> accelerate the intermediates removal reaction. The oxidizing gas of 1000ppm NO+ 1%O<sub>2</sub>/He can remove the intermediate at the lower temperature than 1000ppm NO+ 1000 ppm O<sub>2</sub>/He. Also, The oxidizing gas of 1000 ppm O<sub>2</sub>/He can remove the intermediate at the lower temperature than 1%O<sub>2</sub>/He. It may be due to the increased concentration of the oxidizing gas led to the efficiency of the intermediates removal increased. The order of the efficiency on the intermediate removal of C<sub>3</sub>H<sub>6</sub> and toluene was 1000ppm



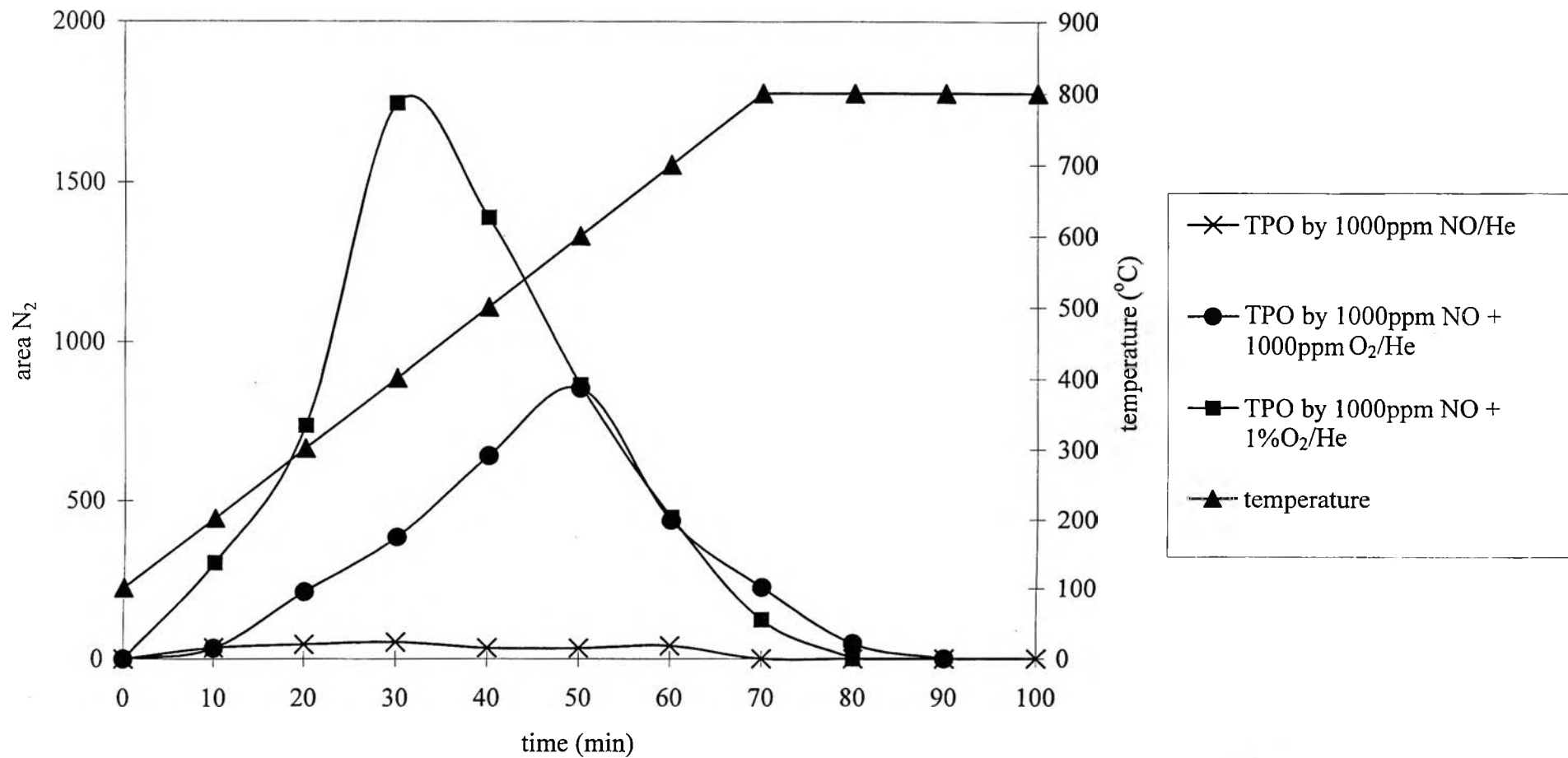
**Figure 5.19** TPO pattern of CO<sub>2</sub> on Cu-ZSM-5 catalyst with various oxidizing gas after adsorption by propene (3% mole C) and balance He, GHSV ~ 20000 h<sup>-1</sup>, reaction temperature 400 °C for 20 min



**Figure 5.20** TPO pattern of CO<sub>2</sub> on Cu-ZSM-5 catalyst with various oxidizing gas after adsorption by toluene (3% mole C) and balance He, GHSV ~ 20000 h<sup>-1</sup>, reaction temperature 400 °C for 20 min



**Figure 5.21** TPO pattern of N<sub>2</sub> on Cu-ZSM-5 catalyst with various oxidizing gas after adsorption by propene (3% mole C) and balance He, GHSV ~ 20000 h<sup>-1</sup>, reaction temperature 400 °C for 20 min



**Figure 5.22** TPO pattern of CO<sub>2</sub> on Cu-ZSM-5 catalyst with various oxidizing gas after adsorption by toluene (3% mole C) and balance He, GHSV ~ 20000 h<sup>-1</sup>, reaction temperature 400 °C for 20 min



NO+ 1%O<sub>2</sub>/He > 1%O<sub>2</sub>/He > 1000ppm NO+1000ppm O<sub>2</sub>/He > 1000ppm NO/He > 1000 ppmO<sub>2</sub>/He, respectively.

Although the amount of CO<sub>2</sub> emerged from the effluent gas between TPO by O<sub>2</sub> and TPO by NO+O<sub>2</sub> was not much different, the N<sub>2</sub> concentrations in both cases were remarkably different as illustrated in figures 5.21 and 5.22. TPO by NO+O<sub>2</sub> resulted in the amount of N<sub>2</sub> emerged and N<sub>2</sub> emerged at the same temperature of CO<sub>2</sub> emerged from system. This result implies that the increased amount of nitrogen may be attributed to nitrogen in oxidizing gas that can interact with intermediate and form nitrogen products. Thus, nitrogen products observed were from both nitrogen-containing intermediate and nitrogen from gas phase. This is in agreement to the results show before and the literature of Chen *et al.* (1998) which uses isotopic labeling technique on Fe-ZSM-5 and found that one nitrogen atom in every nitrogen produced come from the intermediates, the other comes from gas phase NO<sub>2</sub>.

