

## CHAPTER V

### RESULTS AND DISCUSSION

The characteristics and activities of various types of ZSM-5 zeolite catalysts were investigated. The results and discussion in this chapter were separated into four main parts, catalyst characterization, steady state tests, effect of feed concentration on activities and transient reaction tests, respectively.

#### 5.1 Catalyst Characterization

All catalysts used in this study were first characterized to overview the difference of their characteristics and properties. The specific surface area and amount of Si, Al, Na and Cu in catalysts were measured to considered their physical differences.  $\text{Cu}^{1+} / \text{Cu}^{2+}$  was also evaluated CO adsorption. The oxygen adsorption capacity of catalysts was also determined. XRD and ex-situ FT-IR were used to investigate the structure of catalysts. Finally, Acid properties as well as Brønsted and Lewis acidic sites on catalysts was additional observed by pyridine adsorption method.

##### 5.1.1 Physical Properties

The specific surface area estimated by BET, and composition of catalysts used in this study were determined and are shown in table 5.1 and 5.2, respectively. Surface area of all catalysts is around  $370 \text{ m}^2/\text{g cat}$ . There are no significant difference of surface area among all catalysts used. This implies that the exchanged Cu ions as well as residual cations do not affect the surface area of zeolite support. The copper ion-exchange procedure does not reduce the surface area of catalysts as well.

Although it was not impossible to directly measure the amount of protons in the catalysts used by an appropriate methods, the Na content will be reversely relate to the proton content among zeolites used in this study. Since the amount of the Al in zeolite is proportional to the content of ion which balance the negative charge of alumina tetrahydra, at a constant Si/Al ratio of various zeolites catalysts used(table

5.2), the total of cations on the surface of zeolites should be constant as well. In table 5.2, Na was measured in Na-ZSM-5 and Cu/Na-ZSM-5, but was negligible in H-ZSM-5 and Cu/H-ZSM. This could be expected that the Cu/H-ZSM-5 still contain significant residual protons.

**Table 5.1** Specific surface area of catalysts

Catalyst	BET surface area (m <sup>2</sup> /g.catalyst)
Na-ZSM-5	374.6
H-ZSM-5	386.8
Cu/Na-ZSM-5	353.6
Cu/H-ZSM-5	370.6

**Table 5.2** Quantities of substances in catalysts

Catalyst	Observed Si/Al	Cu content (wt %)	Na content (wt %)
Na-ZSM-5	40.4	-	1.84
H-ZSM-5	40.0	-	-
Cu/Na-ZSM-5	37.2	1.06	0.38
Cu/H-ZSM-5	39.0	1.09	< 0.09

### 5.1.2 CO Adsorption

Although the total copper content on both Cu/ZSM-5 zeolites was carefully controlled to be about the same, differences in the copper state may have occur. It is generally accepted that several oxidation states of Cu can exist on Cu/ZSM-5 surface

[37, 75]. The residual cations could affect the distribution of states in each of the zeolite. Thus, copper in each oxidation state was examined. CO adsorption is a simple method to determine the amount of  $\text{Cu}^{1+}$  [131]. The amount of CO adsorbed on the catalyst surface represents the amount of  $\text{Cu}^{1+}$ . The results are shown in table 5.3. The amount of  $\text{Cu}^{1+}$  in Cu/H-ZSM-5 appears to be about double in Cu/Na-ZSM-5. Since the total copper content of the two catalysts was equal, Cu/H-ZSM-5 had a higher  $\text{Cu}^{1+}/\text{Cu}^{2+}$  ratio. The difference in  $\text{Cu}^{1+}/\text{Cu}^{2+}$  could have an affect on the activity in the copper exchanged zeolites. One possibility for the different ratio is that the reducibility of Cu in the zeolites is affected by the residual cations.

**Table 5.3** Amount of  $\text{Cu}^{1+}$  in catalysts estimated by CO adsorption

Catalyst	Amount of CO adsorbed ( $\mu\text{mol/g.cat}$ )	Number of $\text{Cu}^{1+}$ ( $\times 10^{19}$ site/g.cat.)
Cu/Na-ZSM-5	1.121	1.35
Cu/H-ZSM-5	2.247	2.71

### 5.1.3 Oxygen Adsorption

Oxygen adsorbed on acid site might play the essential role for the reactions in the absence of oxygen. Performance of oxygen adsorption over catalysts, therefore, are examined. Amount of oxygen desorbed on various catalysts at room temperature are summarized in table 5.4. The result in table 5.4 indicates that oxygen does not adsorb on Na-ZSM-5 but can adsorb on acid site in H-ZSM-5 and Cu site in Cu/ZSM-5 zeolites. However, capacity of oxygen adsorbed on acid site is much less than Cu site. This illustrates the oxygen adsorption capacity of acid site is not as much as Cu site. However, oxygen adsorption capacity of Cu/Na-ZSM-5 and Cu/H-ZSM-5 are the same. This adsorption property might be mostly result from Cu ion site which mostly exist on the catalyst surface. They dominate the different characteristic between proton and  $\text{Na}^+$  ion. Thus, their difference between Cu/Na-ZSM-5 and Cu/H-ZSM-5 was not observed.

**Table 5.4** Amount of oxygen adsorbed on catalysts at room temperature

Catalyst	O <sub>2</sub> adsorption at rt. ( $\mu\text{mol/g}$ . catalyst)
Na-ZSM-5	0
H-ZSM-5	4.13
Cu/Na-ZSM-5	8.00
Cu/H-ZSM-5	8.04

#### 5.1.4 X- Ray Diffraction pattern

The structure of various types of ZSM-5 were analyzed by X-ray diffraction (XRD) as shown in figure 5.1. The XRD patterns of all Na-ZSM-5, H-ZSM-5, Cu/Na-ZSM-5 and Cu/H-ZSM-5 are the same as expected because all of catalyst used in this study were prepared from the same parent Na-ZSM-5 zeolite. Hence, crystal structure should not be affected by cations exchanged. Ciambelli et al.[74] noticed that CuO formed after passing a feed stream over an over-exchanged Cu/ZSM-5 could be observed by XRD. However, expectantly, CuO was not detected in the catalysts in this study.

#### 5.1.5 FT-IR pattern

FT-IR was also used in this study to characterize the catalysts. There is no difference in IR spectra of all four catalysts as shown in figure 5.2. Although Spoto et al.[81] claimed they could measure the hydroxyl group( -OH ) on H-ZSM-5 by IR at around  $3600\text{ cm}^{-1}$ , they were not detected in this experiment. This may due to limitation of our instrument or to sample preparation or to interference by the other peak of ZSM-5 spectra.

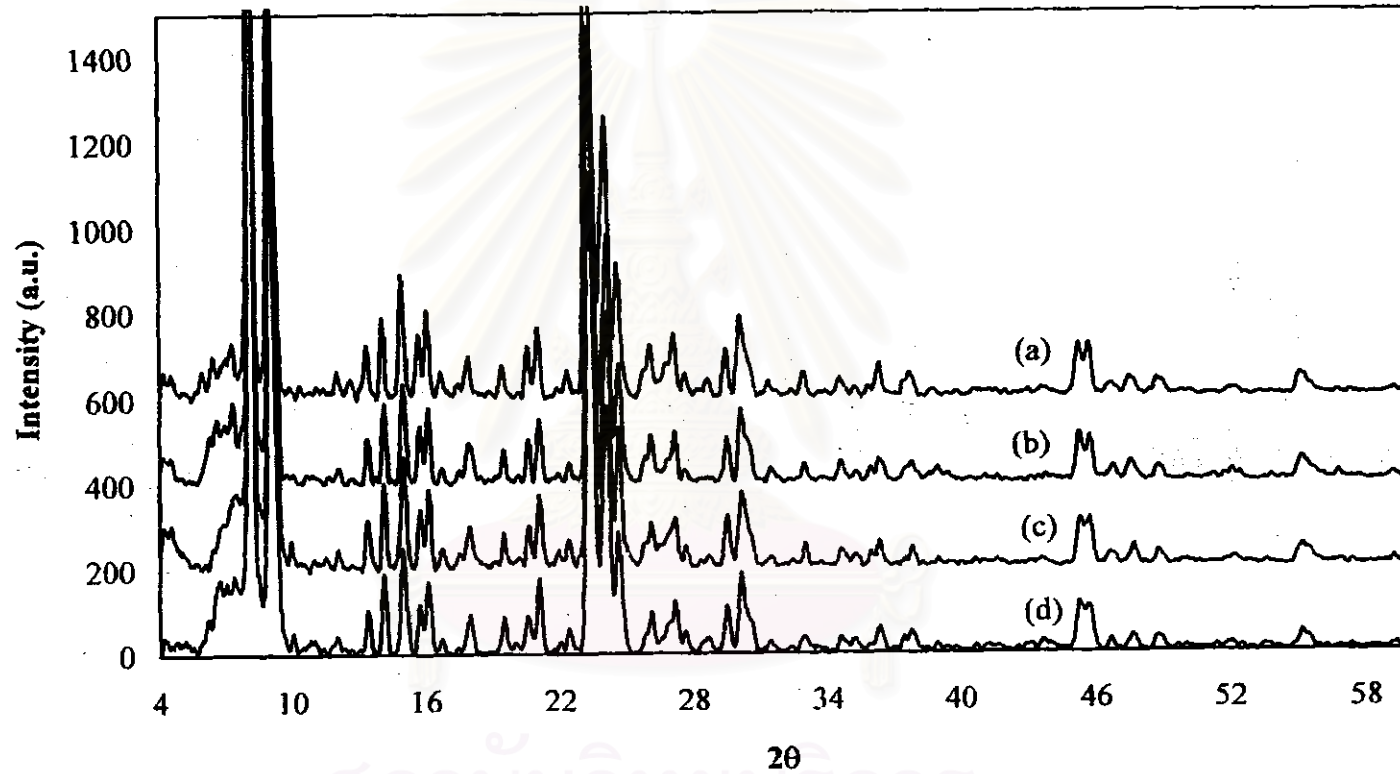


Figure 5.1 X-ray diffraction pattern of (a) Na-ZSM-5 (b) H-ZSM-5 (c) Cu/Na-ZSM-5 (d) Cu/H-ZSM-5

