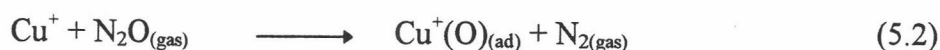
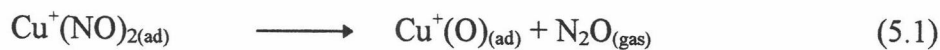


## CHAPTER V

### RESULTS AND DISCUSSION

#### 5.1 Effect of O<sub>2</sub> to SCR of NO by propylene

This experiment was performed on the microreactor. The Cu/Na-ZSM-5 catalyst was exposed to the gas mixture, contained 1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, various concentration of O<sub>2</sub>, and He balanced. The NO and C<sub>3</sub>H<sub>6</sub> concentrations were closed to the composition of the real exhaust gas. The reaction was performed at 500 °C because NO to N<sub>2</sub> conversion at temperature range 450-550 °C was nearly constant [78]. In order to observe the effect of O<sub>2</sub> on the amount of coke, O<sub>2</sub> concentration was varied. Figure 5.1 shows that the NO to N<sub>2</sub> conversions decrease rapidly at the initial interval of time on stream and then approach some constant values. Furthermore, the values at steady state of NO to N<sub>2</sub> conversion decrease when the O<sub>2</sub> contained in the feed stream was increased. The increasing of O<sub>2</sub> content which affected NO to N<sub>2</sub> conversion probably due to interaction of O<sub>2</sub> with either hydrocarbon or Cu sites of the catalyst. Considered the effect of O<sub>2</sub> to hydrocarbon, the increase of O<sub>2</sub> contained in feed stream enhanced the hydrocarbon combustion and consumed more hydrocarbon. Thus, the hydrocarbon for reacting with NO, in NO reduction, was decreased and the values of NO to N<sub>2</sub> conversion at steady state are found to be dwindled. Considered the effect of O<sub>2</sub> on Cu sites of the catalyst, the first hypothesis based on the mechanism which NO can decomposed by itself on the Cu sites of Cu/ZSM-5 catalyst and the role of hydrocarbon is to remove O<sub>2</sub> adsorbed on the same site which use for converting NO to N<sub>2</sub>, it was suggested that O<sub>2</sub> adsorbed on the Cu sites of Cu/ZSM-5 and protected these sites from reacting with NO as the following scheme which proposed by R. Burch and P.J. Millington. [ 61]



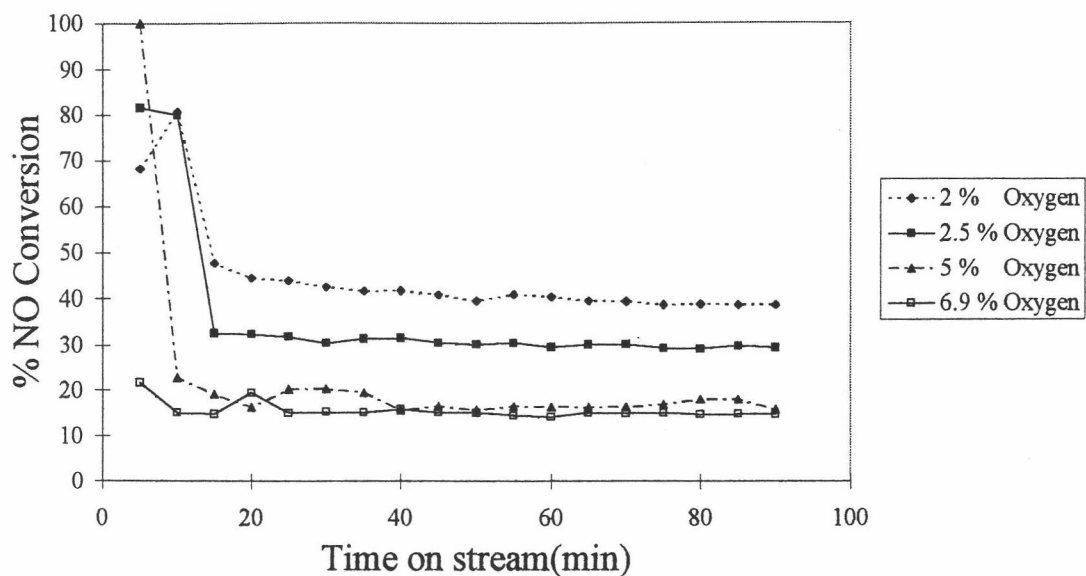
However, a broadly equivalent mechanism can not be rule out, involving  $\text{NO}_2$ - species [30,62], as show in the following reaction scheme.



The only real difference between the two models is the description of the active site as a coordinately unsaturated  $\text{Cu}^+$  ion site on the one hand or as a coordinately unsaturated  $\text{Cu}^+(\text{O})_{(\text{ad})}$  ion site on the other. Further, their observation explained the results which show a maximum activity with gas mixes containing about 2 %  $\text{O}_2$ . Too little oxygen relative to propene, the copper will be reduced to inactivate  $\text{Cu}^0$ : too much oxygen, it will be oxidized to inactive  $\text{Cu}^{2+}$ . In this study, the result that  $\text{O}_2$  enhance the activity of the catalyst at the beginning encourage this mechanism. And the decreasing of the values at steady state of NO to  $\text{N}_2$  conversion when  $\text{O}_2$  was increased may be due to enhance the chance of  $\text{O}_2$  adsorbed and/or reacted with active sites to formed  $\text{Cu-O}_{(\text{ad})}$  which inert for the NO reduction[61].

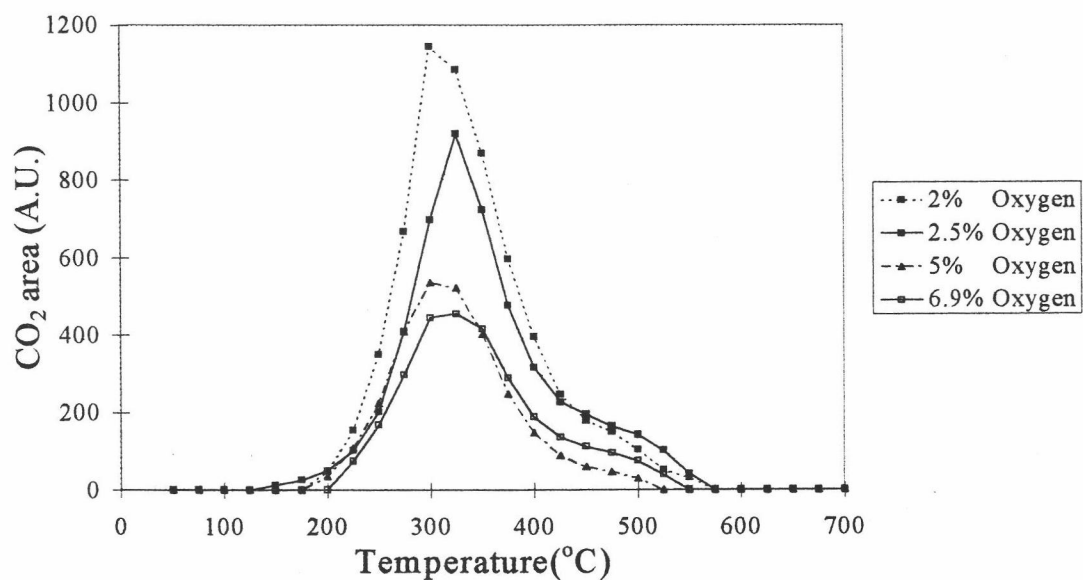
The other hypothesis, based on the  $\text{NO}_2$ -intermediate mechanism, can not be abandoned. The roles of  $\text{O}_2$  are both to formed  $\text{NO}_2$  [55] and to formed  $\text{Cu-O}_{(\text{ad})}$  [61]. Since  $\text{NO}_2$  is necessary for SCR [19,27,32,34,35,39,68-74], the increasing of  $\text{O}_2$  content enhance the conversion of NO to  $\text{NO}_2$  and consequently increase the values at initial interval of NO to  $\text{N}_2$ . On the other hand, The large amount of  $\text{O}_2$  may increase the chance of  $\text{Cu-O}_{(\text{ad})}$  formation which reduce the values at steady state of NO to  $\text{N}_2$  conversion.

Figure 5.2 exhibits the TPO patterns of spent catalysts refer to the figure 5.1. From the experimental result in both figures, it was clearly shown that the increase of  $\text{O}_2$  affect to enhance the coke combustion.



**Figure 5.1** Effect of  $O_2$  contained in feed stream on NO conversion on Cu/Na-ZSM-5.

1000 ppm NO, 3000 ppm  $C_3H_6$ , various %  $O_2$ , and balanced He,  
GHSV  $4000\ h^{-1}$ , reaction temperature  $500^\circ C$ .



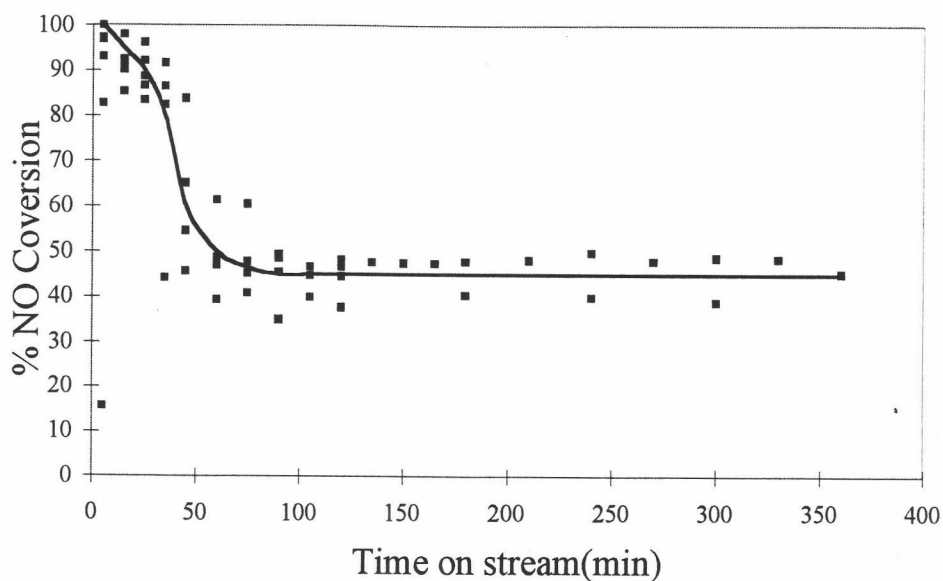
**Figure 5.2** Effect of  $O_2$  contained in feed stream to TPO patterns on Cu/Na-ZSM-5.