## 5.2 Characterization of the intermediates species

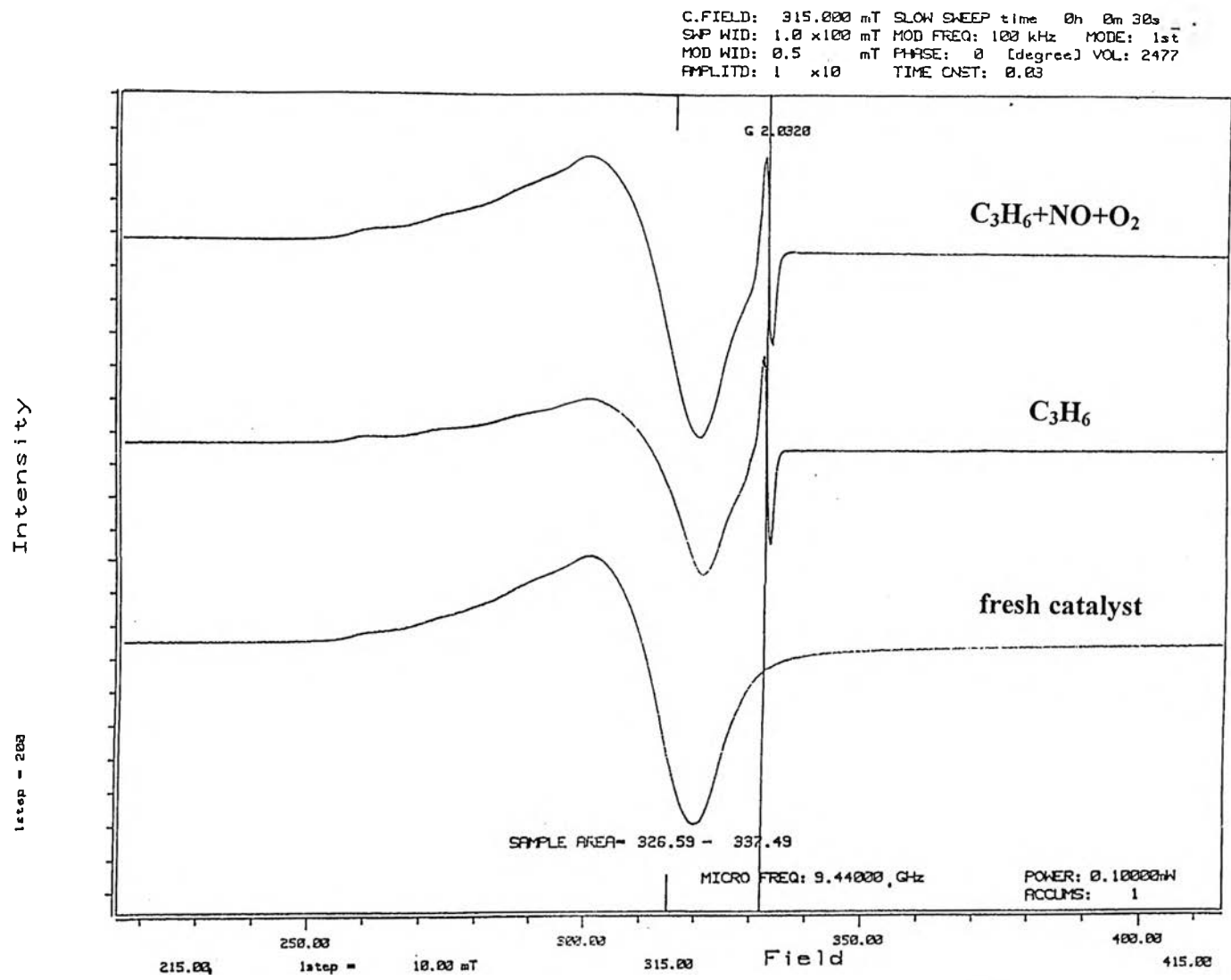
### 5.2.1 Electron Spin Resonance (ESR)

In order to examine the effect of  $\text{NO}+\text{O}_2$  addition on the formation of intermediates in more details, the ESR experiment was studied. Electron Spin Resonance (ESR) has long been an effective technique to estimate the radical density of carbonaceous deposits [Peri (1988), Lange *et al.* (1988)]. ESR spectroscopic studies of the radicals accompanying the formation of the intermediates allow one to estimate the amount of carbonaceous deposits and to obtain information concerning its nature. ESR spectra are obtained by measuring the intensity versus wavelength (or frequency) of a beam of electromagnetic radiation as it passes through a sample or matter, which is presented, in a derivative trace of adsorption curve. Then, the radical density can be computed from the integrated area of the spectra obtained [Lunsford (1972)]. Further carbon radicals are representative of the overall carbonaceous deposits, for both its nature and its amount because the amount of olefin or allylic radicals are characteristic of the intermediates. In earlier study [Lange *et al.* (1988)], they found that olefinic or allylic oligomeric species were low temperature carbon radicals while highly unsaturated species were high-temperature carbon radicals.

#### a.) Effect of $\text{NO}+\text{O}_2$

In order to examine the species of the intermediates that formed on the catalyst after adsorption by different reactants ( $\text{C}_3\text{H}_6$  only and  $\text{C}_3\text{H}_6+\text{NO}+\text{O}_2$ ), we fixed the amount of carbon on the intermediates from TPO and measured the density of carbon radicals by ESR. A comparison between ESR and TPO results exhibited a good correlation between the number of carbon radicals and the amount of carbon on the intermediates.

The effect of  $\text{NO}+\text{O}_2$  on the ESR spectra of carbon radicals that were recorded at room temperature on Cu-ZSM-5 and H-ZSM-5 are illustrated in figures 5.23 and 5.24, respectively.



·Figure 5.23 ESR spectra of the effect of NO+O<sub>2</sub> on the intermediates over Cu-ZSM-5