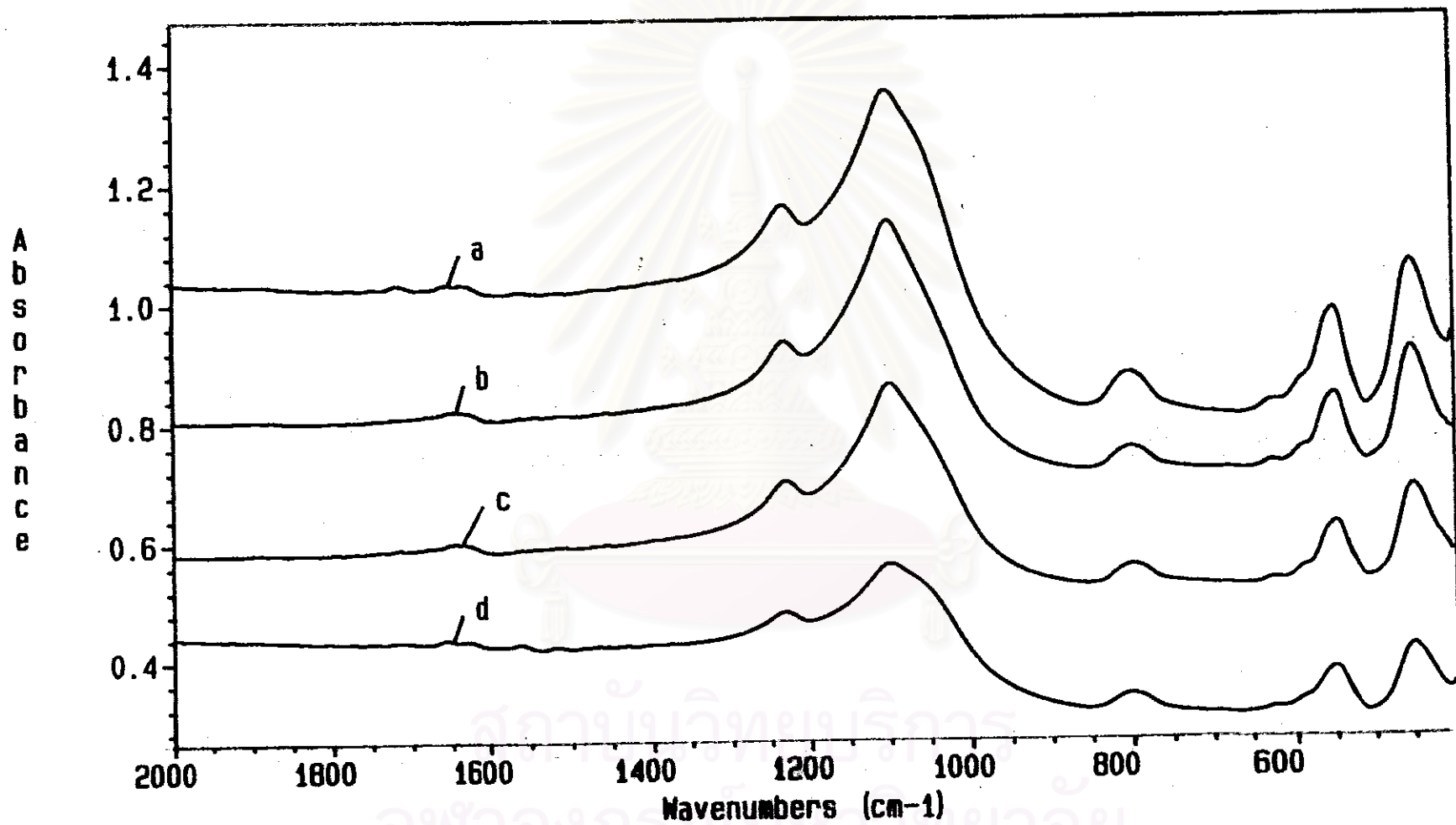


Figure 5.2 IR spectra of (a) H-ZSM-5, (b) Cu/ZSM-5, (c) Cu/Na-ZSM-5 and (d) Na-ZSM-5



### 5.1.6 Pyridine Adsorption

Pyridine adsorption studies of the catalyst surface was additionally made by IR. The peaks of pyridinium ion at Brønsted acid site can be typically observed at 1540 and 1640  $\text{cm}^{-1}$ . Pyridine coordinately bonded to surface Lewis acid site shows peaks at 1450 and 1600  $\text{cm}^{-1}$  [100, 109, 132]. The band at 1490  $\text{cm}^{-1}$  represents all adsorbed pyridine species [132]. The IR spectra of adsorbed pyridine on Na-ZSM-5, H-ZSM-5, Cu/Na-ZSM-5 and Cu/H-ZSM-5 are shown in figures 5.3, 5.4, 5.5 and 5.6, respectively. Both Brønsted and Lewis acid sites were found on all catalysts. Pyridine gradually desorbed at higher temperature. These peaks are associated with the disappearance of a protonated pyridine peak (1540  $\text{cm}^{-1}$ ) and a nonprotonated pyridine peak (1450  $\text{cm}^{-1}$ ). Pyridine adsorbed on both Brønsted and Lewis sites are found in Na-ZSM-5 (figure 5.3). Nevertheless, they are weak since all pyridine disappeared after heating in vacuum to 200 °C.

In comparison, H-ZSM-5 (figure 5.4) has more Brønsted and Lewis acid sites than Na-ZSM-5 in terms of both quantity and strength. Peaks of pyridinium ion at Brønsted acid sites are still observed at 500 °C whereas pyridine on Lewis disappeared above 400 °C. Copper ions exchanged into ZSM-5 change the acidic properties of these catalysts as shown in figures 5.5 and 5.6. Copper ions minimize the acid strength of Brønsted acid sites of H-ZSM-5 and these now disappear at 400 °C. All pyridine species were removed by 450 °C on both Cu/Na-ZSM-5 and Cu/H-ZSM-5 catalysts. The amount and strength of pyridine adsorbed on both catalysts were almost the same. The study of Connerton et al. [109] also reported this result.

Copper sites are supposed to exhibit as Lewis acid rather than Brønsted acid properties [131], hence, pyridine may also adsorb on copper sites. Characteristics of Brønsted acid sites of both catalysts are similar. This suggests that there may be some residual protons on Cu/Na-ZSM-5 as well. These protons may have come from water used for washing the catalyst [3, 100]. However, perhaps there is interference among Cu, protons and Na ion remaining in Cu/ZSM-5 because the difference between IR spectra of both catalysts was not clearly observed.

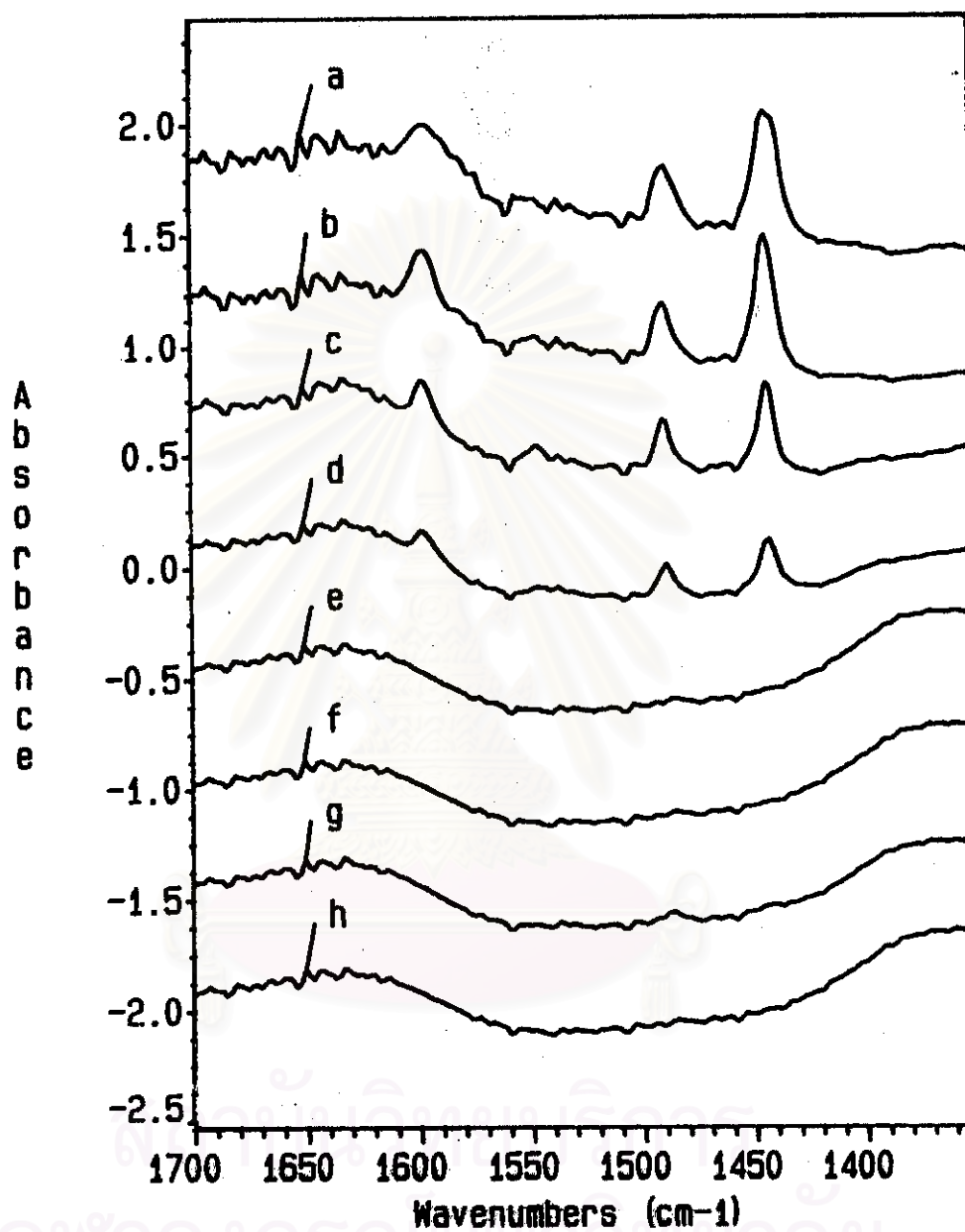


Figure 5.3 IR spectra of Na-ZSM-5 after saturated adsorption with pyridine (a) followed by evacuating and measured at room temperature (b), 100 °C (c), 200 °C (d), 300 °C (e), 400 °C (f), 450 °C (g), and 500 °C (h)