1000 ppm NO, 3000 ppm  $C_3H_6$ , various %  $O_2$  and balanced He,  
GHSV  $4000\ h^{-1}$ , reaction temperature  $500\ ^\circ C$ .

## 5.2 Relationship between the amount coke and time on stream

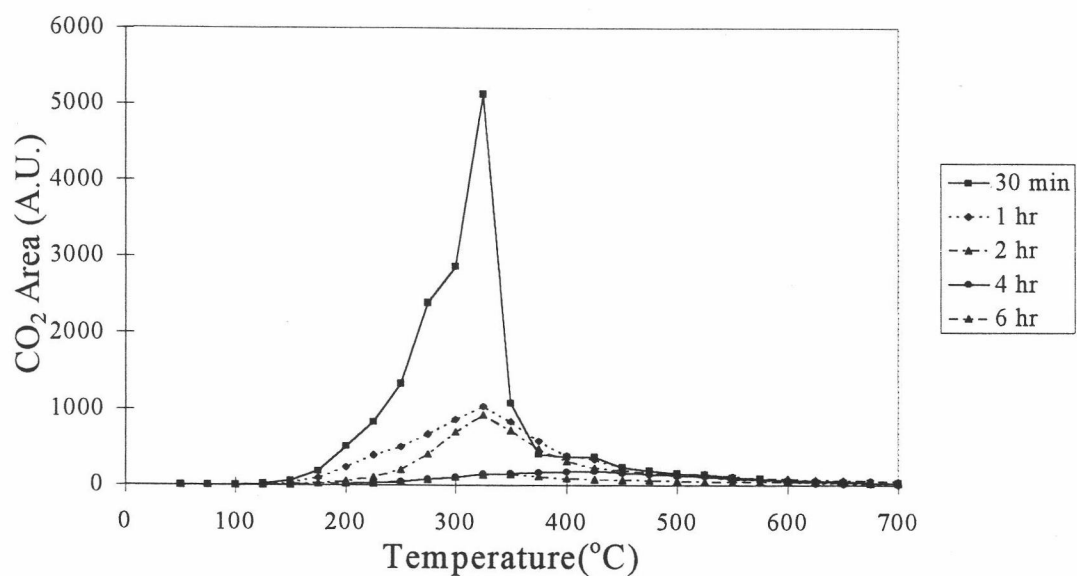
This experiment was performed on Cu/Na-ZSM-5 at 500 °C in order to study the relationship between quantity of coke and time on stream. The NO to N<sub>2</sub> conversion as a function of time on stream is shown in the figure 5.3. The hydrocarbon conversion reached 100 % in a few minutes at the beginning of every experiments. Figure 5.4 illustrates the TPO patterns of the spent catalysts at time on stream 0.5, 1, 2, 4 and 6 hours, respectively. Both NO to N<sub>2</sub> conversion and the amount of coke decreased when time on stream increased. These results may be due to rate of coke combustion from the catalyst surfaces are higher than rate of coke formation. The highest coke content was found at 30 minutes of the reaction, when compare with others in this experiment, can be caused by most of the sites which proper for coke formation opened for hydrocarbon to form coke on them. Figure 5.5 shows the comparison between NO to N<sub>2</sub> conversion and amount of coke. This experiment which operated at high temperature does not give enough detail about the reaction mechanism of SCR because the hydrocarbon conversion is 100% and it is obvious that NO conversion is increase when amount of coke on the catalyst increase. Thus, in the section 5.3, the reaction temperature is decrease to 207 °C which hydrocarbon conversion does not reach 100% and NO to N<sub>2</sub> conversion is not zero. Furthermore, at 207 °C, it is supposed that the rate of coke formation is higher than the rate of coke combustion.





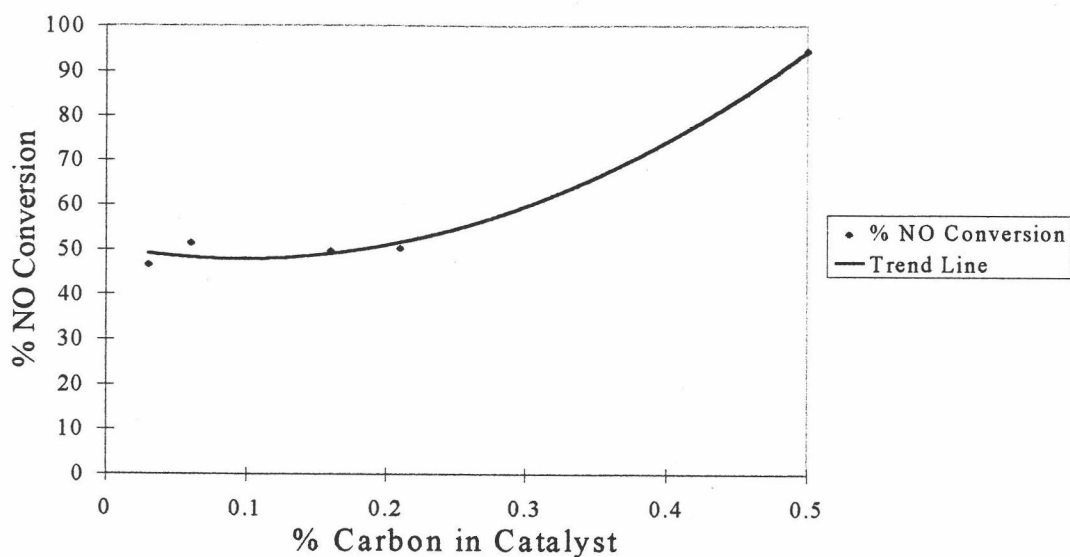
**Figure 5.3** NO conversion as function of time on stream of Cu/Na-ZSM-5.

1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5% O<sub>2</sub>, and balanced He,  
GHSV 4000 h<sup>-1</sup>, reaction temperature 500 °C.



**Figure 5.4** TPO patterns of Cu/Na-ZSM-5 in various time on stream.

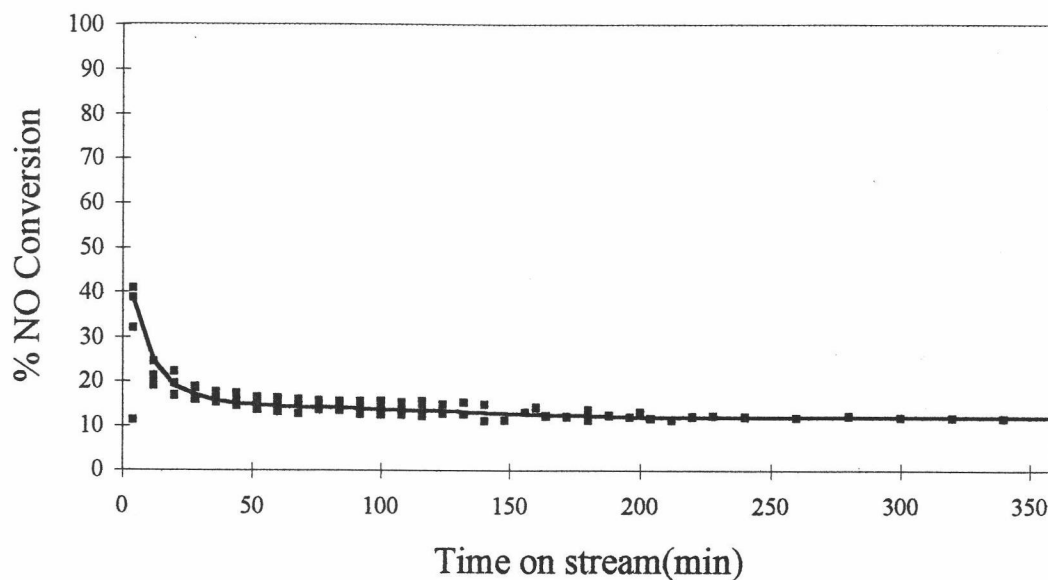
1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5% O<sub>2</sub>, and balanced He,  
GHSV 4000 h<sup>-1</sup>, reaction temperature 500 °C.



**Figure 5.5** Relationship between % carbon on catalyst and NO conversion of Cu/Na-ZSM-5. 1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5% O<sub>2</sub>, and balanced He, GHSV 4000 h<sup>-1</sup>, reaction temperature 500 °C.

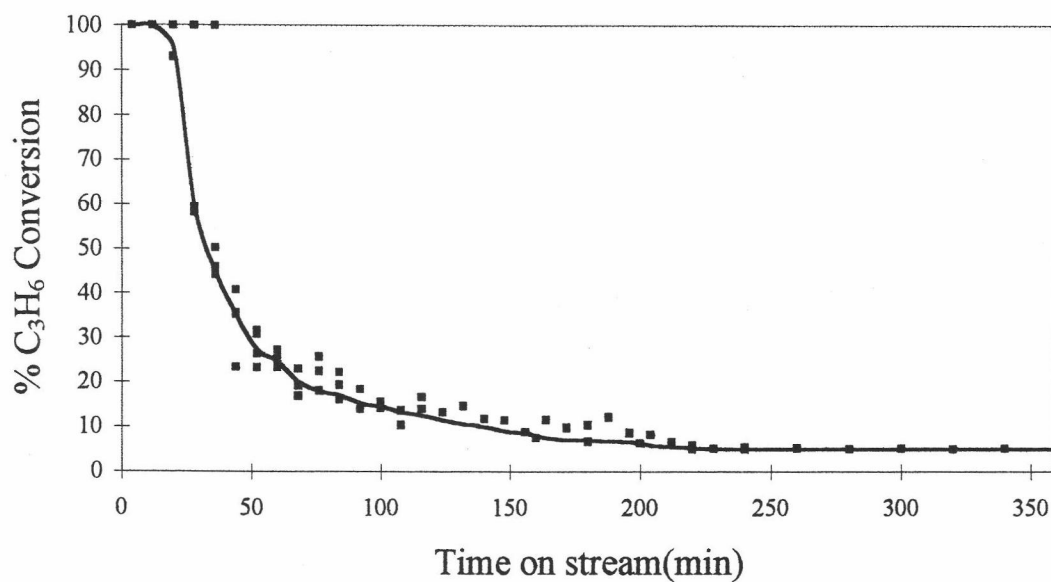
### 5.3 Effect of Coke on Cu/Na-ZSM-5 at 207 °C

The NO to N<sub>2</sub> and hydrocarbon conversions on Cu/Na-ZSM-5 are shown in figures 5.6 and 5.7, respectively. The TPO patterns of spent Cu/Na-ZSM-5 catalysts are shown in figure 5.8. Figure 5.9 exhibits NO and hydrocarbon conversions as a function of coke quantities. The coke content on the catalyst surfaces increased with time on stream at this temperature which contrasted with the result at 500 °C which the coke content decreased when time on stream increased. From this result, it is clearly shown that the rate of coke combustion for this temperature is lower than at 500 °C. It was confirmed by the result that the amount of coke which deposited on the catalysts operated at 207 °C are much more than that ones at 500 °C. From figure 5.9, the hydrocarbon conversion increased and NO conversion kept nearly constant while the amount of coke increased with time on stream. It is clearly shows that the coke formed on the site for converting hydrocarbon but did not deposited on the site which converted NO to N<sub>2</sub>.