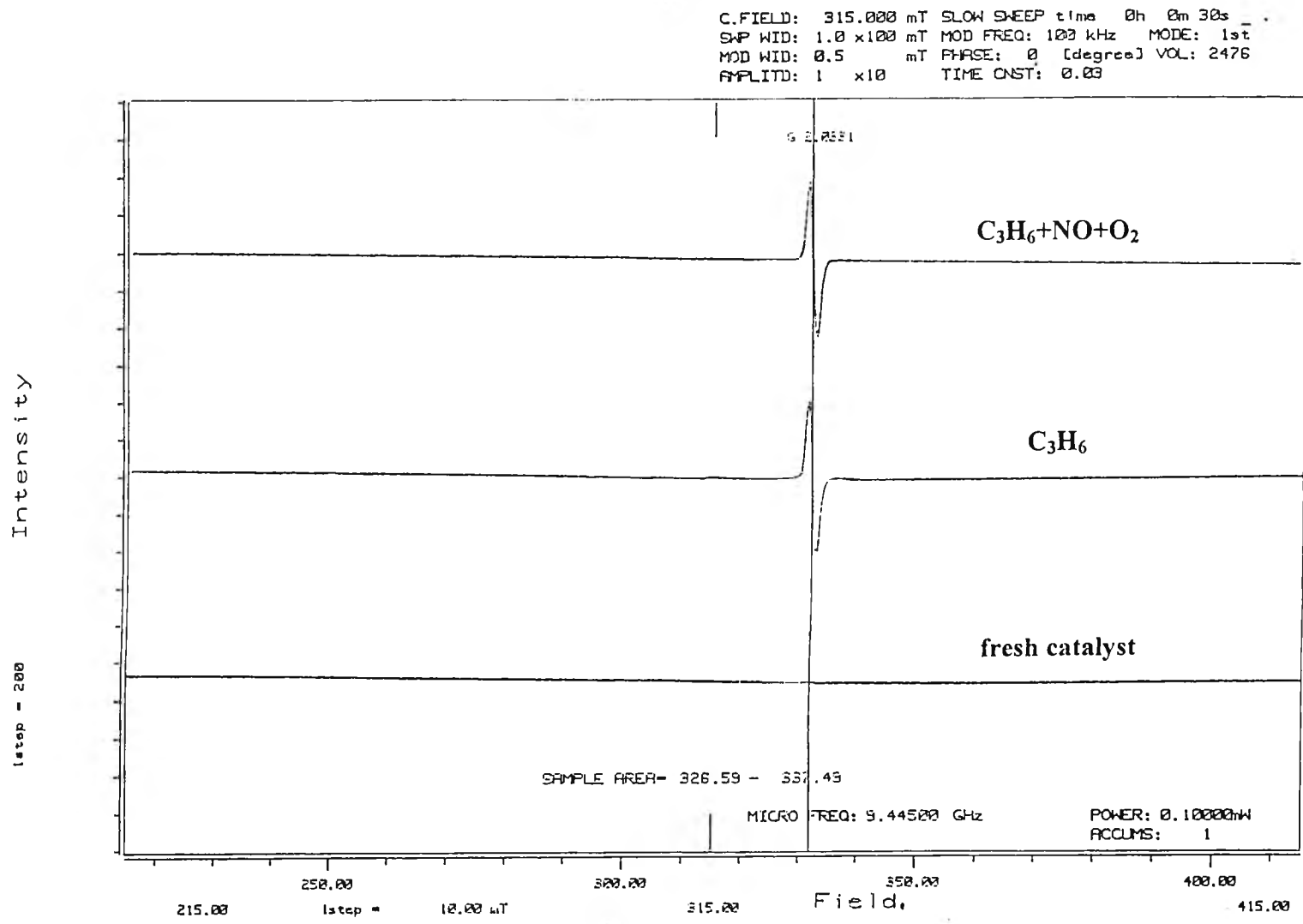


Figure 5.24 ESR spectra of the effect of NO+O<sub>2</sub> on the intermediates over H-ZSM-5

These signal intensities from figures 5.23 and 5.24 are not seemed to be different. Thus, the amount of carbonaceous radicals integrated from ESR spectra, list in table 5.7 is considered instead. However, the adsorbed g values for the intermediates catalysts at different reactants are similar to each other. The g value of the carbon radicals was estimated to be 2.03 in agreement with earlier literatures [Mann (1997)] that observed for  $sp^2$  hybridized aromatic carbon. The corresponding radicals are referred to intermediate radicals, i.e., olefinic or allylic radicals [Lange *et al.* (1988), Kucherov *et al.* (1986)].

**Table 5.7** The density of carbon radicals of intermediates per gram Cu-ZSM-5 ad H-ZSM-5 catalysts with various reactants for the same amount of carbon

catalyst	reactant	%(wt.) carbon (from TPO)	the density of carbon (from ESR)
Cu-ZSM-5	$C_3H_6$	0.62	$1.15 \times 10^5$
Cu-ZSM-5	$C_3H_6+NO+O_2$	0.65	$1.23 \times 10^5$
H-ZSM-5	$C_3H_6$	0.42	$8.57 \times 10^4$
H-ZSM-5	$C_3H_6+NO+O_2$	0.48	$9.26 \times 10^4$

From the ESR spectra, the fresh Cu-ZSM-5 catalyst showed only ESR signal of copper radical whereas the used Cu-ZSM-5 catalyst showed both copper and carbon radical indicating the presence of carbon species ( $C_xH_y$  species) on them. This is accounting for the observed decrease in the number of radicals as a function of decreasing amount of carbon as demonstrated in table 5.7. It can suggest that the effect of  $NO+O_2$  do not affect the  $C_xH_y$  species of intermediate that detected by ESR. The corresponding radicals of  $C_3H_6+NO+O_2$  and  $C_3H_6$  on Cu-ZSM-5 and H-ZSM-5 are referred to olefinic or allylic radicals.

From these results, it can conclude that the same amount of carbon from the intermediates of  $C_3H_6+NO+O_2$  and  $C_3H_6$  has the same amount of  $C_xH_y$  species that detect by ESR.

### b.) Effect of time on stream

The identities of sets of ESR spectra as a function of various times on stream of selective catalytic reduction by  $C_3H_6+NO+O_2$  over H-ZSM-5 are shown in figure 5.25. Exactly, the time affects the ESR signal as can be seen in figure 5.25 and the amount of carbon radicals is ascribed in table 5.8. From the ESR spectra, the fresh catalyst showed no ESR signal, indicating the absence of any paramagnetic species on them. The ESR spectra showed a strong ESR signal at increased time. It is indicated that the observed strong ESR signal for the time presented a high concentration of paramagnetic carbon species. This is accounting for the observed decrease in the number of radicals as a function of decreasing time as demonstrated in table 5.8. However, the absorbed g-values for the intermediates catalyst at different reaction times were quite close to each other (average value  $\sim 2.3$ ).

**Table 5.8** The density of carbon radicals of intermediates per gram H-ZSM-5 catalyst with various times on stream.

time	%(wt.) carbon (from TPO)	the density of carbon (from ESR)
3	0.30	$4.33 \times 10^4$
5	0.48	$9.26 \times 10^4$
15	0.75	$1.45 \times 10^5$