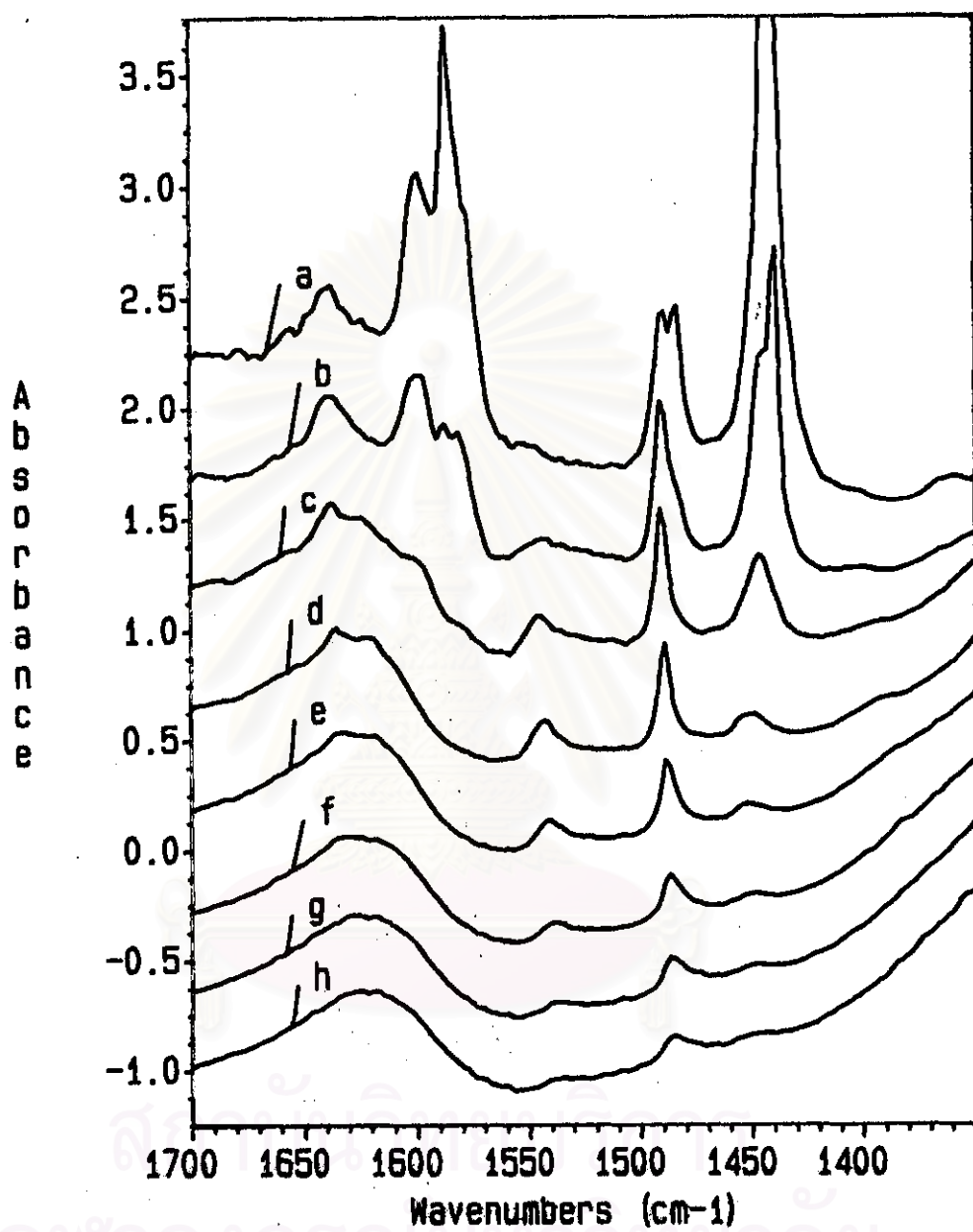


Figure 5.4 IR spectra of H-ZSM-5 after saturated adsorption with pyridine (a) followed by evacuating and measured at room temperature (b), 100 °C (c), 200 °C (d), 300 °C (e), 400 °C (f), 450 °C (g), and 500 °C (h)

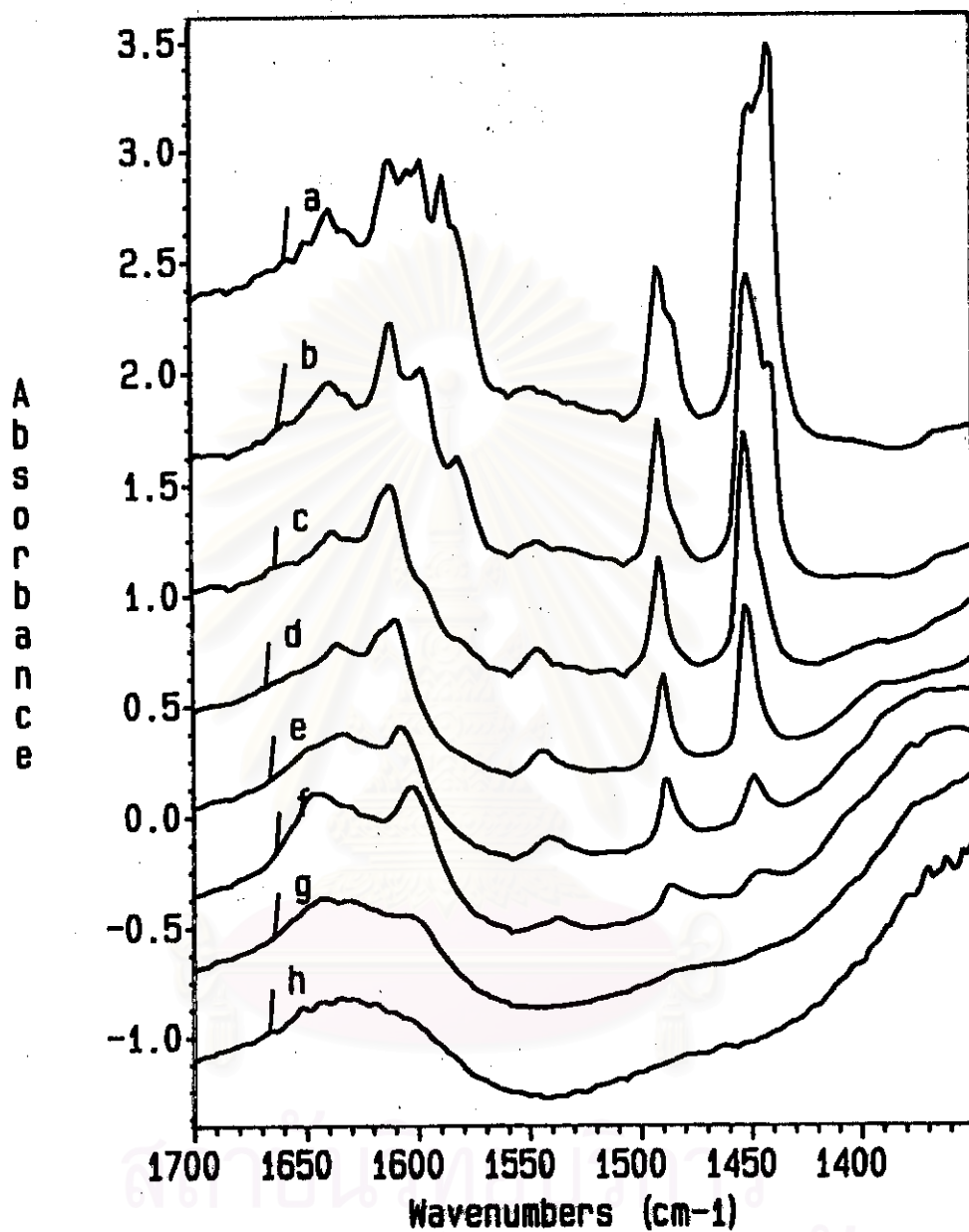


Figure 5.5 IR spectra of Cu/Na-ZSM-5 after saturated adsorption with pyridine (a) followed by evacuating and measured at room temperature (b), 100 °C (c), 200 °C (d), 300 °C (e), 400 °C (f), 450 °C (g), and 500 °C (h)

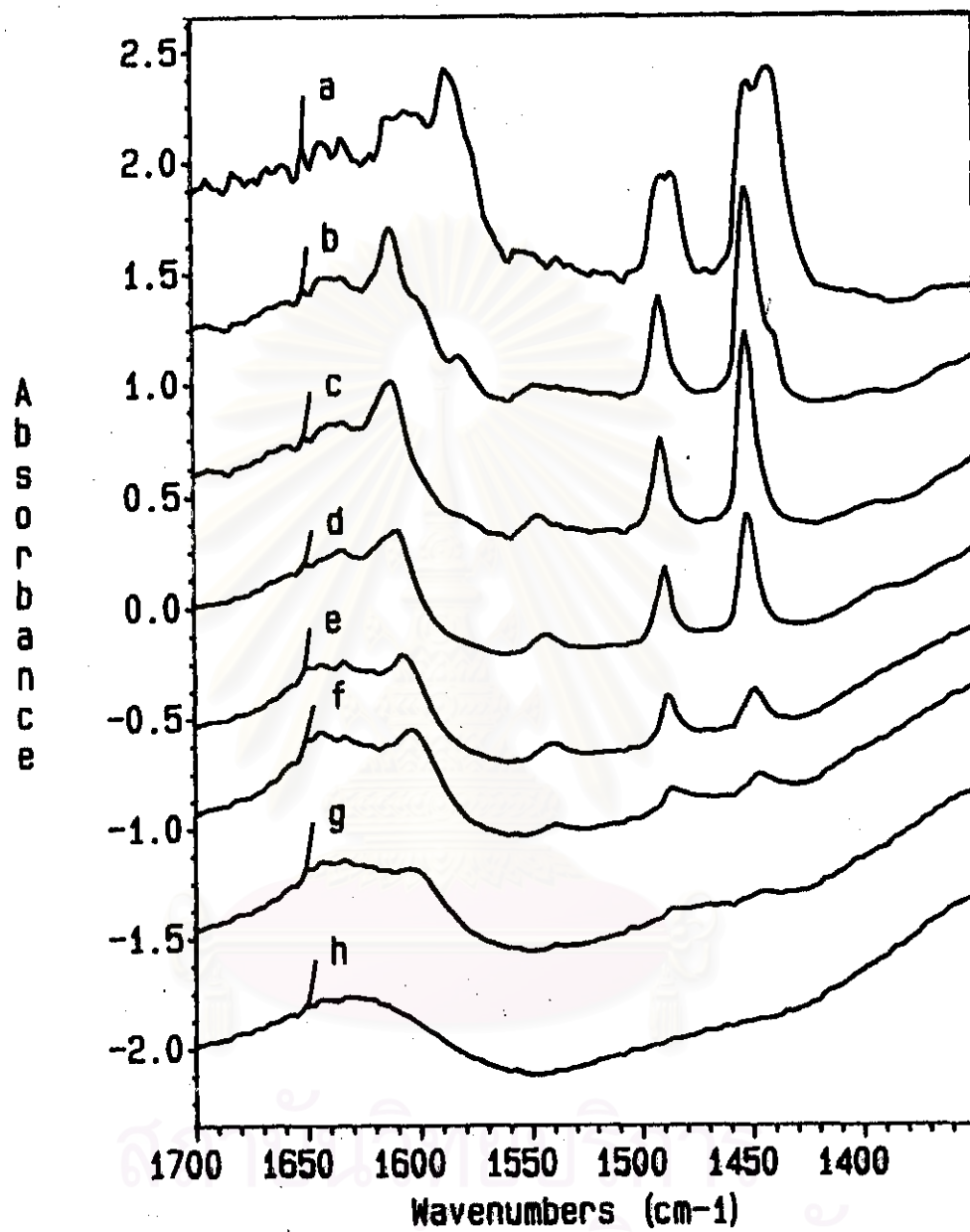


Figure 5.6 IR spectra of Cu/H-ZSM-5 after saturated adsorption with pyridine (a) followed by evacuating and measured at room temperature (b), 100 °C (c), 200 °C (d), 300 °C (e), 400 °C (f), 450 °C (g), and 500 °C (h)

Quantitative analysis confirm the different residual cations between Cu/Na-ZSM-5 and Cu/H-ZSM-5 (table 5.2). Because significant amount of Na was detected in Cu/Na-ZSM-5, it would be expected that the Cu/H-ZSM-5 will contain significant residual protons as well. However, structure from XRD pattern and FT-IR spectra and also acidic property from pyridine adsorption of both catalysts are similar. Moreover, Na-ZSM-5 does not adsorb oxygen while H-ZSM-5 could slightly adsorb. Due to high oxygen adsorption capacity of copper site, oxygen adsorption between Cu/Na-ZSM-5 and Cu/H-ZSM-5 was not observed. Although total Cu content of Cu/Na-ZSM-5 and Cu/H-ZSM-5 are the same, the  $\text{Cu}^{2+}/\text{Cu}^{1+}$  estimated by CO adsorption of both catalysts are different.