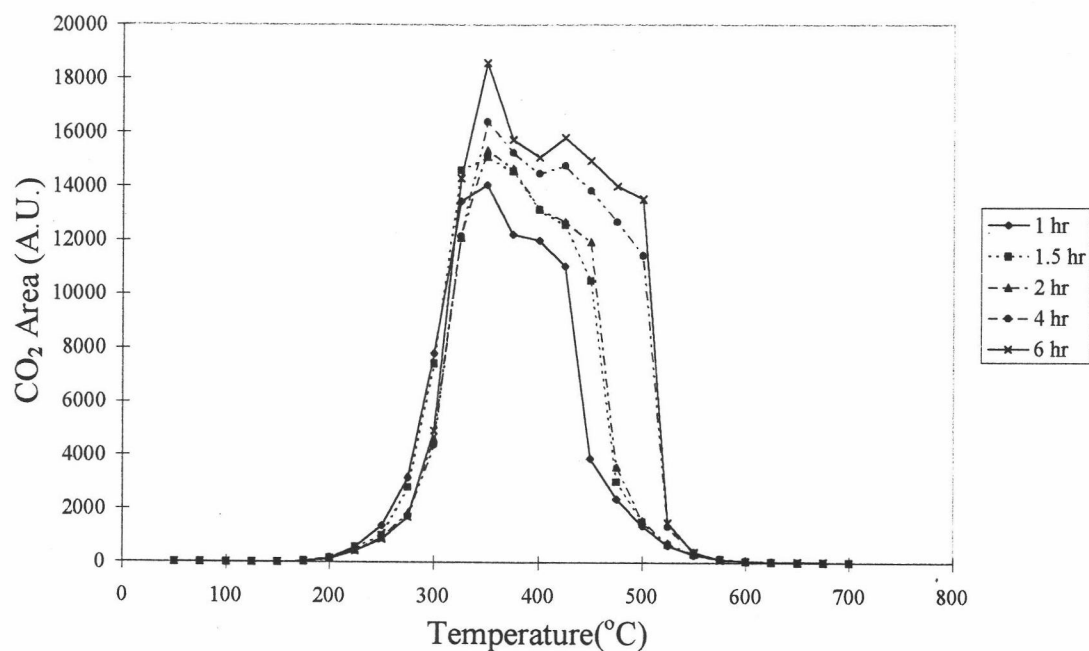
**Figure 5.6** NO conversion as function of time on stream of Cu/Na-ZSM-5.

1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5% O<sub>2</sub>, and balanced He,  
GHSV 4000 h<sup>-1</sup>, reaction temperature 207 °C.



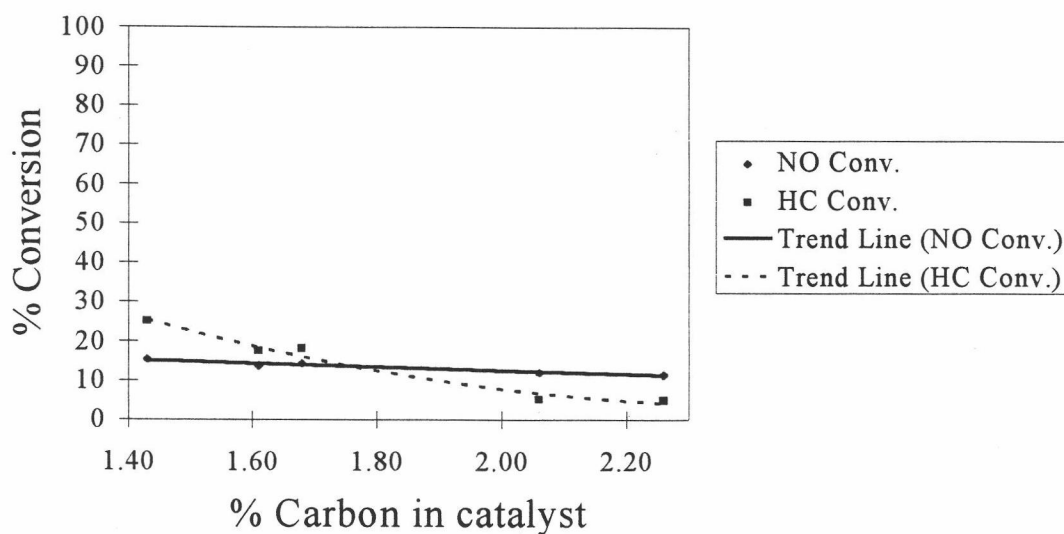
**Figure 5.7** C<sub>3</sub>H<sub>6</sub> conversion as a function of time on stream of Cu/Na-ZSM-5.

1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5% O<sub>2</sub>, and balanced He,  
GHSV 4000 h<sup>-1</sup>, reaction temperature 207 °C.

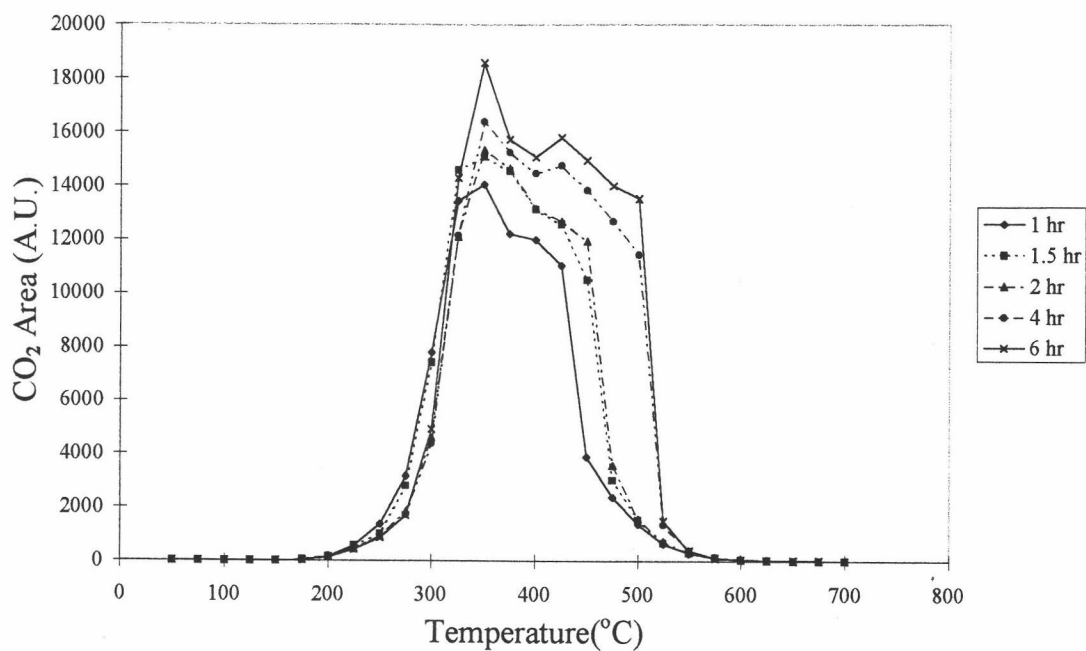


**Figure 5.8** TPO patterns of Cu/Na-ZSM-5 in various time on stream.

1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5% O<sub>2</sub>, and balanced He,  
GHSV 4000 h<sup>-1</sup>, reaction temperature 207 °C.

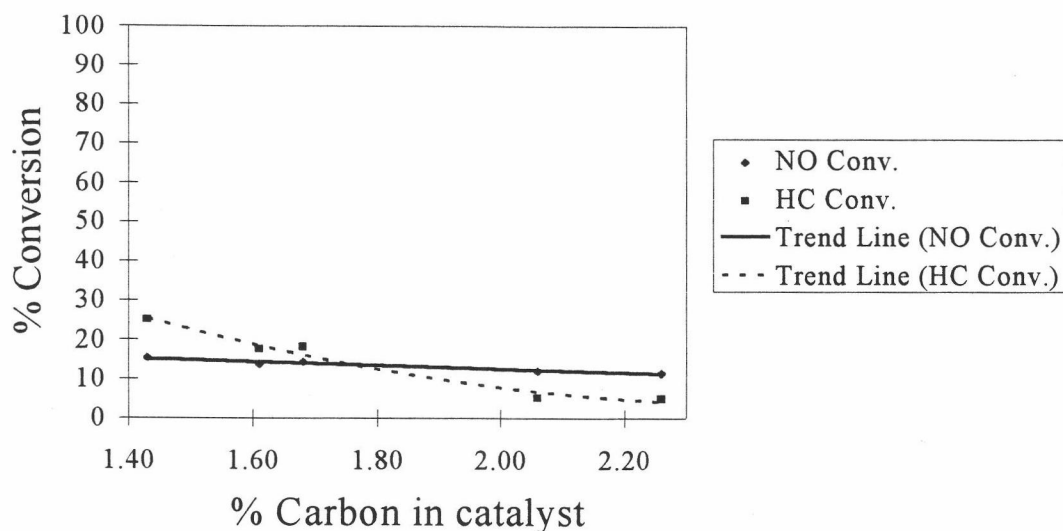


**Figure 5.9** Relationship between % carbon on catalyst and NO conversion of Cu/Na-ZSM-5. 1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5% O<sub>2</sub>, and balanced He, GHSV 4000 h<sup>-1</sup>, reaction temperature 207 °C.