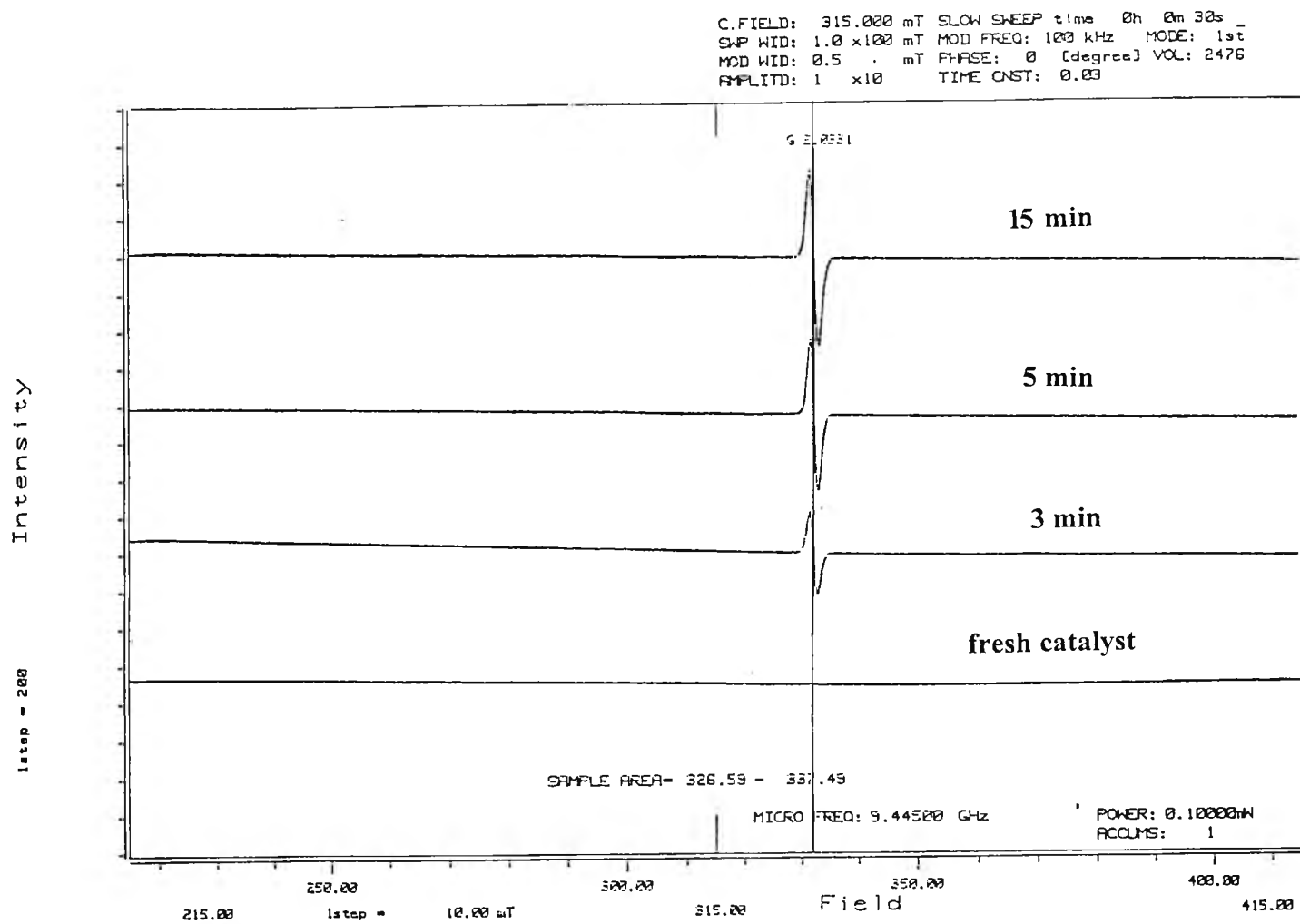


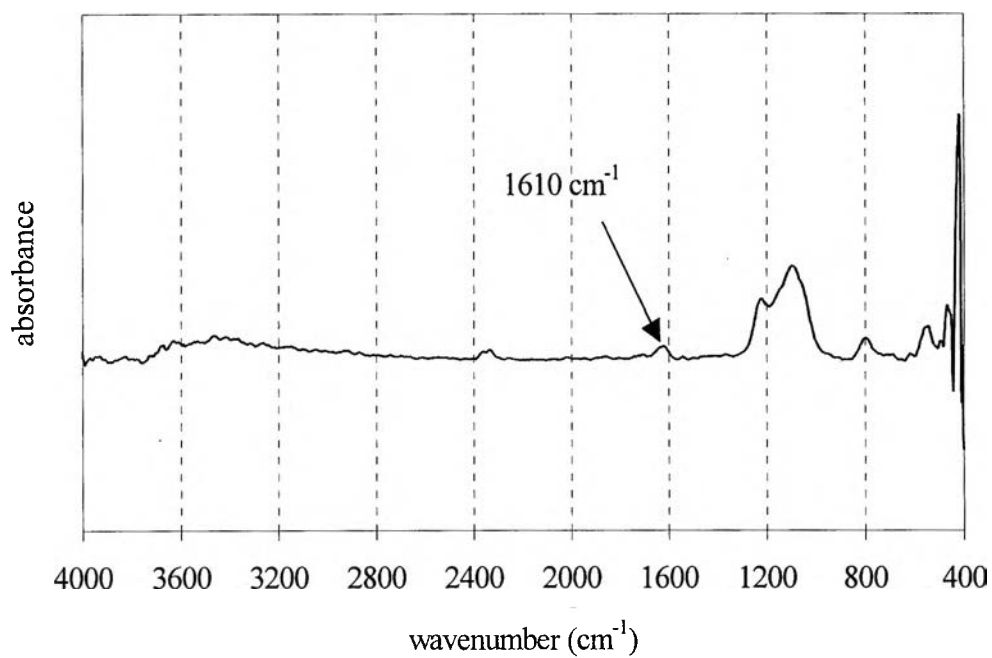
Figure 5.25 ESR spectra of intermediates on H-ZSM-5 with various times on stream

### 5.2.2 Infrared spectroscopy (IR)

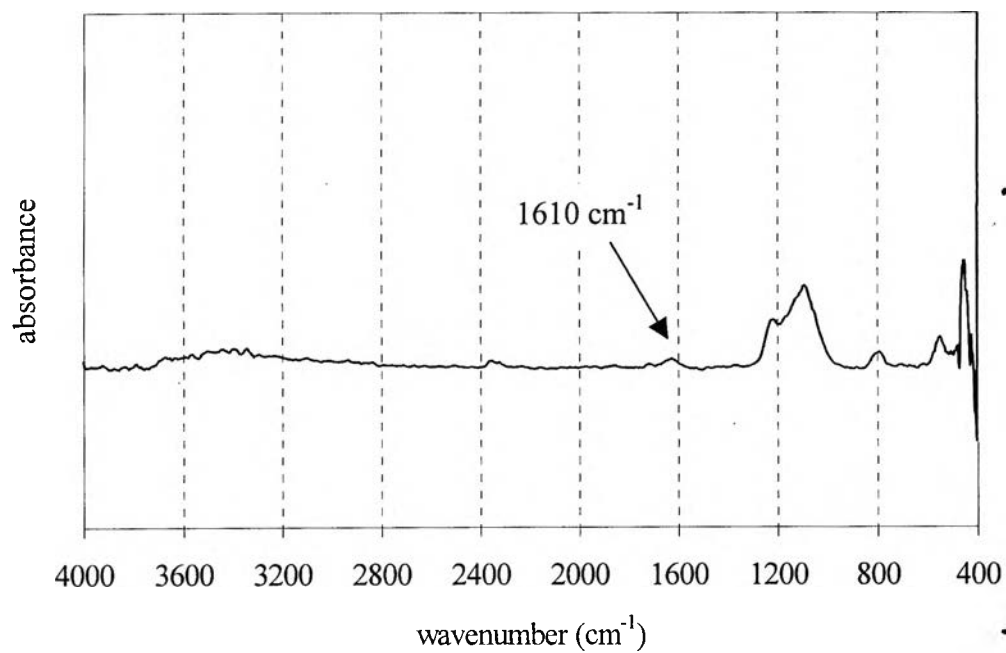
IR studies give information concerning the chemical identity of the carbonaceous deposits components. The structure of  $C_xH_y$  species on the intermediates was additionally monitored by means of the corresponding bands determined IR adsorption bands after each reaction carried out by varying reactants. IR spectra of catalysts with various reactants,  $C_3H_6$  and  $C_3H_6+NO+O_2$ , for the same amount of carbon on H-ZSM-5 and Cu-ZSM-5 catalysts are illustrated in figures 5.26-5.29. An intensity band was detected at approximately  $1610\text{ cm}^{-1}$ . Normally, the band in this region is specific to stretching mode of aromatic system [Pieck *et al.* (1992)]. The band at wave number about  $1610\text{ cm}^{-1}$  indicates the formation of graphite-like coke [Mann (1997)]. No IR adsorption bands of aliphatic hydrocarbons at  $2960$  and  $2800\text{ cm}^{-1}$  for  $CH_3$  and  $2930\text{ cm}^{-1}$  for  $CH_2$  were observed of the intermediates catalysts. Thus, only aromatic ring structure can be identified. However, IR spectra of the various reactants,  $C_3H_6$  and  $C_3H_6+NO+O_2$ , were not different. They were the same position at  $1610\text{ cm}^{-1}$ , the so called-coke band. The suggestions are in agreement with earlier results obtained in TPO and ESR.