Accordingly, from all above characterizations made in this study, the residual cations remained in Cu/ZSM-5 zeolites do not affect the structure and acidic properties but are likely affect oxidation state of Cu site. This difference probably affect the catalytic performance of Cu/Na-ZSM-5 and Cu/H-ZSM-5. Nevertheless, the activity test would be additional studied to observe the catalytic performance between Cu/Na-ZSM-5 and Cu/H-ZSM-5.

## **5.2 Steady State Reactions Tests.**

To study the performances between Cu/Na-ZSM-5 and Cu/H-ZSM-5, the activities of both catalysts were examined. The various reactions were studied in order to investigate the effect of types of feed on these catalysts.

### **5.2.1 NO + C<sub>3</sub>H<sub>8</sub> + O<sub>2</sub> system**

The typical reactions of the selective catalytic reduction (SCR) of nitrogen monoxide by hydrocarbon was first studied. The activity of Cu/Na-ZSM-5 and Cu/H-ZSM-5 was also compared. NO conversion to N<sub>2</sub> and propane conversion at temperatures from 150 °C to 600 °C in the presence of excess oxygen over Cu/Na-ZSM-5 and Cu/H-ZSM-5 are shown in figures 5.7 and 5.8, respectively. Both zeolite catalysts illustrated typical features of NO reduction by hydrocarbon in excess of oxygen. These have been identical by studies carried out so far [11-15]. Dinitrogen gas

begins to appear at 200 °C and then the NO conversion rapidly increases until a maximum conversion is reached at around 300 to 400 °C (figure 5.7). The active region of reduction is 300 - 500 °C. Cu/H-ZSM-5 reached the maximum conversion (about 60 %) at 500 °C. Above 500 °C, the NO conversion dropped because hydrocarbon combustion becomes dominant [3]. The propane conversion shown in the figure 5.8 appears at 200 °C and rises to 100 % conversion at about 350 °C. It did not fall at higher temperature.

In comparison, the activity of Cu/Na-ZSM-5 is about the same as that of Cu/H-ZSM-5 as measured by both NO conversion to N<sub>2</sub> and propane conversion. However, the system over Cu/Na-ZSM-5 had light off temperature --the temperature that give 50 % conversion that is slightly lower than that over Cu/H-ZSM-5. In addition, at 350 - 450 °C, conversion to N<sub>2</sub> of Cu/H-ZSM-5 system is more than that for Cu/Na-ZSM-5 whereas above 450 °C, the system on Cu/Na-ZSM-5 has more NO conversion.

Since both types of catalysts gave high activity in the SCR of NO in the excess of oxygen which made the conversion of NO in both systems are almost 100 % at low gas space velocity (GHSV), the difference activities was not observed at such condition. Therefore, another set of experiments would be tested at a high GHSV. Figure 5.9 illustrates the NO conversion to N<sub>2</sub> of the NO reduction with propane in the excess of oxygen at 12000 h<sup>-1</sup> over Cu/Na-ZSM-5 and Cu/H-ZSM-5. It is noticed that Cu/Na-ZSM-5 is a little more active than Cu/H-ZSM-5. This difference was not found in the previous tests(figure 5.7). This may be because of the difference of feed concentrations and gas space velocity of the reaction. However, it can be roughly concluded that, Cu/Na-ZSM-5 is more active than Cu/H-ZSM-5 in the reduction of NO by propane with excess oxygen condition. These results are in the line with studies of Engopasanan[108] and Torr-Abrev[92]. Engopasanan[108] found that there was no different activity between Cu/Na-ZSM-5 and Cu/H-ZSM-5 which identical with our results at low GHSV. In other words, Torr-Abrev[92] found that Cu/Na-ZSM-5 was more active than Cu/H-ZSM-5 which also accord with the results at high GHSV.

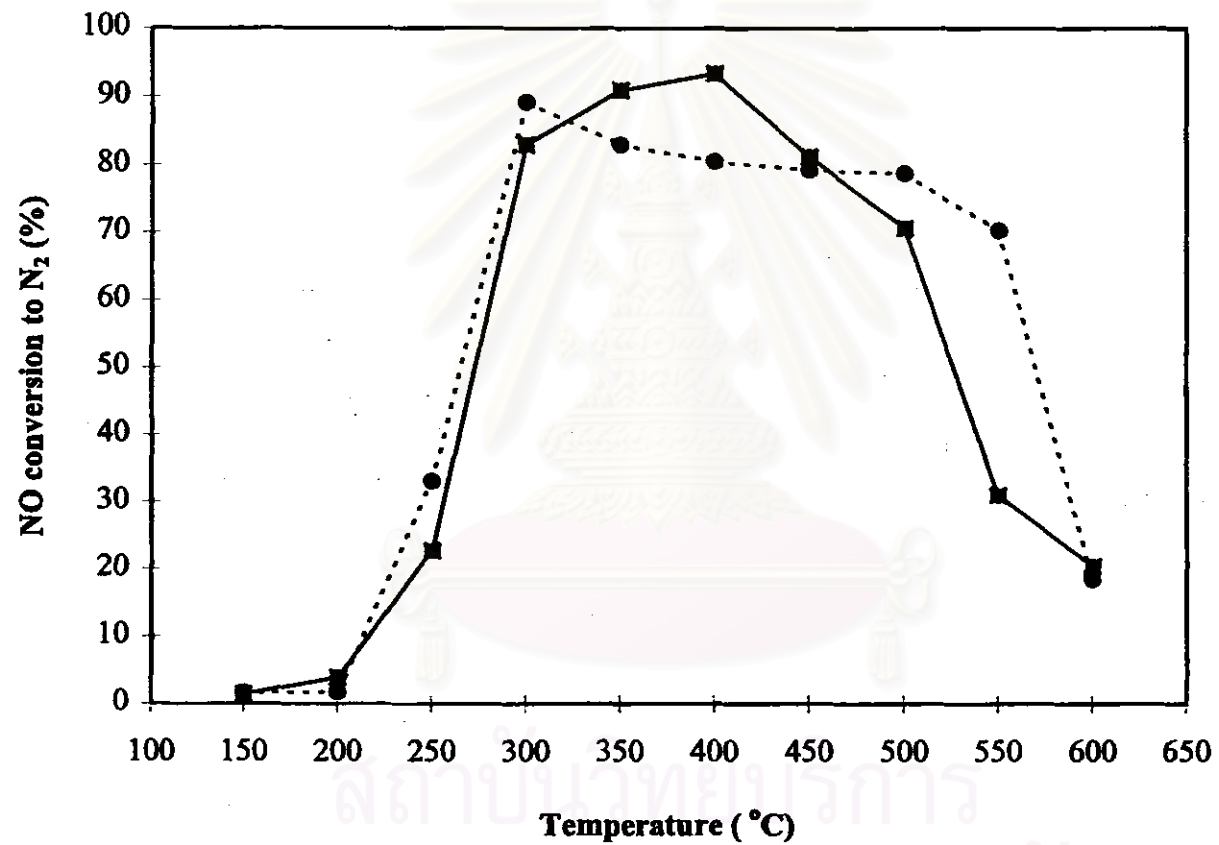


Figure 5.7 NO conversion to N<sub>2</sub> in the system of 1000 ppm NO, 3000 ppm propane, 10% O<sub>2</sub> and He Bal. at GHSV: 4000 h<sup>-1</sup> over Cu/Na-ZSM-5 (---●---), Cu/H-ZSM-5(—■—).



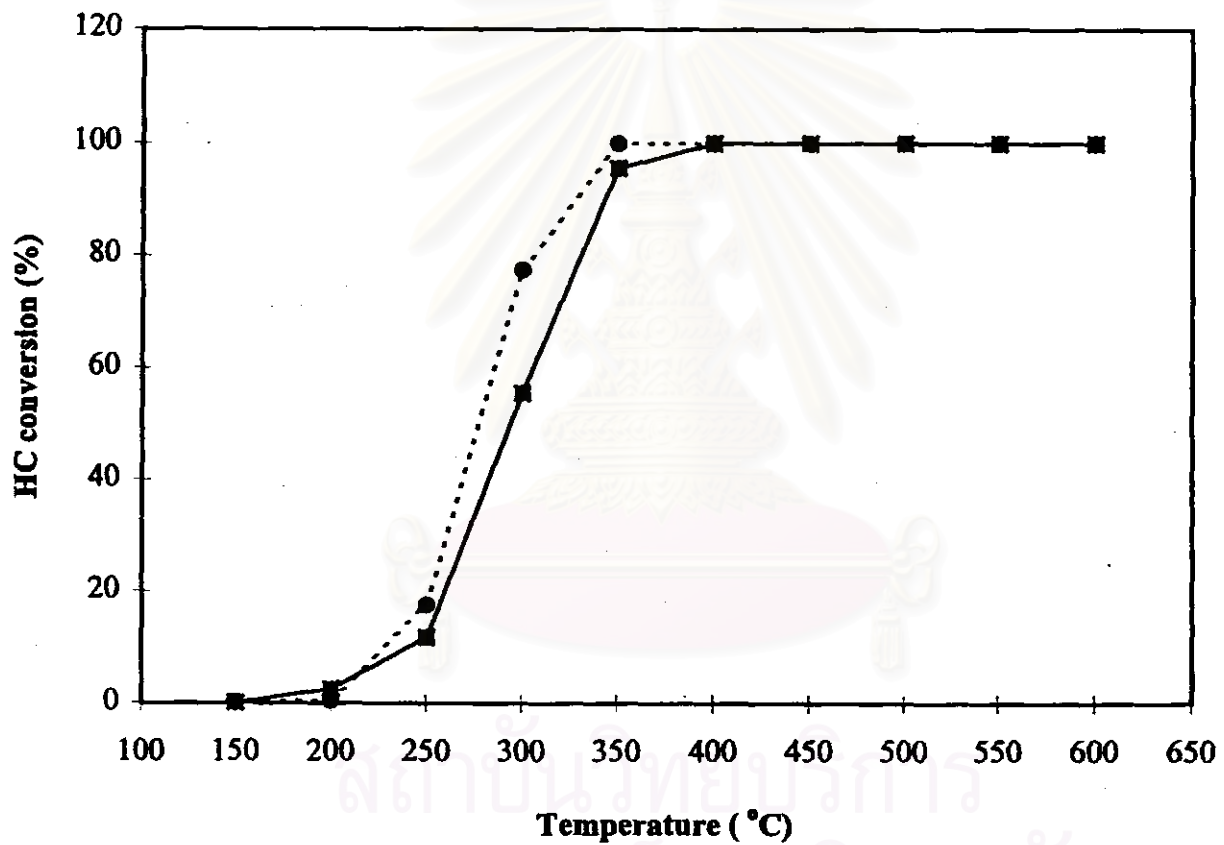


Figure 5.8 Propane conversion in the system of 1000 ppm NO, 3000 ppm propane, 10% O<sub>2</sub> and He Bal. at GHSV: 4000 h<sup>-1</sup> over Cu/Na-ZSM-5 (---●---), Cu/H-ZSM-5(—■—).