**Figure 5.8** TPO patterns of Cu/Na-ZSM-5 in various time on stream.

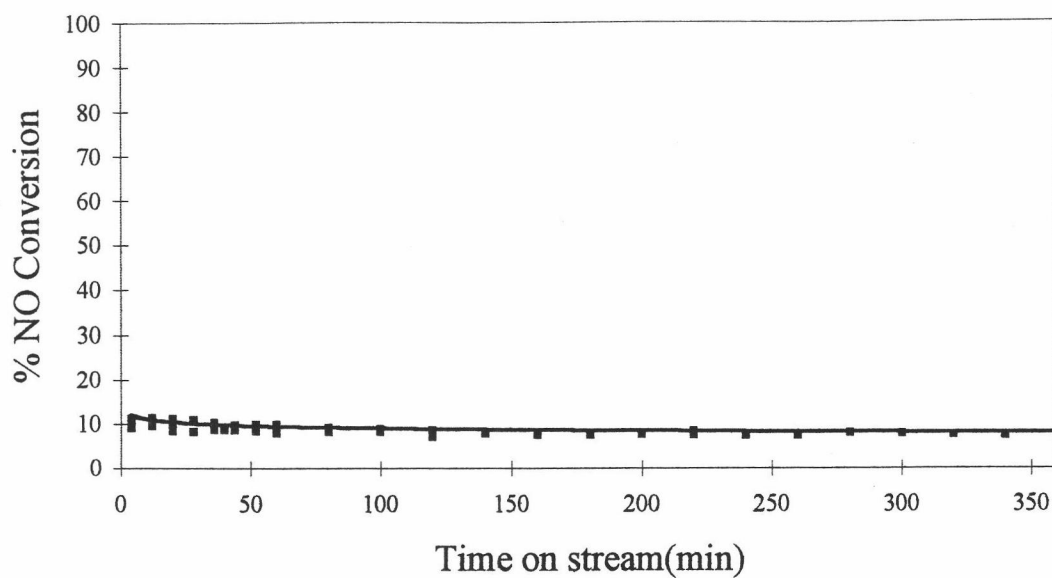
1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5% O<sub>2</sub>, and balanced He,  
GHSV 4000 h<sup>-1</sup>, reaction temperature 207 °C.



**Figure 5.9** Relationship between % carbon on catalyst and NO conversion of Cu/Na-ZSM-5. 1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5% O<sub>2</sub>, and balanced He, GHSV 4000 h<sup>-1</sup>, reaction temperature 207 °C.

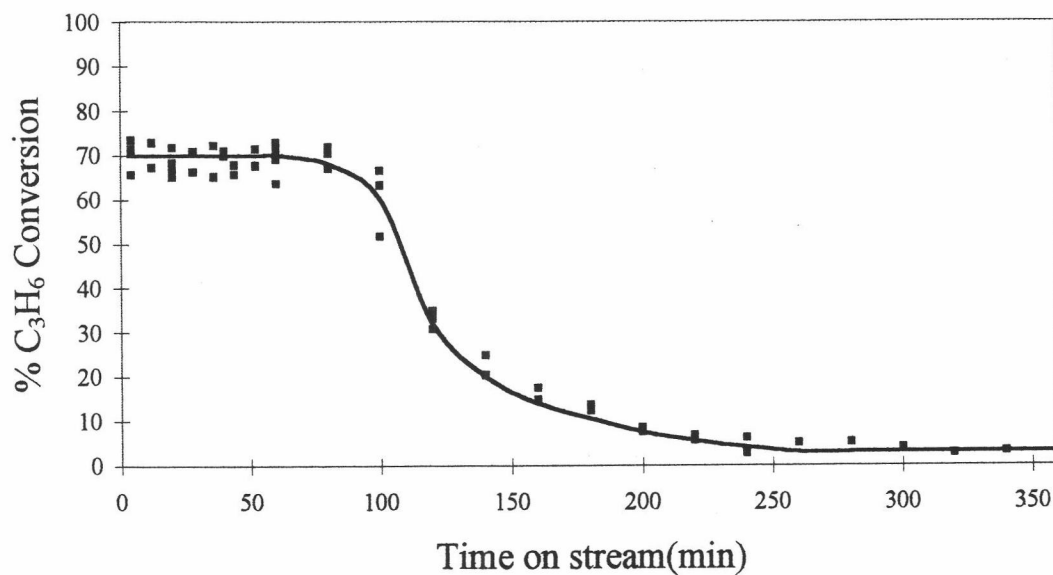
#### 5.4 Effect of Coke on H-ZSM-5 at 207 °C

In order to find the reaction mechanism, the result will be compared between Cu/Na-ZSM-5 and H-ZSM-5. This study chose H-ZSM-5 catalyst because it can catalyze the SCR of NO by hydrocarbon [27,31,42] and it is also the same type of zeolite with Cu/Na-ZSM-5. The NO and hydrocarbon conversions on H-ZSM-5 catalyst is shown in figures 5.10 and 5.11, respectively. Figure 5.12 exhibits the TPO patterns of this catalyst obtained from various time on stream. From figure 5.12, the coke deposited on the catalyst is reacted with O<sub>2</sub> at high temperature, approximately 600 °C, which is much more than Cu/Na-ZSM-5, 350 °C. This result indicates that coke deposited on the H-ZSM-5 catalyst is harder than in the case of Cu/Na-ZSM-5. This means that carbon deposited on the H-ZSM-5 is more difficult to be combusted with O<sub>2</sub> than the one on Cu-ZSM-5. Figure 5.13 exhibits the relationship between coke quantity and NO and hydrocarbon conversion. This figure gives the same clues with the figure 5.9 that the coke formation affected only hydrocarbon conversion. It means that coke deposited on the site for converted hydrocarbon but does not form on the sites for converted NO to N<sub>2</sub>.



**Figure 5.10** NO conversion as function of time on stream of H-ZSM-5.

1000 ppm NO, 3000 ppm  $C_3H_6$ , 2.5%  $O_2$ , and balanced He,  
GHSV  $4000\ h^{-1}$ , reaction temperature  $207\ ^\circ C$ .



**Figure 5.11**  $C_3H_6$  conversion as function of time on stream of H-ZSM-5.

1000 ppm NO, 3000 ppm  $C_3H_6$ , 2.5%  $O_2$ , and balanced He,  
GHSV  $4000\ h^{-1}$ , reaction temperature  $207\ ^\circ C$ .

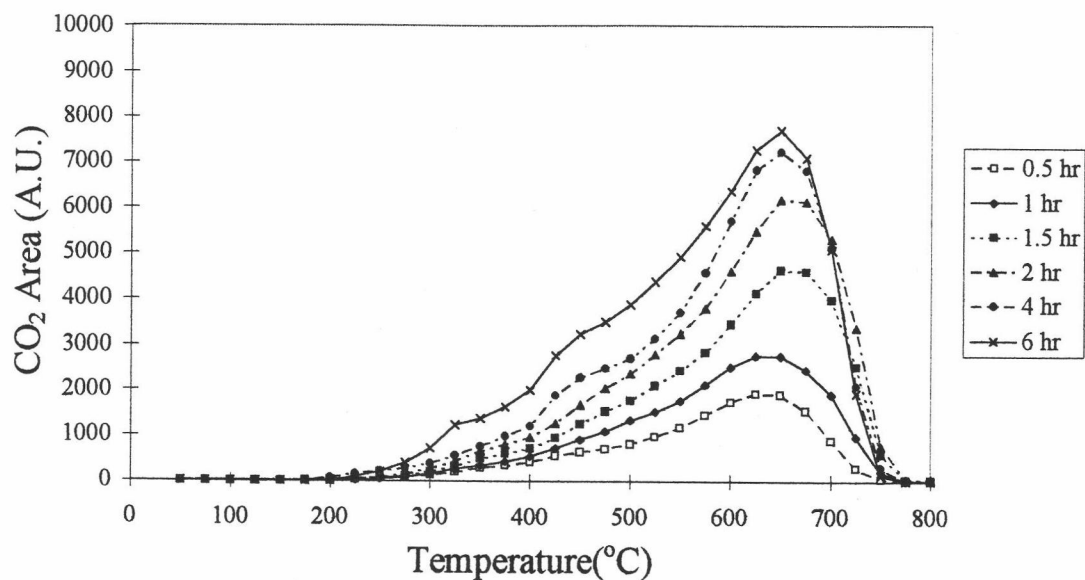


Figure 5.12 TPO patterns of H-ZSM-5 in various time on stream.

1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5% O<sub>2</sub>, and balanced He,  
GHSV 4000 h<sup>-1</sup>, reaction temperature 207 °C.

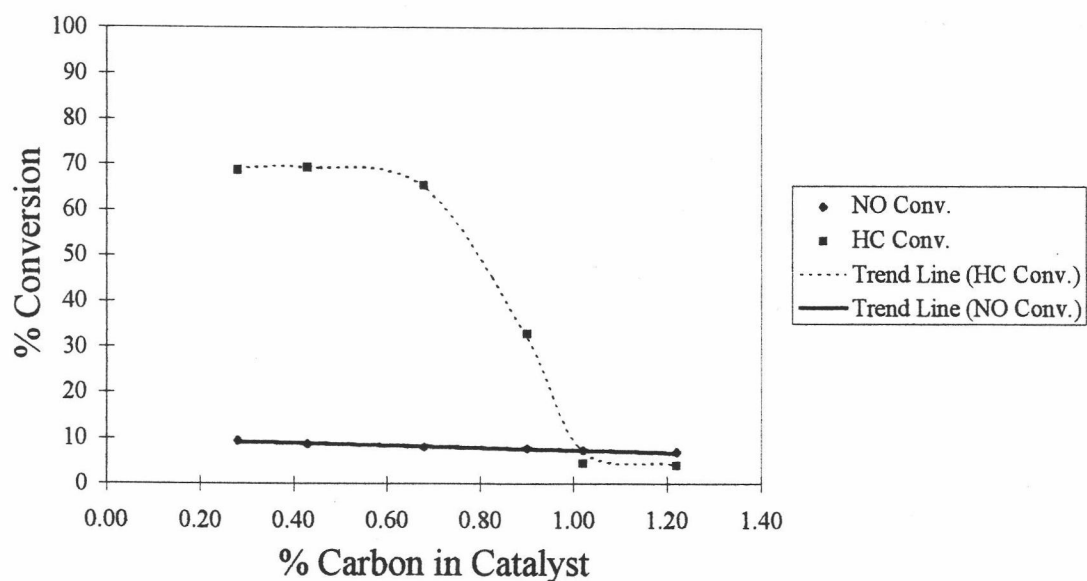


Figure 5.13 Relationship between % carbon on catalyst and NO conversion of

H-ZSM-5. 1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5% O<sub>2</sub>, and balanced He,  
GHSV 4000 h<sup>-1</sup>, reaction temperature 207 °C.