Importantly, the addition of  $NO+O_2$  did not affect the chemical structure of intermediates that are detected by IR. Additionally, the corresponding IR bands of  $C_3H_6+NO+O_2$  and  $C_3H_6$  on Cu-ZSM-5 and H-ZSM-5 are the same pattern.

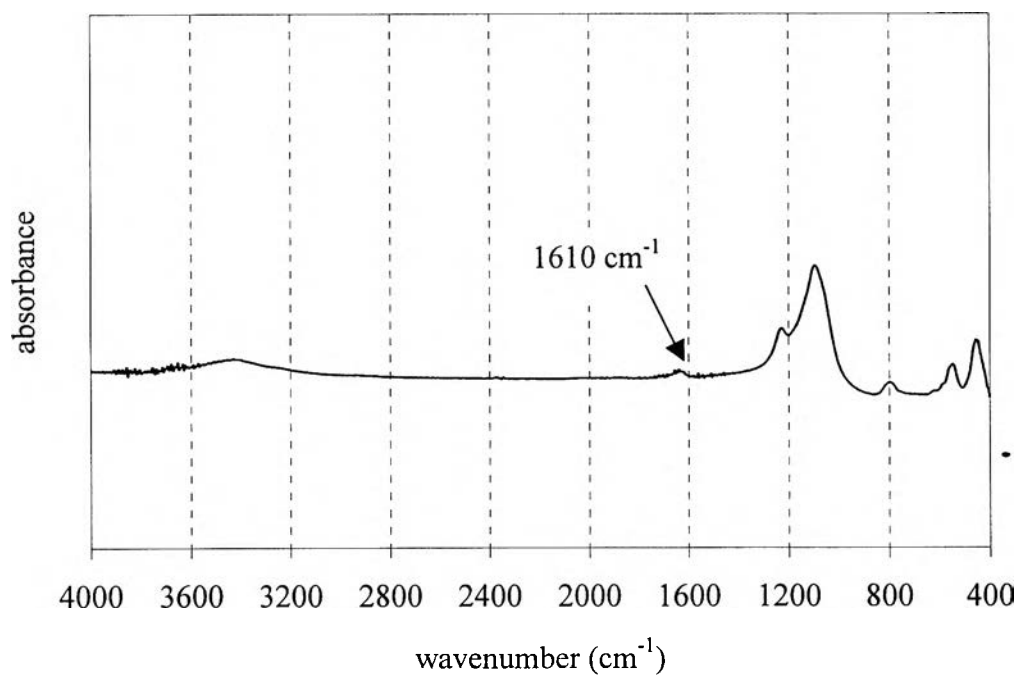




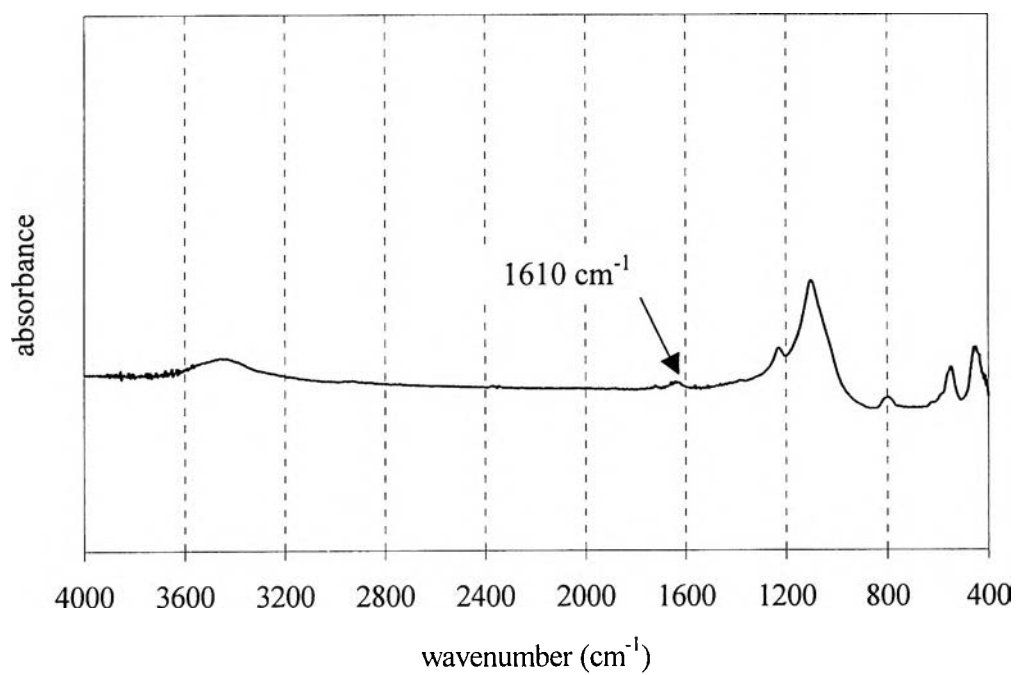
**Figure 5.26** IR spectrum of Cu-ZSM-5 catalyst after adsorption by C<sub>3</sub>H<sub>6</sub>



**Figure 5.27** IR spectrum of Cu-ZSM-5 catalyst after adsorption by C<sub>3</sub>H<sub>6</sub>+NO+O<sub>2</sub>



**Figure 5.28** IR spectrum of H-ZSM-5 catalyst after adsorption by C<sub>3</sub>H<sub>6</sub>



**Figure 5.29** IR spectrum of H-ZSM-5 catalyst after adsorption by C<sub>3</sub>H<sub>6</sub>+NO+O<sub>2</sub>

### 5.3 Physical properties of catalysts

#### 5.3.1 BET surface area of catalysts

In order to investigate the degree of filling of the intermediate into the pore of catalyst, the pore structure of intermediates catalyst was examined with  $N_2$  adsorption isotherms of fresh and used catalysts formed with different adsorbed gas mixtures. By taking the results from  $N_2$  adsorption into consideration, the data was listed in Table 5.10. It is seen that with the intermediates, the BET surface area was decreased. As the amount of carbon was increased the surface areas of spent catalysts were found to be lower on all catalyst because of the intermediates cover on the surface of catalyst. From the previous section, it found that the adsorbed gas mixture of  $C_3H_6+NO+O_2$  formed a larger amount of carbon on the intermediates than  $C_3H_6$ . Thus, the surface area of all catalysts that formed intermediate from  $C_3H_6+NO+O_2$  was found to be lower than all catalysts that formed intermediate from  $C_3H_6$  and the fresh catalyst, respectively.