There have been many reports propose the  $\text{Cu}^{2+}$  as active site for NO reduction by hydrocarbon [3, 37, 57, 63, 85, 133]. From the CO adsorption results in table 5.3, Cu/H-ZSM-5 has more  $\text{Cu}^{1+}$  amount than Cu/Na-ZSM-5. Since the total copper content of both catalysts are identical, Cu/Na-ZSM-5 possibly have more  $\text{Cu}^{2+}$  than Cu/H-ZSM-5. This might be a reason why Cu/Na-ZSM-5 is more active than Cu/Na-ZSM-5 for the SCR of NO by  $\text{C}_3\text{H}_8$  in the oxidizing atmosphere.

### 5.2.2 NO + $\text{C}_3\text{H}_8$ system

When the oxygen is absent in the selective reduction of NO by propane, the activity of both Cu/Na-ZSM-5 and Cu/H-ZSM-5 drop drastically (figure 5.10 and 5.11) although the conversions were more than those in homogeneous reactions. This substantiates the important role of oxygen in the SCR of NO by hydrocarbon as discussed by Iwamoto et al. [14].

In the experiments with oxygen absent, Cu/H-ZSM-5 was obviously more active than Cu/Na-ZSM-5 except above 600 °C. NO conversion to  $\text{N}_2$  over both catalytic system gradually increase beginning at 150 °C. Above 400 °C, the conversion to  $\text{N}_2$  of Cu/H-ZSM-5 system was higher than that of Cu/Na-ZSM-5, particularly at 500 °C where Cu/H-ZSM-5 gave 90 % conversion whereas Cu/Na-ZSM-5 gave 40 % conversion. The non catalytic reduction at 500 C contributed less than 10% conversion. In contrast, propane conversion in the experiments over both catalysts were very similar (figure 5.11). Propane conversion is negligible below 400 °C and gradually increases at higher temperature. However, carbon dioxide production in these experiments, as shown in table 5.5, was different over both Cu/ZSM-5. Table 5.5 shows quite large differences cracking more extensive on Cu/H-ZSM-5 also more  $\text{N}_2\text{O}$  and  $\text{CO}_2$ . In this study, the propane conversion is calculated from the consumption of propane or the disappearance of propane in gas stream. Hence, these results illustrate that the propane consumption does not relate totally with the production of  $\text{CO}_2$ . Some propane must be converted to gas species other than  $\text{CO}_2$  particularly in the Cu/Na-ZSM-5 system. These are perhaps CO or carbonaceous deposits.

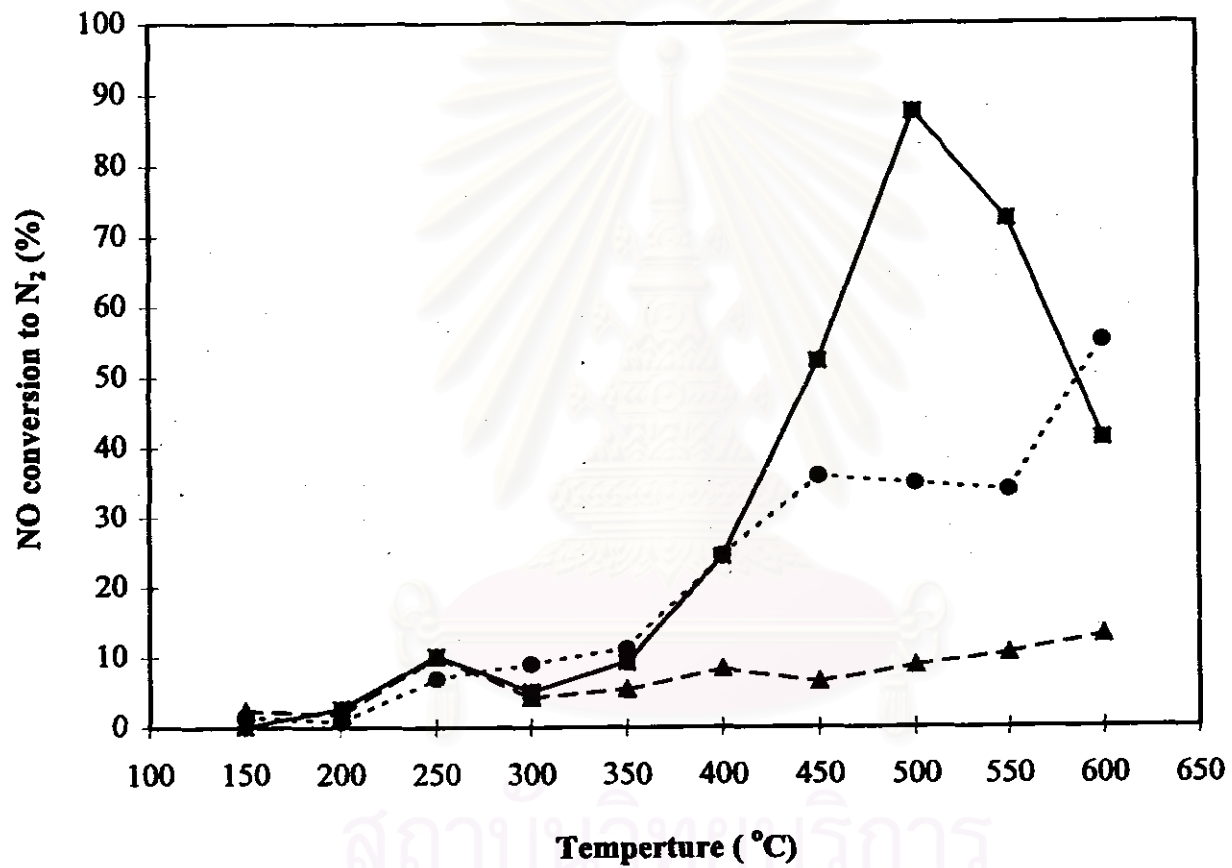


Figure 5.10 NO conversion to N<sub>2</sub> in the system of 1000 ppm NO, 3000 ppm propane and He Bal. at GHSV: 4000 h<sup>-1</sup> over Cu/Na-ZSM-5 (---●---), Cu/H-ZSM-5 (—■—) and without catalyst (—▲—).

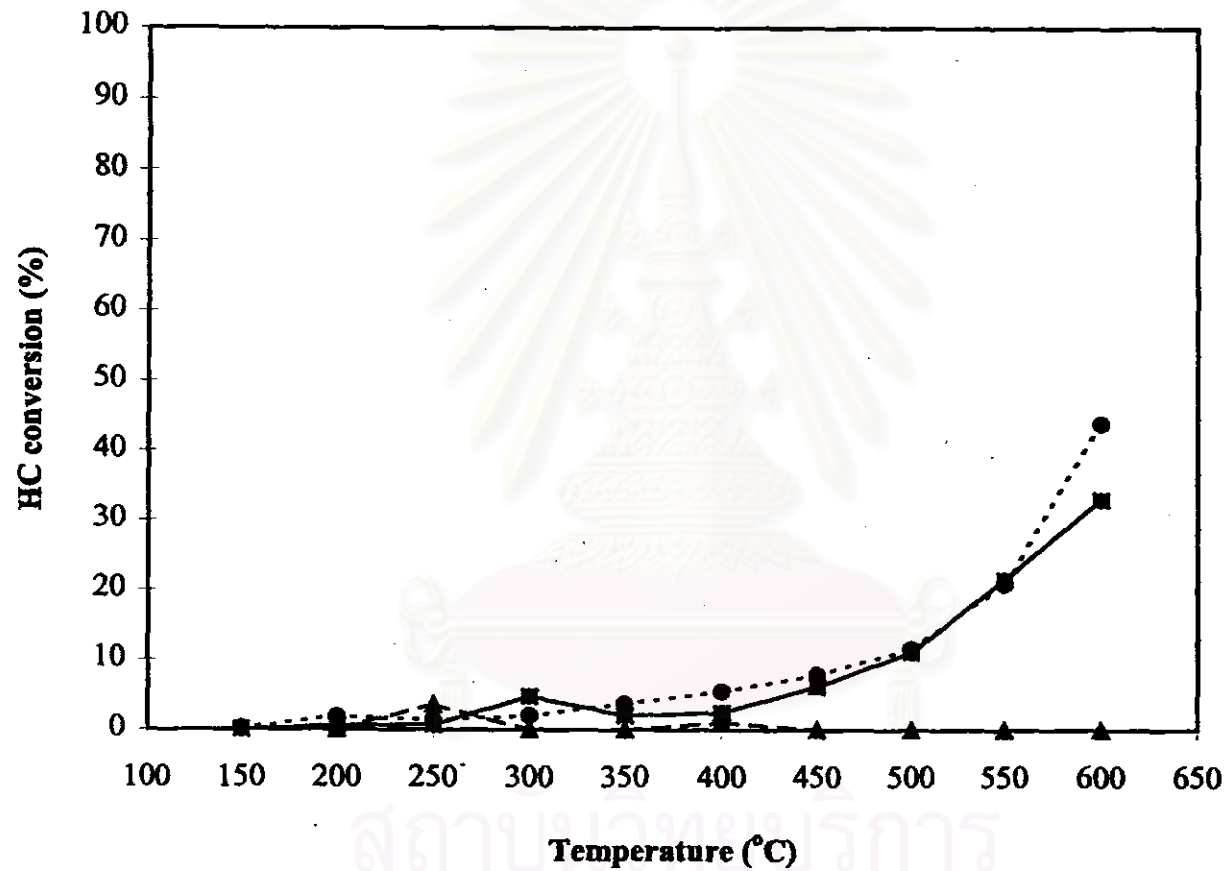


Figure 5.11 Propane conversion in the system of 1000 ppm NO, 3000 ppm propane and He Bal. at GHSV:  $4000 \text{ h}^{-1}$  over Cu/Na-ZSM-5 (---●---), Cu/H-ZSM-5(—■—) and without catalyst(---▲---).