### 5.5 Comparison between the Cu/Na-ZSM-5 and H-ZSM-5

From figures 5.6, 5.7, 5.10 and 5.11 in sections 5.3 and 5.4, the differences of NO and hydrocarbon conversions between Cu/Na-ZSM-5 and H-ZSM-5 are as follow:

- (1) The hydrocarbon conversion of Cu/Na-ZSM-5 starts at 100 % and decreases very rapidly after 10 minute. In case of H-ZSM-5, hydrocarbon conversion is kept near a constant value , approximately at 70 %, about 80 minutes. Next, their hydrocarbon conversion decrease to about 5 %.
- (2) At the early stage of reaction, from 0 to 10 minute, the NO to N<sub>2</sub> conversion of Cu/Na-ZSM-5 drops from about 40 % to 15 %. On the other hand, NO to N<sub>2</sub> conversion of H-ZSM-5 remain nearly constant value about 10 %.

This phenomena may be caused by the formation of coke deposited on the active site for converting hydrocarbon, may be some of the Cu-sites and/or the acidic site of zeolite , will be discuss in detail later in section 5.9 . From the phenomena (1) above , there may be explained by one of these two reasons. First, there are many sites for converting hydrocarbon on H-ZSM-5 and more than on the Cu/Na-ZSM-5 catalyst. At the beginning, coke deposited on the active site and hydrocarbon conversion can occur on the vacant site which was not covered by coke. Then, after the catalyst was deactivated by coke covered most of the active sites, the hydrocarbon conversion decreased very rapidly and went to a nearly constant value at steady state. The other reason, it is well known that the presence of transition metal accelerates the formation of coke [80]. Thus, rate of coke formation on Cu/Na-ZSM-5 can be higher than H-ZSM-5 and makes the hydrocarbon conversion of Cu/Na-ZSM-5 decreases faster than H-ZSM-5. Our experiments satisfies the latter reason. Probably, the Cu sites on Cu/Na-ZSM-5 accelerate coke formation by spillover the oxygen to the zeolite surfaces. This O<sub>2</sub> spillover not only establish high rate of hydrocarbon combustion but also make high rate of coke formation.

The following phenomena can be explained by the above reason.

- 1) Hydrocarbon conversion on Cu/Na-ZSM-5 reaches 100 % but that on H-ZSM-5 approaches to only 70 %
- 2) Hydrocarbon conversion on Cu/Na-ZSM-5 drops faster than H-ZSM-5.

For NO to N<sub>2</sub> conversion on Cu/Na-ZSM-5, the cause of decreasing of NO to N<sub>2</sub> conversion on Cu/Na-ZSM-5 catalyst in the early stage of the reaction due to various reasons which point on the Cu sites of the catalys. Many researchers suggested that exchanged copper sites play an important role on SCR by changed NO to NO<sub>2</sub>-intermediate [19,29,32,34,35,39,68-74]. First, it was considered that the coke formation on Cu sites can be neglected. In our experiment, we did not find any significant decreasing of Cu sites on the spent Cu/Na-ZSM-5 catalyst, as shown in table 5.1 . Thus, this phenomena can occur from other effect, such as can be by the effect of O<sub>2</sub> as the result shown previously in section 5.1.

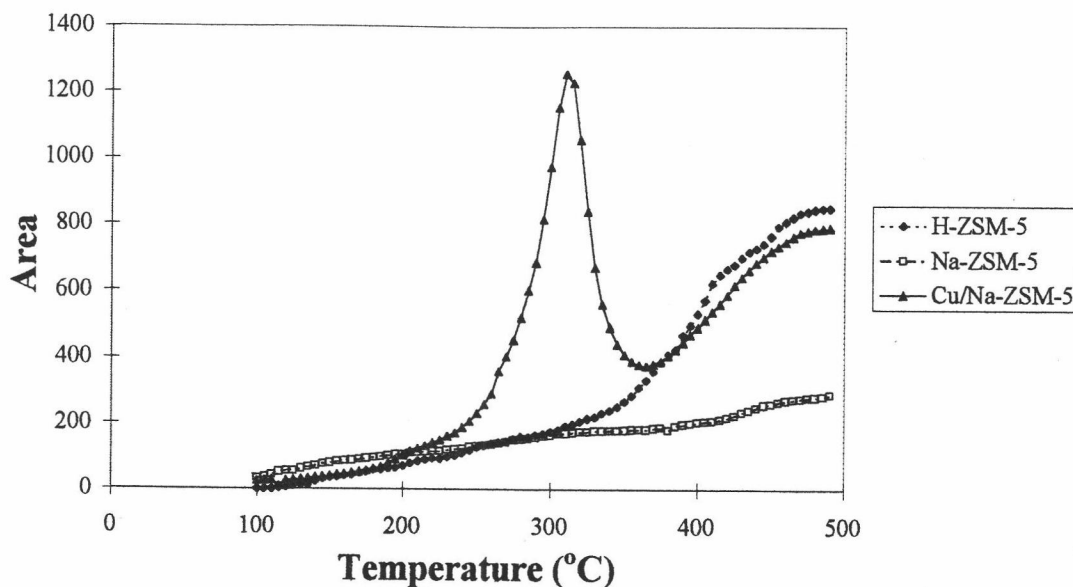
The TPO patterns, in figures 5.8 and 5.12 for Cu/Na-ZSM-5 and H-ZSM-5, respectively, not only show that coke on H-ZSM-5 is more difficult to be combusted by O<sub>2</sub> than that on Cu/Na-ZSM-5 but also exhibit that the amount of coke on H-ZSM-5 is lower than Cu/ZSM-5. These results can indicate that coke on Cu/Na-ZSM-5 is disturbed by something and made it difficult to be hard coke like that on H-ZSM-5. By the nature of coke, coke must be developed from coke precursor and then grows up to the coke and hard coke, respectively. Soft and hard cokes are defined by their combustion ability. The soft coke is easier to be combusted with oxygen than hard coke (used lower temperature). It is suggested that the development of coke is resisted by oxygen. However, it is clearly shown in figures 5.8 and 5.12 that O<sub>2</sub> in the gas phase may not react with the carbon deposited on catalyst surfaces at 207 °C. It probably has O<sub>2</sub>, which is adsorbed, on the Cu metal spillover from Cu site to react with coke on the catalyst surfaces [63,64].

Since the enlargement of coke content on the catalyst surfaces has some limitations, as shown in figures 5.9 and 5.13, the explanation of this phenomena have two hypothesis. First, the coke deposition goes to equilibrium stage by the rate of coke formation equals to the rate of coke combustion. The other is the active sites for coke

formation may not be proper because of ensemble effect [79]. In this experiment, reaction temperature was 207 °C which is too to burn coke at high enough rate. Then, the ensemble effect is more probably the main cause of these phenomena at this temperature.

### **5.6 Temperature Programmed Reduction (TPR) experiment**

In order to find the amount of oxygen on the catalyst surfaces, the TPR experiment was used. Basis on the reduction properties of H<sub>2</sub>, TPR experiment performed by adsorbed O<sub>2</sub> onto the catalyst surface and then exposed the catalyst to the H<sub>2</sub>-flow and heated at a heating rate of 10 °C/min.. The H<sub>2</sub> consumption shows the amount of oxygen on the catalyst and the temperature which H<sub>2</sub> reacted with oxygen indicates the strength of interaction between oxygen and catalyst surfaces. Figure 5.14 shows the TPR profiles on Cu/Na-ZSM-5, Na-ZSM-5 and H-ZSM-5. The peak located at 310 °C shows that there is O<sub>2</sub> on Cu sites of the catalyst. These experimental data are similar to report of R.burch and S. Scire [73]. Furthermore, there are broad peaks at about 450-500 °C for Cu/Na-ZSM-5 and H-ZSM-5 only. Probably, the adsorption of O<sub>2</sub> on the catalyst surface plays an important role to the SCR of NO by hydrocarbon since NO to N<sub>2</sub> conversion on Cu/Na-ZSM-5 was the highest and NO to N<sub>2</sub> conversion on Na-ZSM-5 was the lowest.



**Figure 5.14** TPR profiles of Cu/Na-ZSM-5, Na-ZSM-5 and H-ZSM-5.

### 5.7 Cu-site measurement by $N_2O$ probe molecules adsorption

The result of  $N_2O$  probe molecules adsorption, which was used to measure the Cu sites, is shown in Table 5.1. The experimental data do not show any major change of the content of Cu on the catalyst surface when coke was formed. This indicates that there is little amount of coke deposited on the Cu site of the spent catalyst. This result is close to the study of G.P. Ansell et al.[30]. The nitric oxide uptake traced on a sample of Cu/ZSM-5 which has been coked in  $C_3H_6/O_2$  at 160 °C and then TPD (Temperature Programmed Desorption) to 400 °C. The TPD profile looked very similar with that observed over fresh Cu/ZSM-5, indicating that similar processes were occurring. This result reveals that the coke is not deposited on the copper sites.

**Table 5.1** The amount of Cu sites on the Cu/Na-ZSM-5 surfaces.

Catalyst	molecule Cu/g catalyst
fresh	$2.19 \times 10^{22}$
run 0.5 hr.	$1.84 \times 10^{22}$
run 1 hr.	$2.03 \times 10^{22}$
run 4 hr.	$1.93 \times 10^{22}$
run 6 hr.	$1.69 \times 10^{22}$

### 5.8 BET Surface Area and Pore Size Distribution

The BET surface area and the average pore size of Cu/Na-ZSM-5 are shown in Table 5.2. It is suggested that the formation of coke enlarges the average pore size due to the pore of coke bigger than the micropore of the zeolite. The coke formed in the macro pore of the catalyst and increased the average pore size of the catalysts.