**Table 5.9** The textural properties of catalysts samples before and after testing

used catalyst (1) : adsorbed by  $C_3H_6$

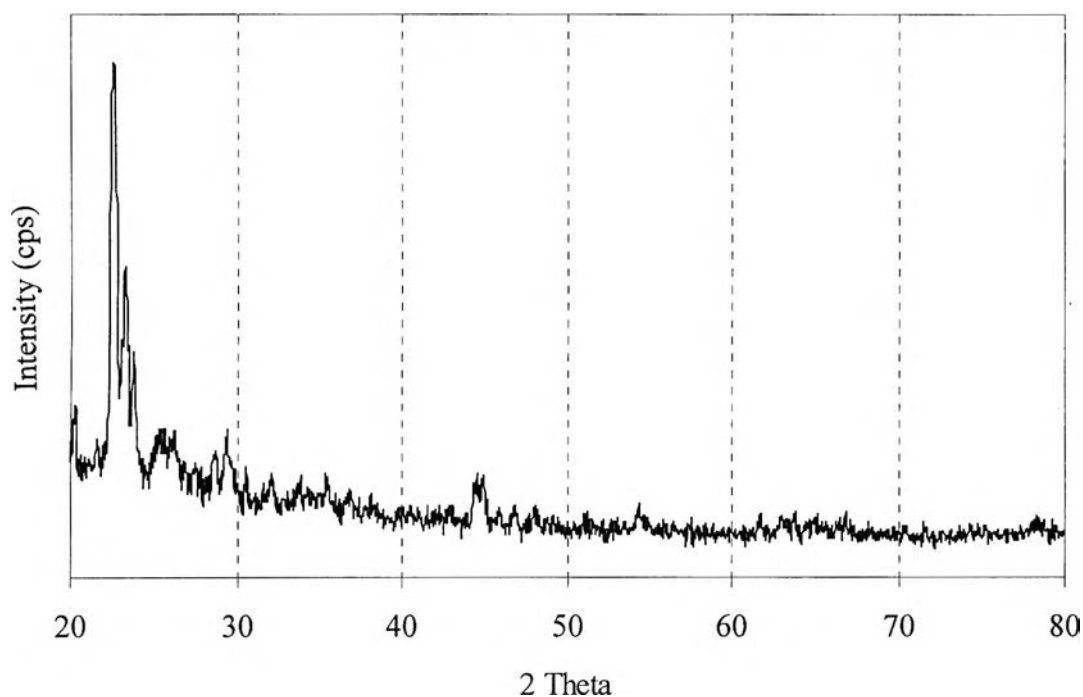
used catalyst (2) : adsorbed by  $C_3H_6+NO+O_2$

Catalyst	surface area ( $m^2/g$ )		
	fresh catalyst	used catalyst(1)	used catalyst(2)
HY	736	725	710
HMOR	869	833	811
H-ZSM-5	337	321	304
Cu-ZSM-5	365	340	302

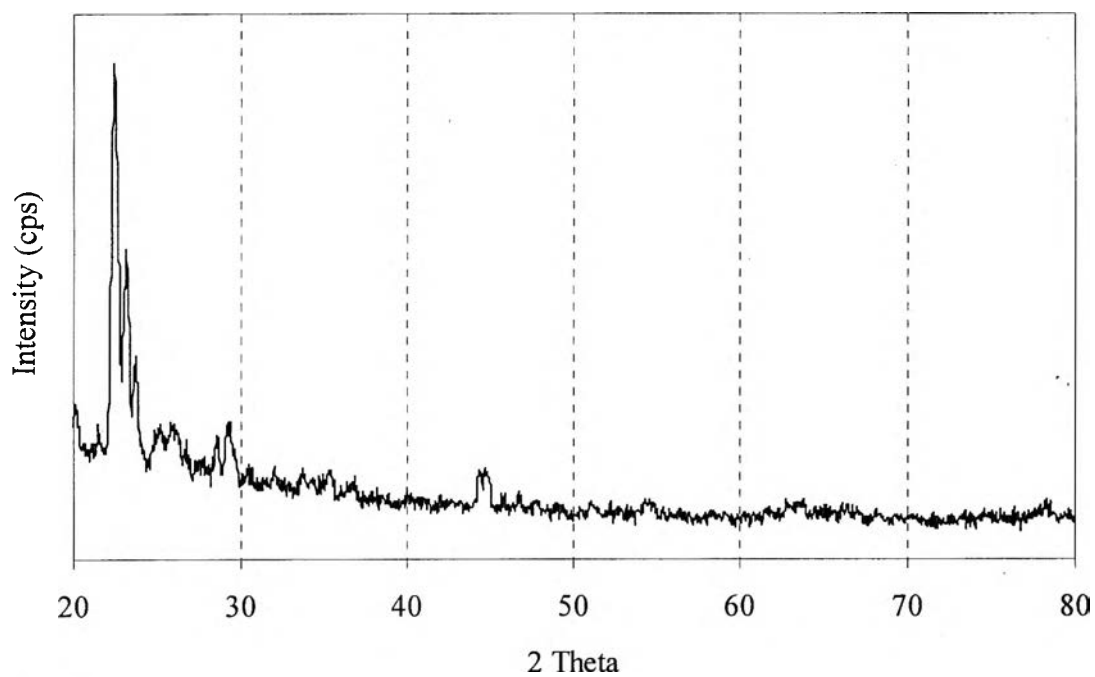
### 5.3.2 X-ray diffraction (XRD)

In this study, crystallinity and crystal structure of the catalyst are analyzed by X-ray diffraction technique.

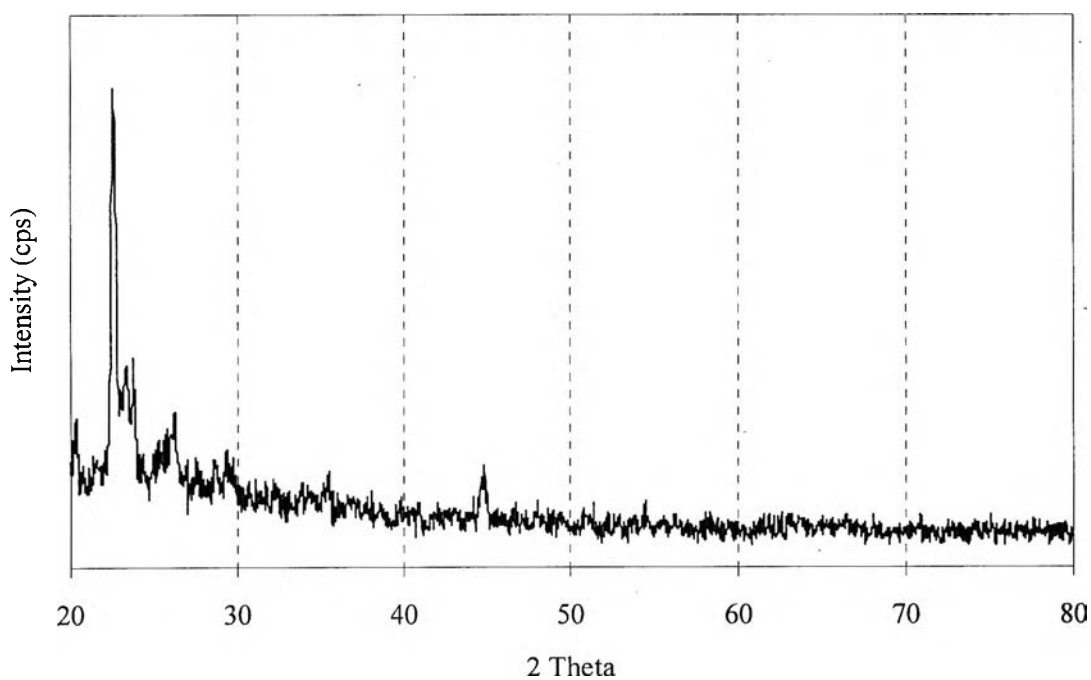
The XRD patterns of fresh Cu-ZSM-5 and that used with the adsorbed gas mixture of  $C_3H_6+NO+O_2$ ,  $C_3H_6$  only, toluene+ $NO+O_2$  and toluene only for 20 min at 400 °C are reported in figures 5.30-5.34. The fresh Cu-ZSM-5 and used Cu-ZSM-5 have the same peak positions. It can conclude that the nature of intermediates may not be formed a crystallographic phases observed. Hence, the intermediates occurred could not be detected by XRD.