**Table 5.5** Formation of gas species in the reaction of 1000 ppm NO ,  
1000 ppm C<sub>3</sub>H<sub>8</sub> and He Bal. at GHSV = 4000 h<sup>-1</sup>

**(a) over Cu/Na-ZSM-5**

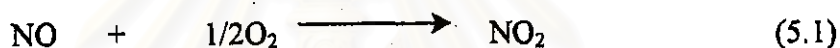
Temp.(°C)	formation of gas (a. u.)					
	methane	CO <sub>2</sub>	N <sub>2</sub> O	ethylene	ethane	propylene
150			52			
200		37	22			
250		33	18			
300		32				
350		31				
400		64				
450	-	-	-	-	-	-
500		71				
550	122	191		41		135
600	182	338		146		250

**(b) over Cu/H-ZSM-5**

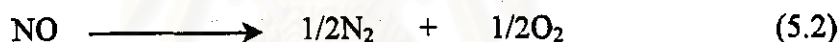
Temp.(°C)	formation of gas (a. u.)					
	methane	CO <sub>2</sub>	N <sub>2</sub> O	ethylene	ethane	propylene
150		10	99			
200		25	53			
250		35	72			
300		30	23			
350		40				
400		125		21		
450		316				
500	67	292		36		68
550	202	394		134		164
600	500	340		332	22	124

Due to the oxygen deficiency, combustion does not occur in such systems to any extent and thermal cracking and/or dehydrogenation preferably take place. As shown in table 5.5, methane, ethylene and propylene were observed at high temperature ( $> 400\text{ }^{\circ}\text{C}$ ).  $\text{N}_2\text{O}$  was also found at below  $300\text{ }^{\circ}\text{C}$ . The formation of  $\text{N}_2\text{O}$  is well known at low temperature due to the disproportionation of  $\text{NO}$  [4]. In the  $\text{NO}$  and hydrocarbon system, there are several reactions which could occur such as the reaction between hydrocarbon and nitrogen monoxide to produce dinitrogen, carbon monoxide and water, direct decomposition to nitrogen gas and oxygen, hydrocarbon combustion and hydrocarbon reforming and cracking as well as coke formation as proposed below:

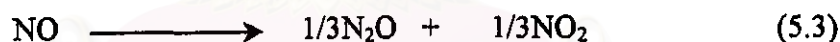
NO Oxidation



NO Decomposition



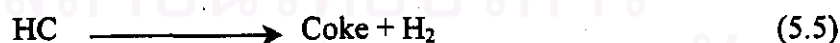
NO Disproportionation



Cracking



Coke Formation



Combustion



Reduction with propane





Which reactions play a dominant role depends on the temperature and the catalyst. However, in this study, all reactions mentioned above seem to occur in the experiments of NO reduction by propane without oxygen over Cu/ZSM-5 zeolites.

The equilibrium constant of some NO reactions were estimated and are shown in table 5.6. From the K constants, NO oxidation and NO disproportionation prefer occur in low temperature. For the NO decomposition, although it have high K constant value, it is difficult occurred in real system and take much time to reach equilibrium even in catalytic reaction [3].

**Table 5.6** Equilibrium constants of NO reactions at various temperatures

Temperature (°C)	Equilibrium constant (K) for		
	NO Decomposition	NO Oxidation	NO Disproportionation
25	$1.51 \times 10^{13}$	$1.35 \times 10^6$	36.77
100	$9.79 \times 10^{11}$	$1.15 \times 10^4$	2.18
150	$3.11 \times 10^{10}$	$1.22 \times 10^3$	0.592
200	$2.05 \times 10^9$	208.353	0.214
250	$2.27 \times 10^8$	50.275	0.0951
300	$3.69 \times 10^7$	15.637	0.0490
350	$8.04 \times 10^6$	5.900	0.0283
400	$2.20 \times 10^6$	2.581	0.0178
450	$7.20 \times 10^5$	1.271	0.0120
500	$2.72 \times 10^5$	0.688	$8.58 \times 10^{-3}$
550	$1.16 \times 10^5$	0.402	$6.40 \times 10^{-3}$
600	$5.44 \times 10^4$	0.250	$4.94 \times 10^{-3}$

In the NO reduction with propane without oxygen condition, the first step of reaction would be the decomposition of NO to N<sub>2</sub> and O<sub>2</sub>. Propane consumption might come from the oxidation with oxygen produced in the reaction, the thermal cracking, the coke formation and NO<sub>x</sub> reduction while nitrogen would produced from the decomposition of NO and the reduction of NO<sub>x</sub> species. Both aspects may not be directly involve each other.

The effect of copper content in Cu/H-ZSM-5 on the activity of NO reduction by propane in the absence of oxygen was studied further. Figure 5.12 illustrates that the temperature of active region of Cu/H-ZSM-5 is above 400 °C. Also, it clearly indicates the important role of copper content in the conversion to N<sub>2</sub> in the absence of oxygen. While the system of Cu/H-ZSM-5 with 1.64 wt.% copper gave 90 % NO conversion to N<sub>2</sub> at 500 °C, the system of 1.06 wt % catalyst gave 60 % conversion and the system of 0.63 wt % catalyst gave about 20 % conversion, respectively.

Iwamoto et al.[11,12,14] observed that the copper content affected on the activity of the selective reduction of NO by hydrocarbon in excess oxygen. Hence, the amount of copper in ZSM-5 zeolites affects the activity in both the presence and the absence of oxygen.

Many authors in the literature [3,15,16,37] suggested that the Cu ions in Cu/ZSM-5 act as the main active sites for the selective catalytic reduction of nitric oxide by hydrocarbon. The remaining cations play just a minor role in the reaction although Shelef [3] noticed the bi-functional active site of Cu sites and acid sites. However, the different activity between Cu/Na-ZSM-5 and Cu/H-ZSM-5 was obviously observed in the NO reduction in the absence of oxygen. This is result from either the direct effect of different residual cations between both zeolite or the different Cu<sup>2+</sup>/Cu<sup>1+</sup> of both catalysts.

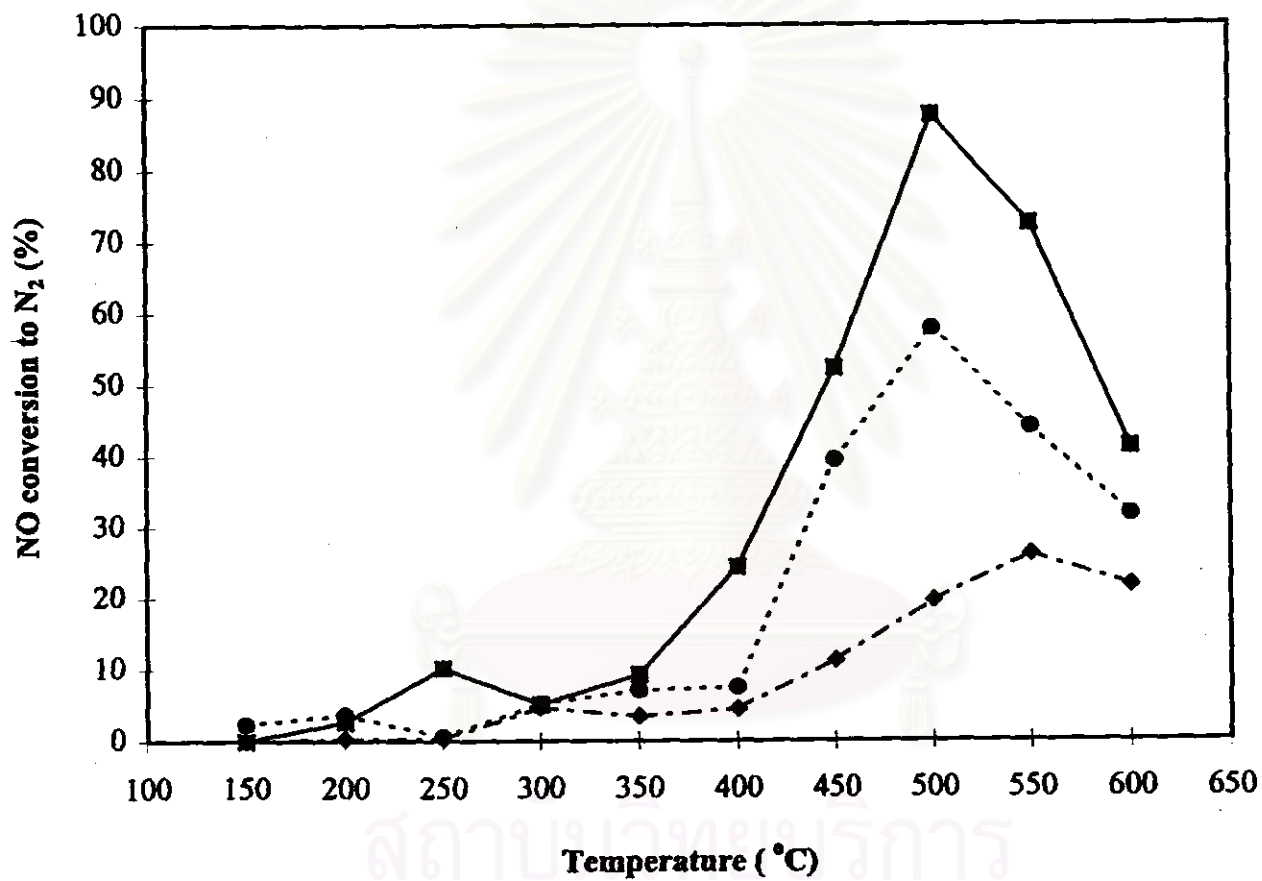


Figure 5.12 NO conversion to N<sub>2</sub> in the system of 1000 ppm NO, 3000 ppm propane and He Bal. at GHSV: 4000 h<sup>-1</sup> over Cu/H-ZSM-5 having 1.64 wt. % (—■—), 1.06 wt. % (---●---) and 0.63 wt. % (---◆---) of copper, respectively.

### 5.2.3 NO system

The activities of Cu/Na-ZSM-5 and Cu/H-ZSM-5 in other reactions were also studied. Figure 5.13 shows the NO conversion to N<sub>2</sub> as a function of temperature for the direct decomposition of NO. Both Cu/Na-ZSM-5 and Cu/H-ZSM-5 are slightly active in NO decomposition when compared with a blank test.

Cu/ZSM-5 has been proposed as the most active catalyst for the NO decomposition[4,5,10,11]. However, the activity is restricted to low GHSV, high concentration of NO and high temperature. In this experiment, the concentration of NO is only 1000 ppm and test at GSHV of 4000 h<sup>-1</sup>. This explains the low activity observed. There is no significant difference of NO conversion to N<sub>2</sub> between the system of Cu/Na-ZSM-5 and Cu/H-ZSM-5 between 300 and 500 °C.

### 5.2.4 C<sub>3</sub>H<sub>8</sub> + O<sub>2</sub> system

Hydrocarbon oxidation over Cu/Na-ZSM-5 and Cu/H-ZSM-5 were also investigated and results are depicted in figure 5.14. Trends of propane conversions as the functions of temperature over Cu/Na-ZSM-5 and Cu/H-ZSM-5 are similar. Only the light off temperatures of Cu/Na-ZSM-5, which is about 275 °C, is lower than that of Cu/H-ZSM-5, which is about 325 °C. Interestingly, this is similar to the conversion of propane in the NO reduction with propane in excess oxygen (figure 5.8). Furthermore, at the temperatures above 400 °C, conversions over both catalysts gradually increase, and Cu/H-ZSM-5 gave more propane conversion than over Cu/Na-ZSM-5.