**Table 5.2** BET surface area and average pore size

Sample Name	BET Surf. Area ( $\text{m}^2/\text{g}$ )	Micropore Area ( $\text{m}^2/\text{g}$ )	Micropore Vol. ( $\text{cc}/\text{g}$ )	Average Pore Dia. ( $\text{\AA}$ )
<b>Cu/Na-ZSM5 fresh</b>	332.09	175.33	0.0812	20.83
Cu/Na-ZSM5 1 hr	316.87	195.70	0.0895	21.69
Cu/Na- ZSM5 2 hr	352.95	196.88	0.0914	21.91
Cu/Na-ZSM5 4 hr	334.60	189.15	0.0878	21.78
Cu/Na-ZSM5 6 hr	307.24	175.85	0.0815	21.75
<b>H-ZSM5 fresh</b>	397.20	215.82	0.0984	19.62
H-ZSM5 1 hr	325.70	190.43	0.0875	20.31
H-ZSM5 6 hr	331.34	191.48	0.0895	20.84
<b>Na-ZSM5 fresh</b>	390.70	267.22	0.1230	19.02

## 5.9 Acidity of Catalyst

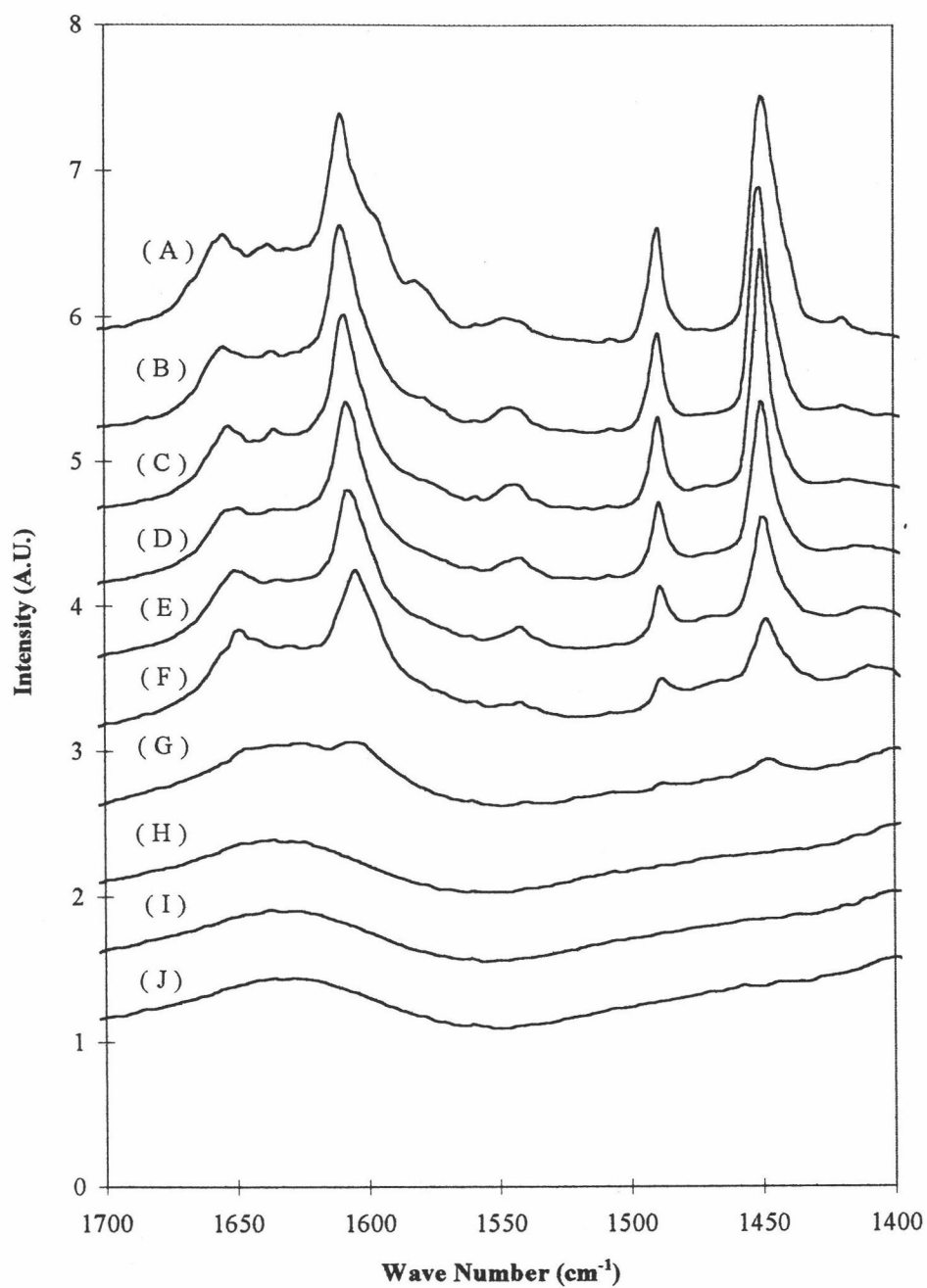
### 5.9.1 Comparison among the types of catalyst

The acidity of the catalysts was observed by using pyridine as a probe molecule. Figures 5.15, 5.16 and 5.17 are the experiments performed on the Cu/Na-ZSM-5, H-ZSM-5 and Na-ZSM-5 catalysts, respectively. From these three figures, peaks at 1610, 1545, 1492 and 1452  $\text{cm}^{-1}$  are adsorbed pyridine on the catalyst surfaces. The experimental data were considered by accepting the assignment of band at 1545  $\text{cm}^{-1}$  to pyridinium ion formed by interaction with Brønsted acid sites, and a band at 1454  $\text{cm}^{-1}$  to pyridine coordinated to Lewis acid sites [65,66] (and the others bands are common to both species). In this experiment, the band at 1492  $\text{cm}^{-1}$  was assigned to pyridinium ions on the Brønsted acid sites like the band at 1545  $\text{cm}^{-1}$ . The amount of Lewis acid sites of Cu/Na-ZSM-5 are higher than H-ZSM-5 and Na-ZSM-5. On the other hand, the amount of Brønsted acid sites of Cu/Na/ZSM-5 are closed to H-ZSM-5 and Na-ZSM-5. The experimental data in figures 5.15 and 5.16 show that at high temperature Brønsted acid sites on H-ZSM-5 still remain while those on Cu/Na-ZSM-5 disappears. It means that the acidity of Brønsted acid sites on H-ZSM-5 is stronger than the Brønsted acid sites on Cu/Na-ZSM-5. When the pyridine adsorption of Cu/Na-ZSM-5 and Na-ZSM-5 are compared, it is clearly shown that exchanged Cu enhances the strength of Lewis acid site of the Na-ZSM-5 catalyst.

### 5.9.2 Comparison between fresh and spent catalysts

Figures 5.18 and 5.19 show the pyridine adsorption measurement on spent Cu/Na-ZSM-5 catalysts operating at 207 °C for 2 and 6 hours, respectively. Figure 5.20 shows the pyridine adsorption measurement on spent H-ZSM-5 operating at 207 °C for 6 hours. The comparison between fresh and spent Cu/Na-ZSM-5, is shown in figures 5.15, 5.18 and 5.19, illustrate that bands which relate to Lewis acid site of spent catalysts are lower than those of fresh catalyst. This result indicates that the

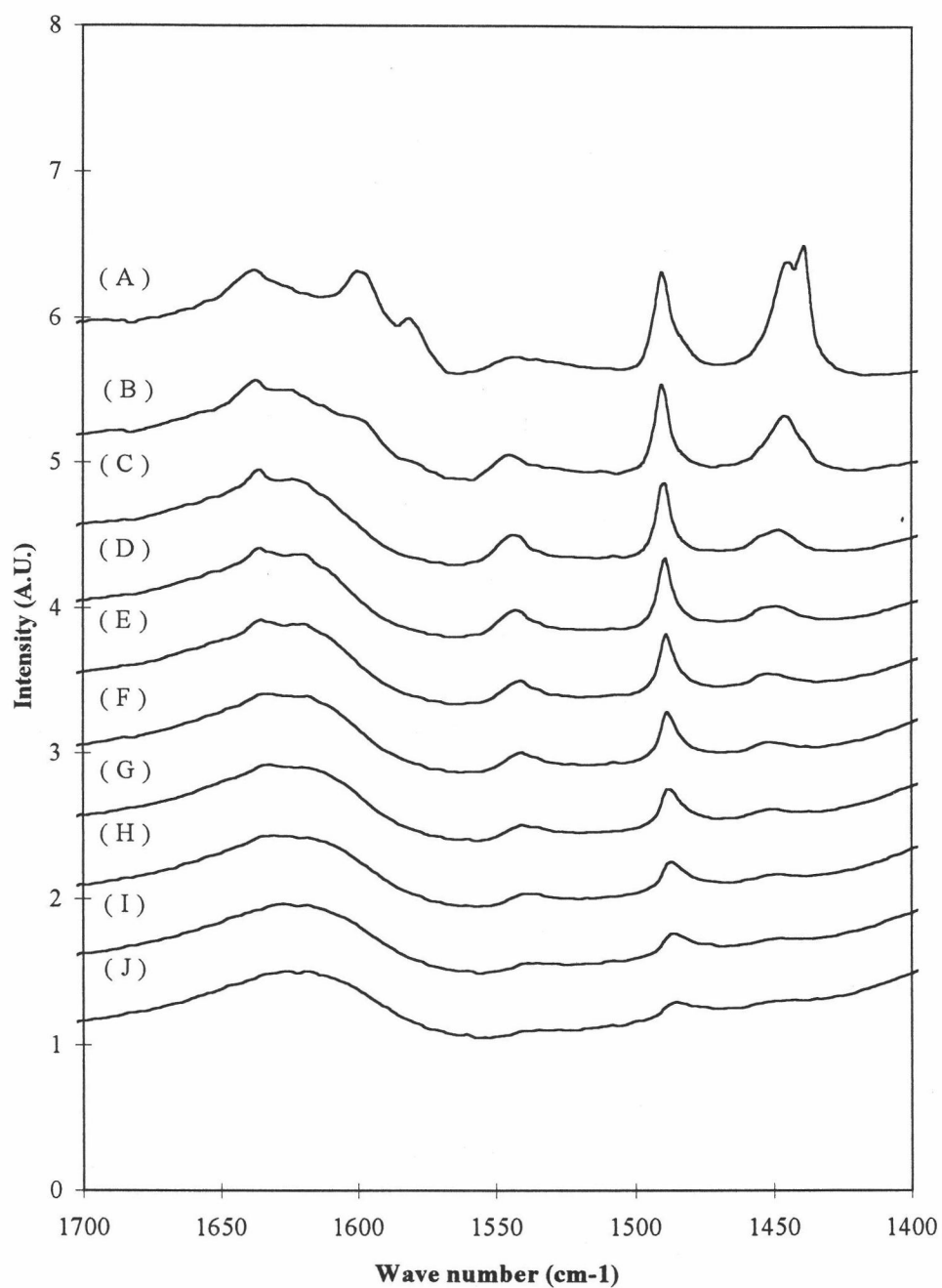
Lewis acid site of Cu/Na-ZSM-5 catalysts decreases when the catalyst was covered by coke. Since coke formation has a little effect on the Cu sites of the catalyst, as shown previously in section 5.7. Thus, the coke may be mainly form on the Lewis acid sites of the zeolite. The result which was observed on H-ZSM-5, figures 5.16 and 5.20, clearly shows the decreasing of the amount of Lewis acid sites. However, the result indicates that the coke forms on both Brønsted and Lewis acid sites. Our results coincided with G.D. Mclellan et al. [65] concluded that acid sites of H-ZSM-5 decreased by coke deposited during the conversion of methanol to gasoline. Moreover, it has been indicated by several investigator ( from ref. [80] ) that strong acids rather than weak acid, Lewis acid than Brønsted acid favor coke formation and that the presence of transition metal ions accelerate the formation of coke on silica-alumina catalyst. In conclusion, coke mainly formed on the Lewis acid sites of the zeolite.