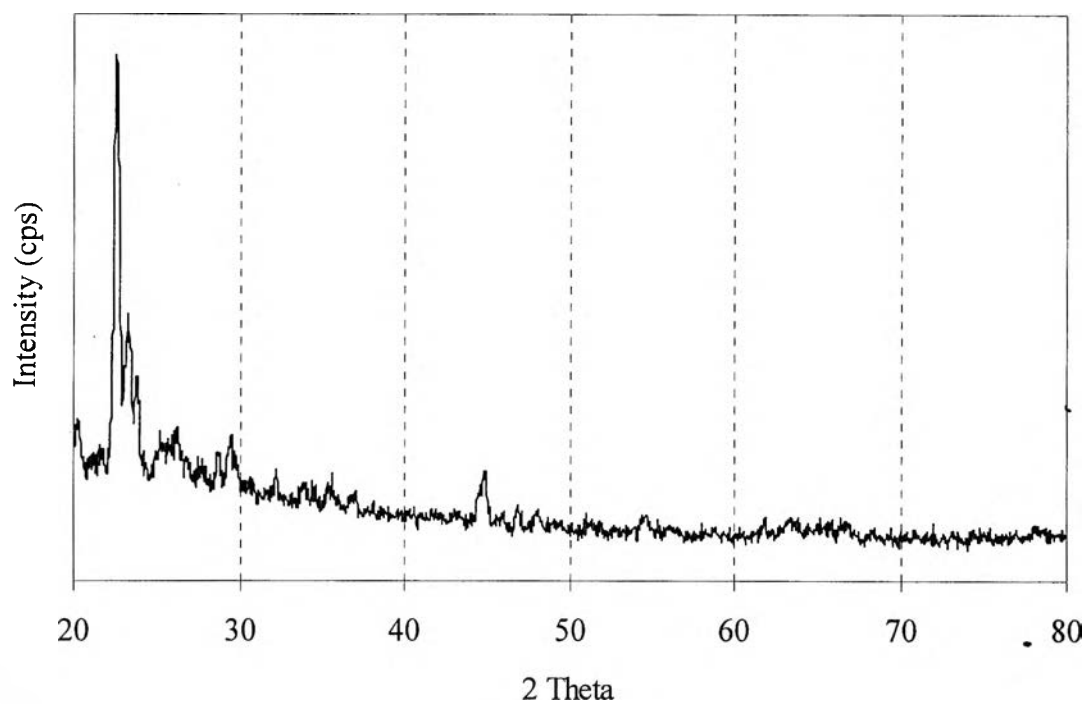
**Figure 5.30** XRD spectrum of fresh Cu-ZSM-5 catalyst



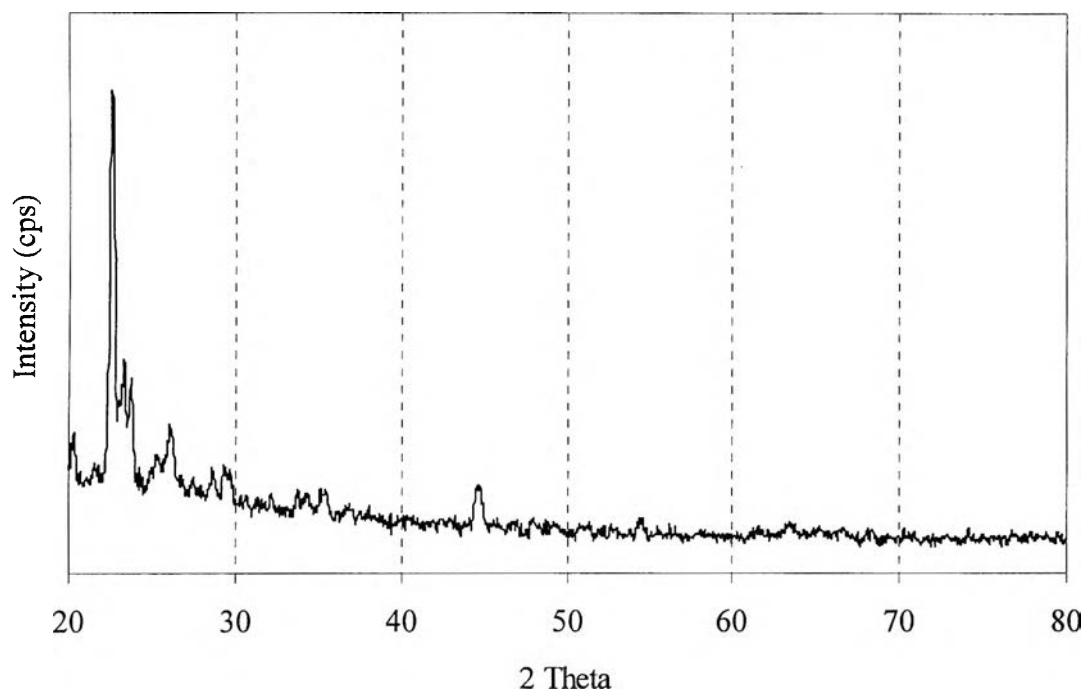
**Figure 5.31** XRD spectrum of carbonaceous deposits sample on Cu-ZSM-5 after adsorption by  $C_3H_6$  (3% mole of C)



**Figure 5.32** XRD spectrum of carbonaceous deposits sample on Cu-ZSM-5 catalyst after adsorption by  $C_3H_6$  (3% mole of C) + 1000 ppm NO + 10%  $O_2/He$



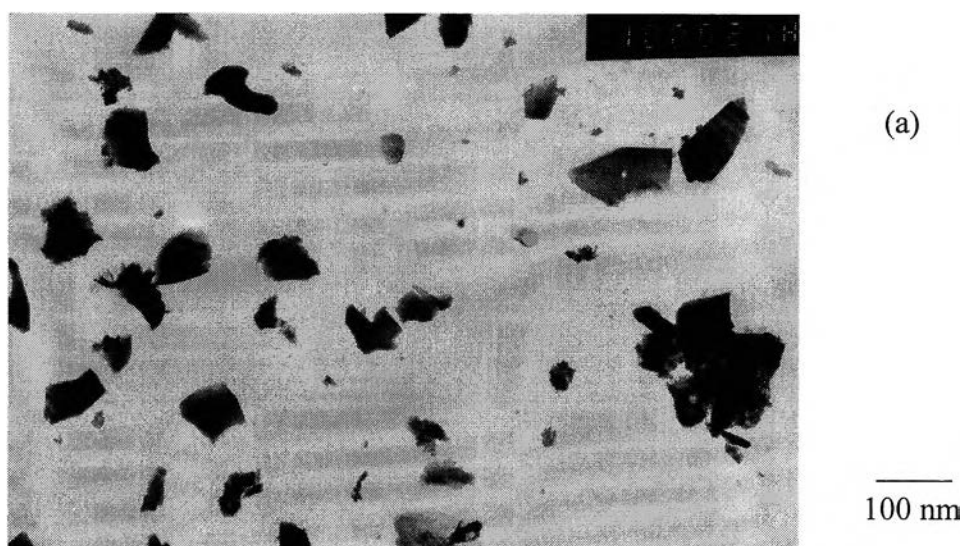
**Figure 5.33** XRD spectrum of carbonaceous deposits sample on Cu-ZSM-5 catalyst after adsorption by toluene (3% mole of C)