From above results, the difference of performance between Cu/Na-ZSM-5 and Cu/H-ZSM-5 was found in some reactions. The significant difference could not be observed in NO decomposition and propane oxidation. However, Cu/Na-ZSM-5 was found to be more active than Cu/H-ZSM-5 in the NO reduction in the condition of oxygen excess, particularly at high GHSV, while Cu/H-ZSM-5 was more active than Cu/Na-ZSM-5 in the NO reduction in the absence of oxygen. However, these results show the independence between the NO reduction by propane with and without oxygen because of the different results received from the different reactions.

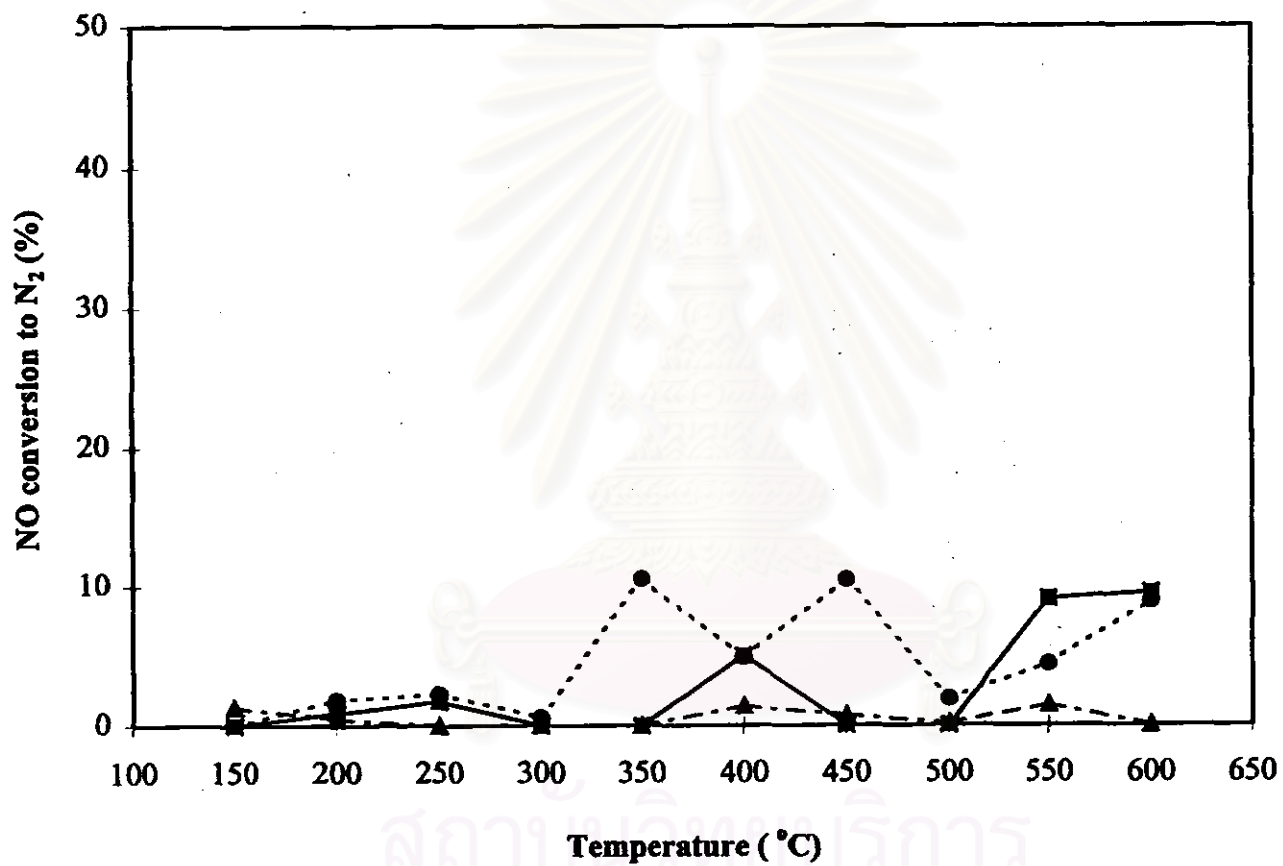


Figure 5.13 NO conversion to  $N_2$  in the system of 1000 ppm NO and He Bal. at GHSV:  $4000 \text{ h}^{-1}$  over Cu/Na-ZSM-5 ( ---●--- ), Cu/H-ZSM-5 ( —■— ) and without catalyst ( ---▲--- ).

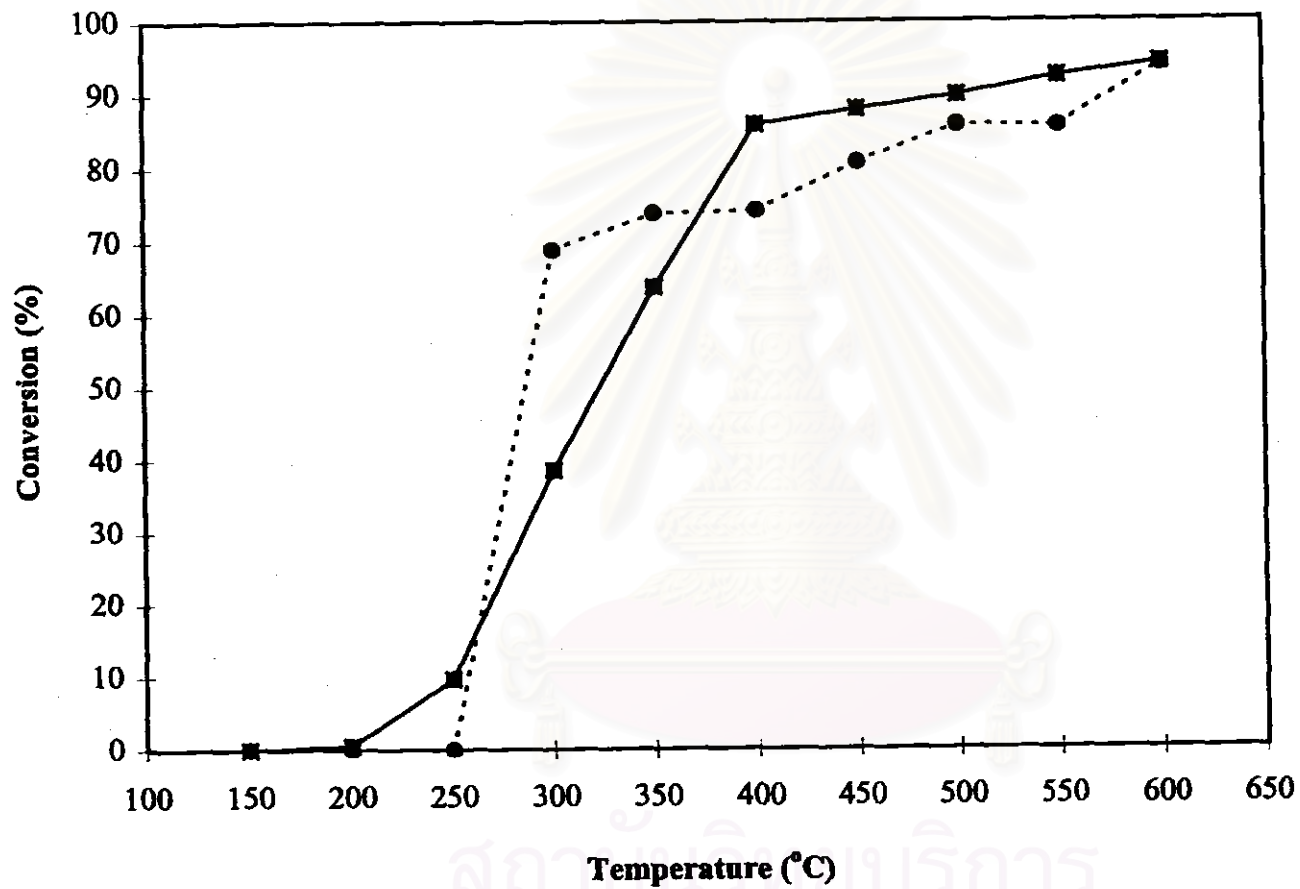


Figure 5.14 Propane conversion in the system of 3000 ppm propane, 1.2 % O<sub>2</sub> and He Bal. at GHSV: 4000 h<sup>-1</sup> over Cu/Na-ZSM-5 ( ---●--- ), Cu/H-ZSM-5( —■—).



It may be imply that the mechanism of the reaction with oxygen is differ from the reaction without oxygen and the main active site may also be different. The residual cations may directly affect on such reactions. Alternatively, the different amount of  $\text{Cu}^{2+}/\text{Cu}^{1+}$  of Cu/Na-ZSM-5 and Cu/H-ZSM-5 might influence the activity of both catalysts in these reactions as well and will clearly distinguish in the oxygen absent reactions.

In the results of this section, the difference between Cu/Na-ZSM-5 and Cu/H-ZSM-5 are certainly observed. The clear explanations for these results, however, would be additional examined in following parts.

### **5.3 Effect of Feed Concentration on the Activity of Catalysts.**

Further from the effect of feed type in reactions on the catalysts studied in the previous section, the effect of feed concentration would be studied to investigate the effect of the remaining cation in Cu/ZSM-5 on the change of feed concentration and also the adsorption and desorption of reactant. In this part, only the SCR reaction of  $\text{NO} + \text{C}_3\text{H}_8 + \text{O}_2$  was studied. Furthermore, in order to clearly observe the effect of concentration of feed gas, nitrogen monoxide, propane and oxygen, on the NO conversion to  $\text{N}_2$ , the experiments would be carried out at a condition that would give the conversion less than 100 %. Hence, 0.1 g of Cu/H-ZSM-5 or Cu/Na-ZSM-5 at GSHV of about  $12000 \text{ h}^{-1}$  were used.

#### **5.3.1 Effect of NO Concentration.**

Figures 5.15 and 5.16 show the NO conversion to  $\text{N}_2$  as a function of concentration of NO at fixed propane and oxygen concentrations in the feed over Cu/Na-ZSM-5 and Cu/H-ZSM-5. NO conversion decreases almost linearly with an increase of NO concentration. Also the reduction at all of the observed temperatures give the same trend. Over both Cu/Na-ZSM-5 and Cu/H-ZSM-5, NO seems to inhibit NO reduction. However, since only 1000 ppm of propane was used in this experiments, the proceed of the reaction might be limited by propane at large concentration of NO. Furthermore, some propane was also combusted with excess

oxygen. These may also cause a lack of reductant for the excess NO. This could also lead to the decrease of NO conversion as well.