**Figure 5.15** Pyridine adsorption of fresh Cu/Na-ZSM-5.

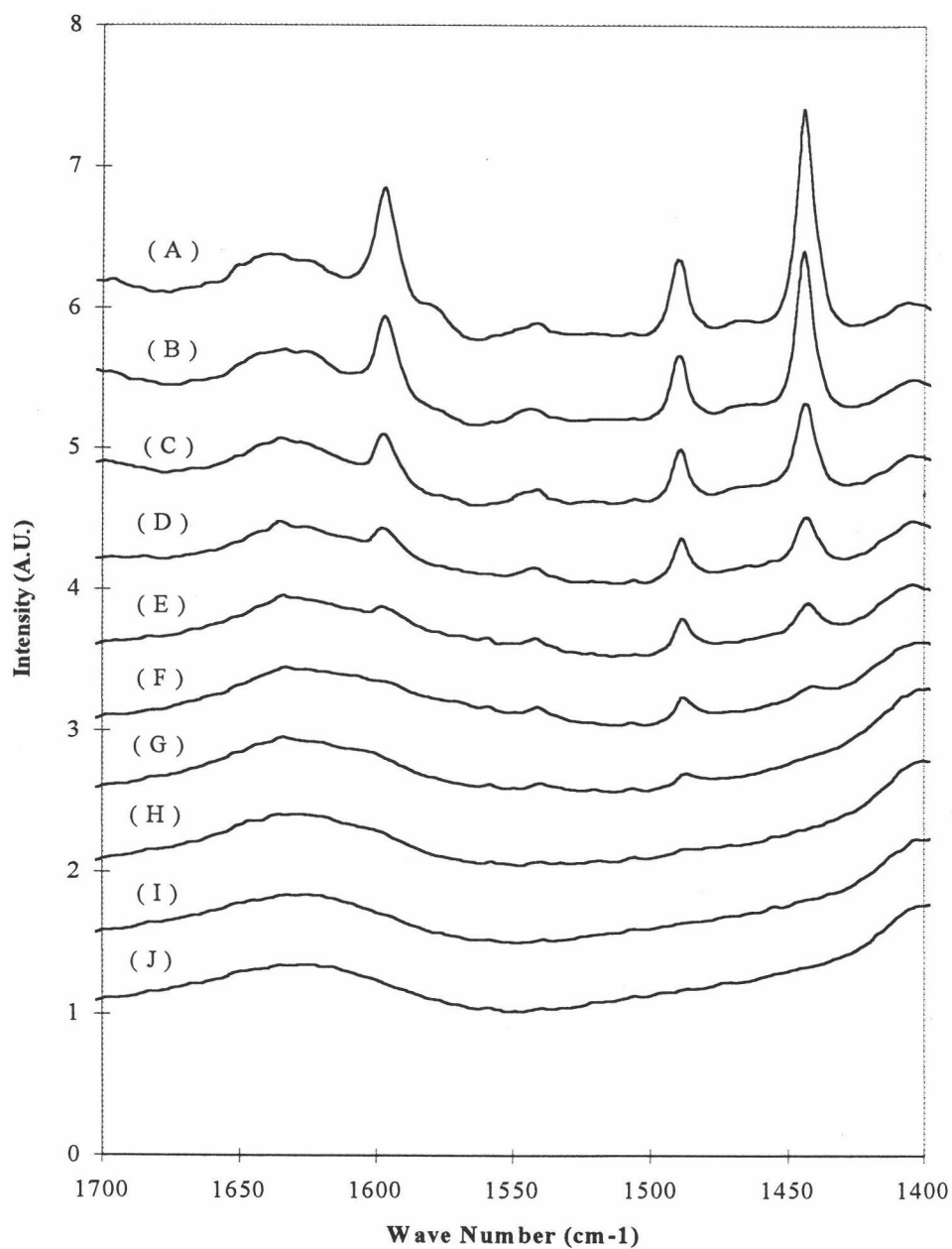
Pyridine adsorbed at room temperature and then heating the catalyst to (A) 50 °C, (B) 100 °C, (C) 150 °C, (D) 200 °C, (E) 250 °C, (F) 300 °C, (G) 350 °C, (H) 400 °C, (I) 450 °C, and (J) 500 °C, consequently





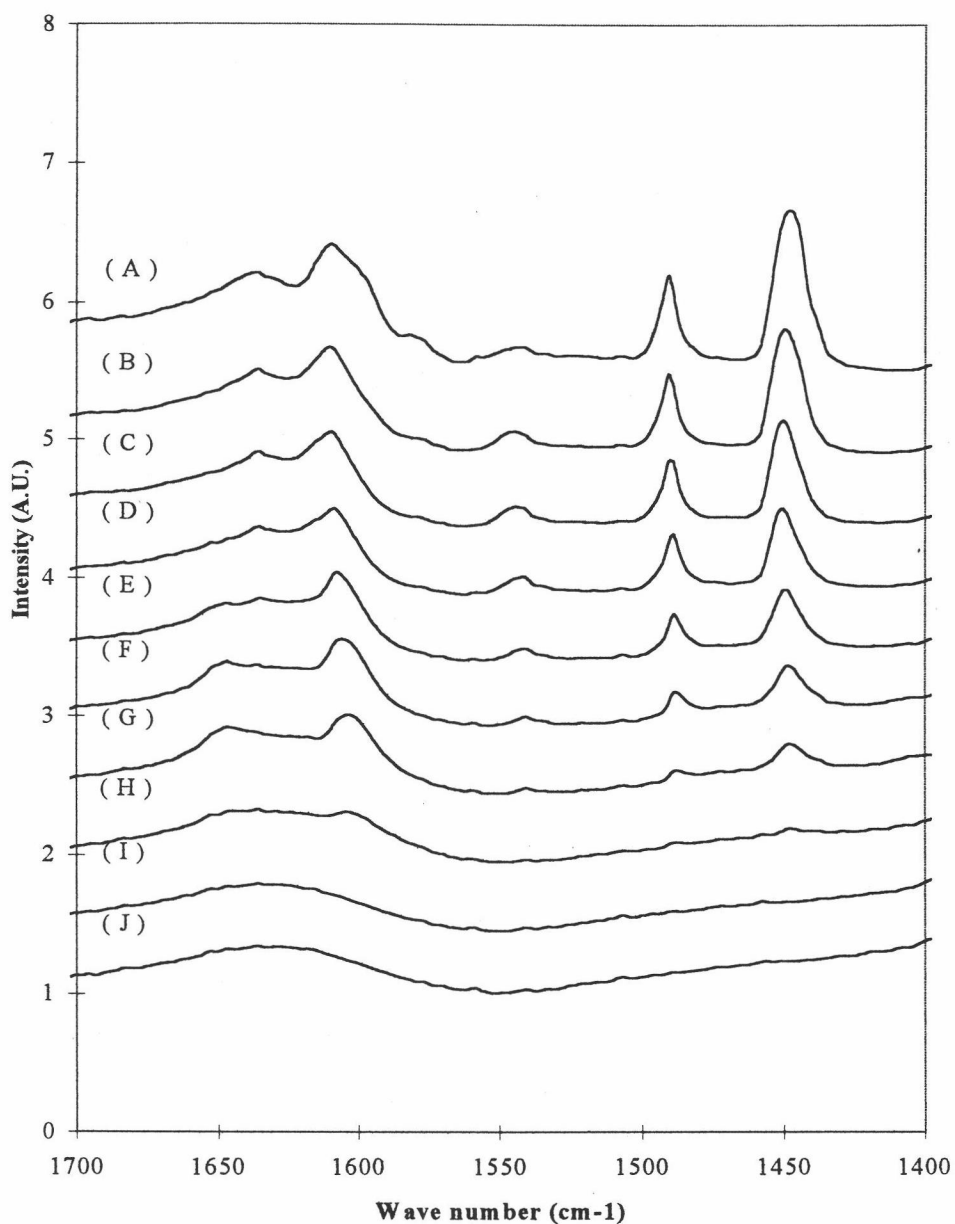
**Figure 5.16** Pyridine adsorption of fresh H-ZSM-5.

Pyridine adsorbed at room temperature and then heating the catalyst to (A) 50 °C, (B) 100 °C, (C) 150 °C, (D) 200 °C, (E) 250 °C, (F) 300 °C, (G) 350 °C, (H) 400 °C, (I) 450 °C, and (J) 500 °C, consequently.



**Figure 5.17** Pyridine adsorption of fresh Na-ZSM-5.

Pyridine adsorbed at room temperature and then heating the catalyst to (A) 50 °C, (B) 100 °C, (C) 150 °C, (D) 200 °C, (E) 250 °C, (F) 300 °C, (G) 350 °C, (H) 400 °C, (I) 450 °C, and (J) 500 °C, consequently.