**Figure 5.34** XRD spectrum of carbonaceous deposits sample on Cu-ZSM-5 catalyst after adsorption by toluene (3% mole of C) + 1000 ppm NO + 10% O<sub>2</sub>/He

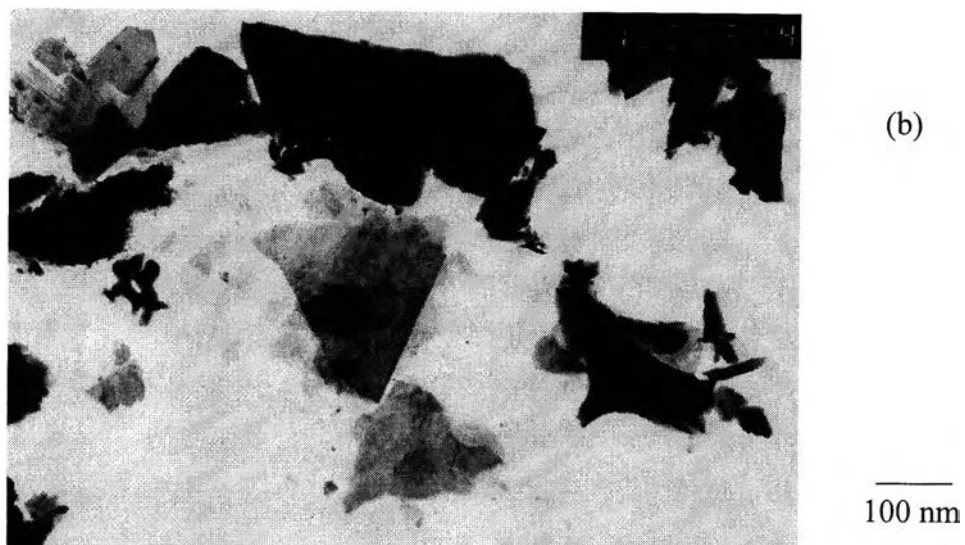
## 5.4 Morphology

Figure 5.35 shows TEM image of the fresh and used Cu-ZSM-5 catalyst by varying gas mixtures at 400°C for 20 min. For fresh catalysts, There is no observation of large dark spot. The carbonaceous coverage on the catalyst was speculate as seen from unclear image of particles. Carbon coverage on the catalyst was found to be a function of type of adsorbed gas mixture. For the adsorbed gas  $C_3H_6+NO+O_2$  (figure 5.35 (c)), it is obvious that the density and coverage of carbon produced were larger than the adsorbed gas mixture of  $C_3H_6$  (figure 5.35 (b)). In the same way, the adsorbed gas toluene+NO+O<sub>2</sub> (figure 5.35 (e)), it is obvious that the density and coverage of carbon produced were larger than the adsorbed gas mixture of toluene (figure 5.35 (d)).



**Figure 5.35** TEM photographs of the intermediates on Cu-ZSM-5 with varying adsorbed gas mixtures

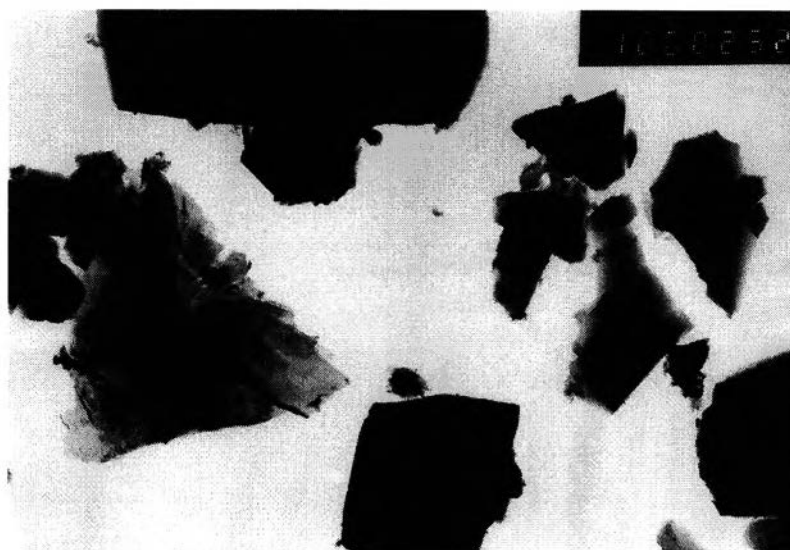
- (a) fresh catalyst,
- (b) used catalyst : adsorbed by  $C_3H_6$
- (c) used catalyst : adsorbed by  $C_3H_6+NO+O_2$
- (d) used catalyst : adsorbed by toluene
- (e) used catalyst : adsorbed by toluene+NO+O<sub>2</sub>



**Figure 5.35 (cont.)** TEM photographs of the intermediates on Cu-ZSM-5 with varying adsorbed gas mixtures

- (a) fresh catalyst,
- (b) used catalyst : adsorbed by  $C_3H_6$
- (c) used catalyst : adsorbed by  $C_3H_6+NO+O_2$
- (d) used catalyst : adsorbed by toluene
- (e) used catalyst : adsorbed by toluene+ $NO+O_2$





(d)

100 nm



(e)

100 nm

**Figure 5.35 (cont.)** TEM photographs of the intermediates on Cu-ZSM-5 with varying adsorbed gas mixtures

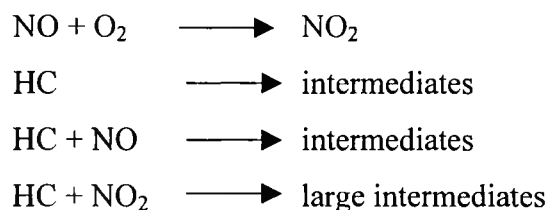
- (a) fresh catalyst,
- (b) used catalyst : adsorbed by  $C_3H_6$
- (c) used catalyst : adsorbed by  $C_3H_6+NO+O_2$
- (d) used catalyst : adsorbed by toluene
- (e) used catalyst : adsorbed by toluene+ $NO+O_2$

## 5.5 The proposed mechanism of the intermediates formation and removal

An overall proposed mechanism of the formation and the removal of the intermediates for NO reduction over Cu-ZSM-5 zeolite can be proposed as follows:

### 5.5.1 The intermediates formation

An intermediate generated over the catalyst from hydrocarbon and NO<sub>2</sub> was significantly larger than the intermediate from hydrocarbon only or hydrocarbon and NO. It may be possible that the intermediate from hydrocarbon and NO<sub>2</sub> was produced by using the selective catalytic reduction mechanism, which the intermediates formation was the rate determining step. Adsorbed NO<sub>2</sub>, reacts with hydrocarbon that can generate the large quantities of intermediates. This can suggest that the presence of O<sub>2</sub> is necessary to the intermediate formation of NO reduction.



### 5.5.2 The intermediates removal

It can suggest that the selective catalytic reduction mechanism was used to explain the intermediates removal by NO+O<sub>2</sub>. The intermediate representing the reductant for the selective catalytic reduction react with NO<sub>2</sub>, occurred from NO and O<sub>2</sub>, to N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O. On the other hand, the intermediates removal by O<sub>2</sub> was assigned by the combustion mechanism. The intermediates react with O<sub>2</sub> to CO<sub>2</sub>, H<sub>2</sub>O. Basically, NO<sub>2</sub> can react with hydrocarbon at lower temperature region than O<sub>2</sub> does. Hence, the intermediate representing hydrocarbon can be removed by NO<sub>2</sub> at lower temperature.