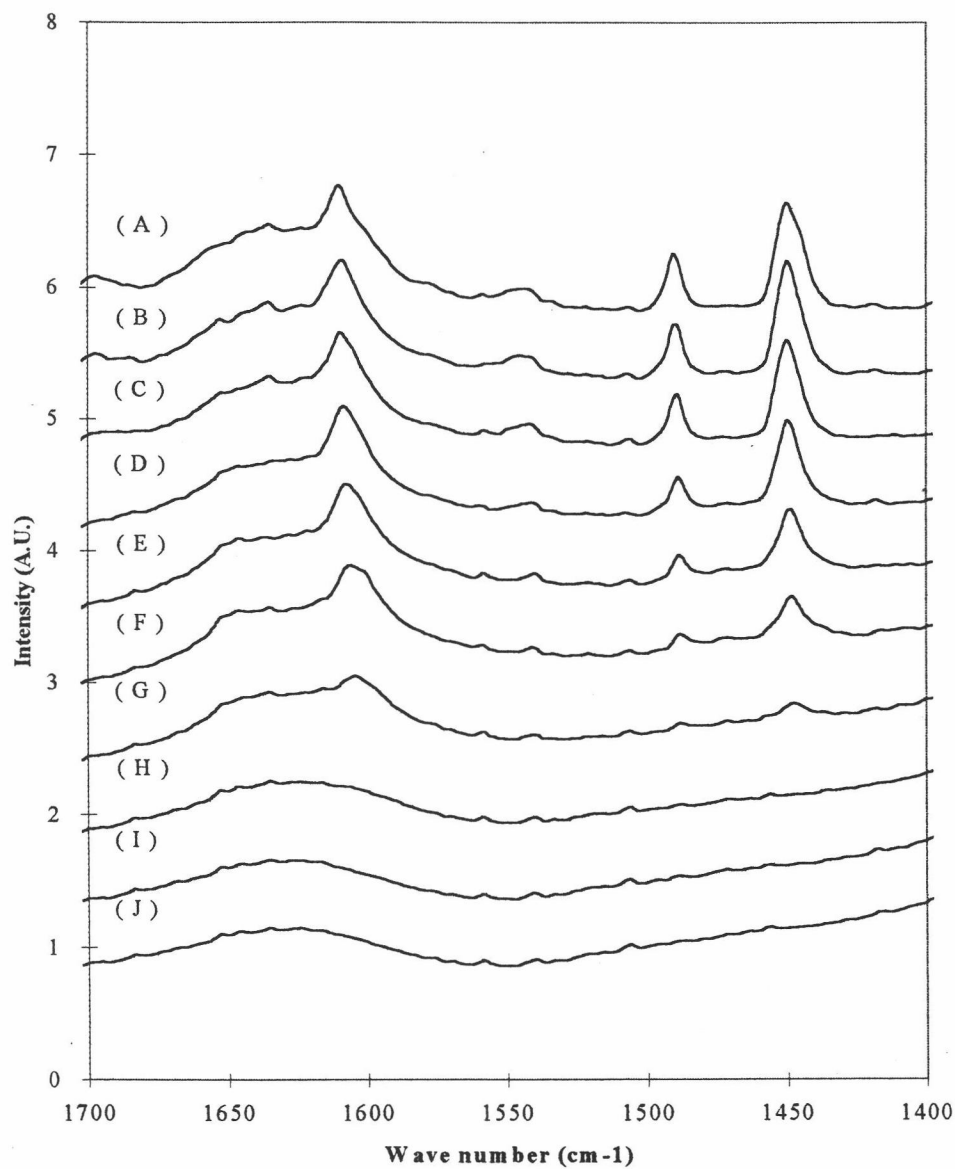


**Figure 5.18** Pyridine adsorption of spent 2 hr Cu/Na-ZSM-5.

(Reaction condition are 1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5 % O<sub>2</sub>, and balanced He, GHSV 4000 h<sup>-1</sup>, reaction temperature 207 °C)

Pyridine adsorbed at room temperature and then heating the catalyst to

(A) 50 °C, (B) 100 °C, (C) 150 °C, (D) 200 °C, (E) 250 °C, (F) 300 °C, (G) 350 °C, (H) 400 °C, (I) 450 °C, and (J) 500 °C, consequently.

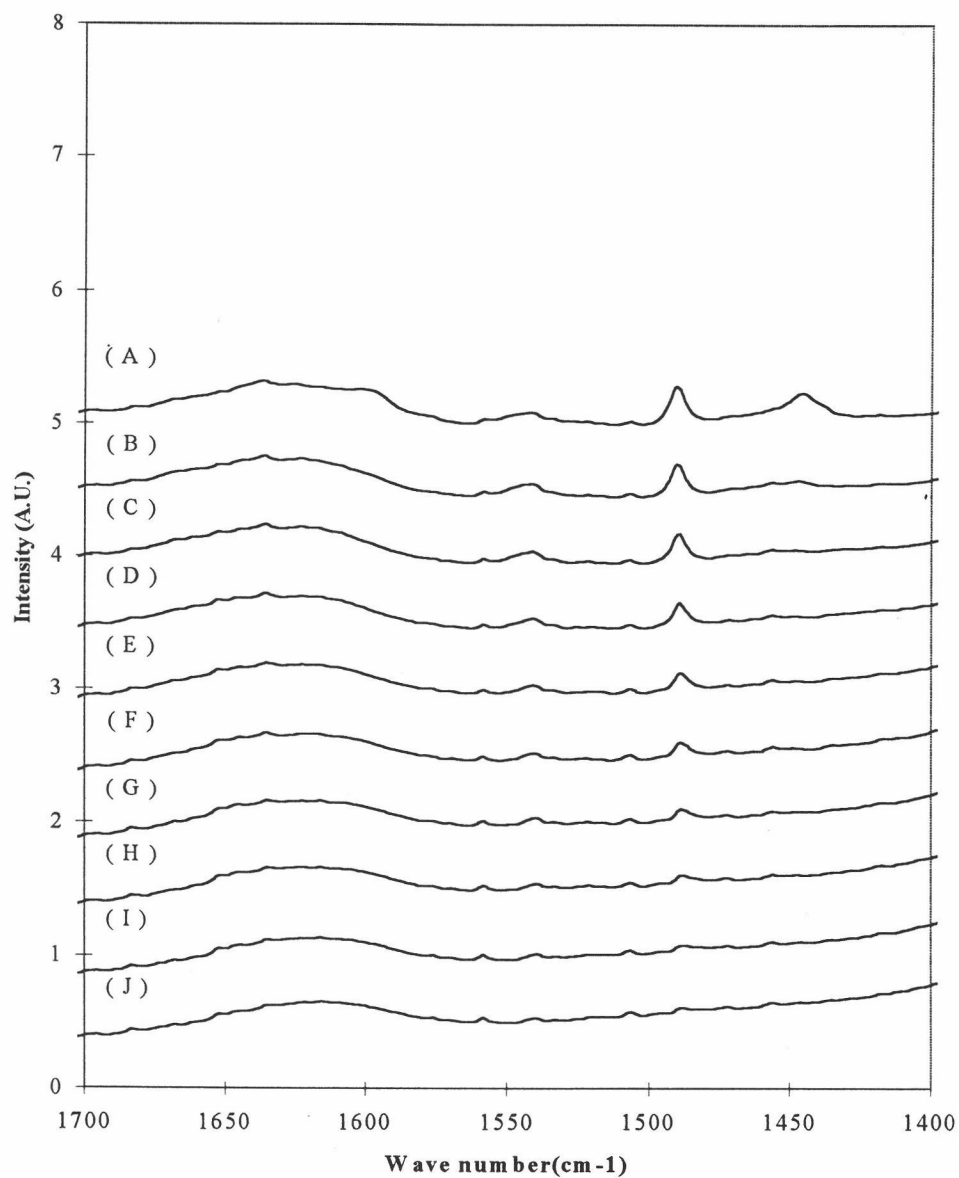


**Figure 5.19** Pyridine adsorption of spent 6 hr Cu/Na-ZSM-5.

(Reaction condition are 1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5 % O<sub>2</sub>, and balanced He, GHSV 4000 h<sup>-1</sup>, reaction temperature 207 °C)

Pyridine adsorbed at room temperature and then heating the catalyst to

(A) 50 °C, (B) 100 °C, (C) 150 °C, (D) 200 °C, (E) 250 °C, (F) 300 °C, (G) 350 °C, (H) 400 °C, (I) 450 °C, and (J) 500 °C, consequently.



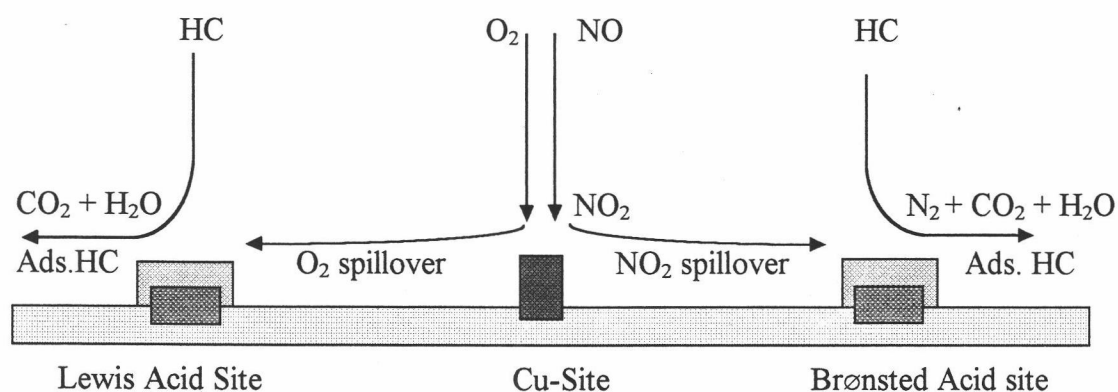
**Figure 5.20** Pyridine adsorption of spent 6 hr H-ZSM-5.

(Reaction condition are 1000 ppm NO, 3000 ppm C<sub>3</sub>H<sub>6</sub>, 2.5 % O<sub>2</sub>, and balanced He, GHSV 4000 h<sup>-1</sup>, reaction temperature 207 °C)

Pyridine adsorbed at room temperature and then heating the catalyst to (A) 50 °C, (B) 100 °C, (C) 150 °C, (D) 200 °C, (E) 250 °C, (F) 300 °C, (G) 350 °C, (H) 400 °C, (I) 450 °C, and (J) 500 °C, consequently.

### 5.10 Mechanism of Selective Catalytic Reduction of NO by Hydrocarbon

Our result indicates that most of the coke formed on the acid site of the catalyst, but preferably on Lewis acid site. From TPO patterns of Cu/Na-ZSM-5 and H-ZSM-5, in sections 5.3 and 5.4, they showed that the coke on H-ZSM-5 is hard coke whereas the coke on Cu/Na-ZSM-5 is soft coke. It was suggested that the  $O_2$  spillover from the Cu sites of Cu/Na-ZSM-5 hindered the formation of hard coke. Thus, the following mechanism model has been proposed as shown in Fig. 5.21.



**Figure 5.21** The mechanism model of SCR of NO by Hydrocarbon on Cu/ZSM-5

This model relates to the well known formation of  $NO_2$  on Cu/ZSM-5 [19,27,32,34,35,39,68-74].  $NO_2$  is likely produced at Cu sites and spillover to acid site that is not covered by coke and then interact with adsorbed hydrocarbon on that sites. Both hydrocarbon species and soft carbonaceous deposited may be able to react with  $NO_2$  to form  $N_2$  and  $O_2$ . From our experiment, the Lewis acid site of the zeolite catalyst is proper for coke formation, as section 5.8.2, and this coke formation lead to the decreasing of hydrocarbon conversion. It is suggested that the Lewis acid site was proper for hydrocarbon combustion. Furthermore, it may be that  $NO_2$  reacts with adsorbed hydrocarbon on the Brønsted acid site easier than on the Lewis acid site.