### 5.3.2 Effect of Propane Concentration

When propane concentration was varied from 400 to 2400 ppm at constant concentrations of NO and oxygen, the conversion of NO to N<sub>2</sub> increased with propane concentration at all temperatures as shown in figures 5.17 and 5.18. At low concentrations of propane, NO conversion increase rapidly whereas at higher concentrations of propane, conversion increased just slightly. Although the NO concentration was fixed at 1000 ppm during this experiment, the reaction, particularly the N<sub>2</sub> production, would not be limited by NO concentration. Thus, increased concentrations of propane promote the reduction. Figure 5.17 and 5.18 do not show C<sub>3</sub>H<sub>8</sub> conversion. Excess propane in the feed is combusted which causes the propane conversion reach 100 % at high temperature (>400 °C) even in runs having 2400 ppm of propane in the feed. On the other hand, NO is not completely reduced by propane. The NO conversion is never 100 % at over the range of reaction temperatures studied. This indicates that in the competition between the propane combustion and the reaction of propane with nitrogen monoxide, combustion predominates high temperature.

In figures 5.17 and 5.18, NO conversion in the system over Cu/Na-ZSM-5 is slightly higher than over Cu/H-ZSM-5 just as found with experiments at various NO concentrations. These results are similar with the result in figure 5.9.

### 5.3.3 Effect of Oxygen Concentration.

NO conversion to N<sub>2</sub> at various O<sub>2</sub> concentrations and temperatures over Cu/Na-ZSM-5 and Cu/H-ZSM-5 are shown in figures 5.19 and 5.20, respectively. It can be observed that O<sub>2</sub> concentration only slightly affects the NO conversion. NO conversion gradually decreases at higher concentrations of oxygen. Iwamoto et al.[15] observed a promotion an effect of oxygen and also found that the highest NO conversion occurred at oxygen concentrations around stoichiometric. NO conversion decrease slightly when higher concentration of oxygen were used. In order to study in

lean burn region, 3-6% of  $O_2$  (at stoichiometric ratio of 6-12) were used in these experiments. Therefore, in highly excess oxygen condition, oxygen concentration does not affect the reactions.

Over the wide range of feed concentrations of the NO reduction with propane in excess of oxygen studied in this section, Cu/Na-ZSM-5 is slightly more active than Cu/H-ZSM-5. It may be because of difference of feed concentrations and gas space velocity (GHSV). Nevertheless, it can be concluded that Cu/Na-ZSM-5 is more active than Cu/H-ZSM-5 in the reduction on NO by propane with excess oxygen. On the other hand, in the previous section, Cu/H-ZSM-5 was seen to be more active than Cu/Na-ZSM-5 in the absence of oxygen.

Furthermore, trends of the NO conversion varied in concentrations of reactants of experiments over Cu/Na-ZSM-5 and Cu/H-ZSM-5 are the quite the same. These results illustrate the same behavior of adsorption mechanism or the route of reaction on both catalysts. Therefore, the difference of activities of Cu/Na-ZSM-5 and Cu/H-ZSM-5 would rather be result from the difference of reactivity or capacity of reactant adsorption or the amount of active sites than the different reaction mechanism of both catalysts.

#### **5.4 Transient Reaction Tests**

Sometimes, the steady state experiment give insufficient information on reaction kinetics. From the steady state studies of several reactions over Cu/Na-ZSM-5 and Cu/H-ZSM-5, we found the just only the different activity of both catalysts on the reduction of NO in both with and without of oxygen while the effect of the different remaining cations on the their activities was not yet clearly known. Thus, unsteady state would be used. Transient experiment is one method to distinguish the dynamics of reaction as well as the adsorption behavior of reactant species. These measurements may contribute to understanding the effect of the residual cations on the activity of Cu/Na-ZSM-5 and Cu/H-ZSM-5.

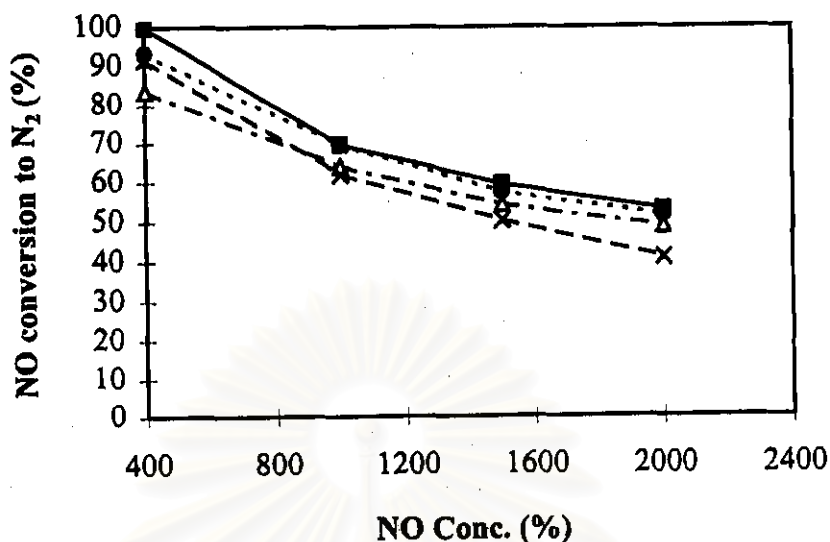


Figure 5.15 Effect of NO concentration on NO conversion to  $N_2$  over Cu/Na-ZSM-5 at 1000 ppm  $C_3H_8$ , 6%  $O_2$  and He Bal., GHSV:  $12000\text{ h}^{-1}$  and at 350 °C (.....●.....), 400 °C (——■——), 450 °C (—△—) and 500 °C (—x—).

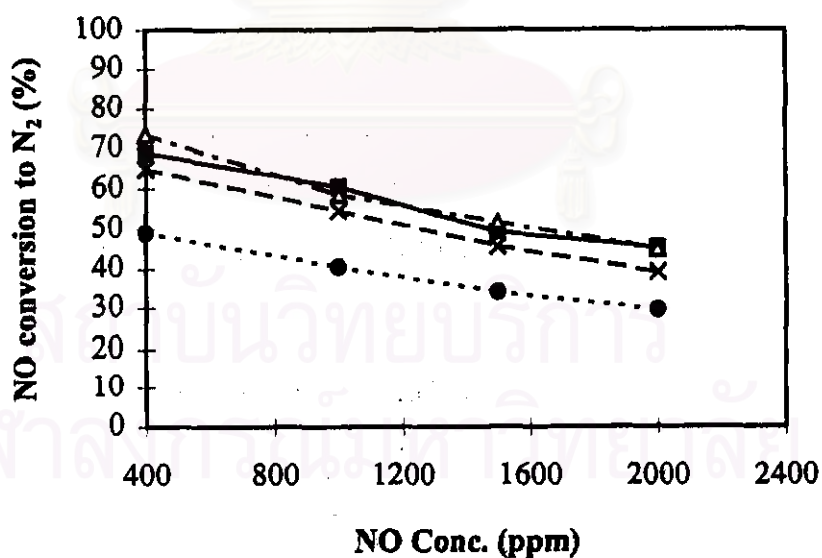


Figure 5.16 Effect of NO concentration on NO conversion to  $N_2$  over Cu/H-ZSM-5 at 1000 ppm  $C_3H_8$ , 6%  $O_2$  and He Bal., GHSV:  $12000\text{ h}^{-1}$  and at 350 °C (.....●.....), 400 °C (——■——), 450 °C (—△—) and 500 °C (—x—).

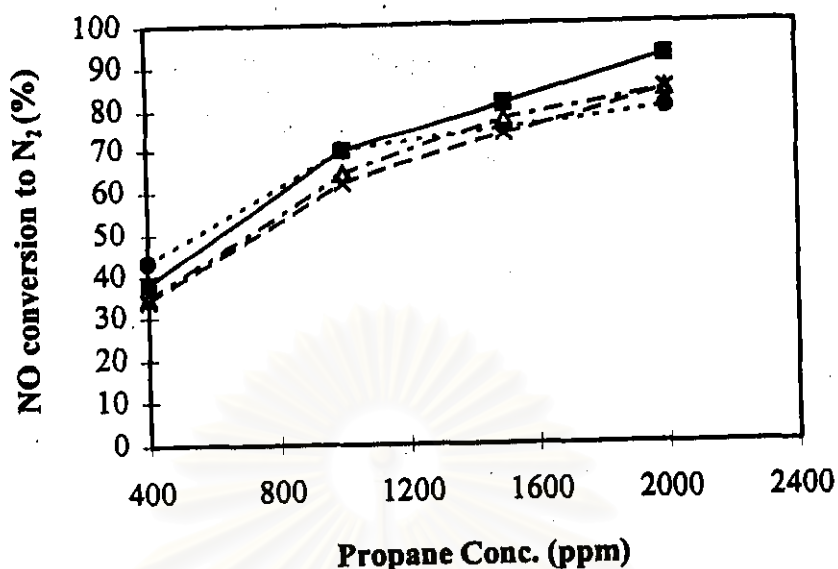


Figure 5.17 Effect of propane concentration on NO conversion to N<sub>2</sub> over Cu/Na-ZSM-5 at 1000 ppm NO, 6 % O<sub>2</sub> and He Bal. , GHSV: 12000 h<sup>-1</sup> and at 350 °C ( .....●..... ), 400 °C ( —■— ), 450 °C ( - -△- ) and 500 °C ( - -x- ).

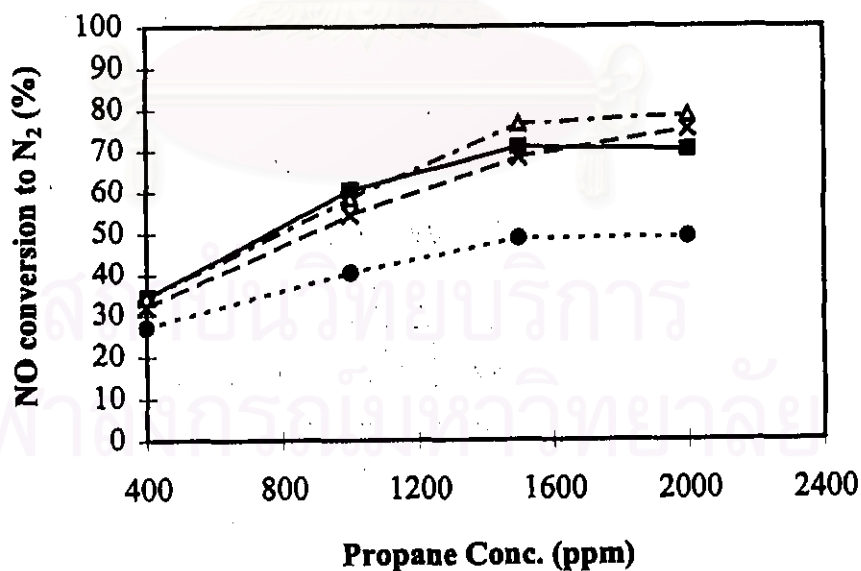


Figure 5.18 Effect of propane concentration on NO conversion to N<sub>2</sub> over Cu/H-ZSM-5 at 1000 ppm NO, 6 % O<sub>2</sub> and He Bal. , GHSV: 12000 h<sup>-1</sup> and at 350 °C ( .....●..... ), 400 °C ( —■— ), 450 °C ( - -△- ) and 500 °C ( - -x- ).

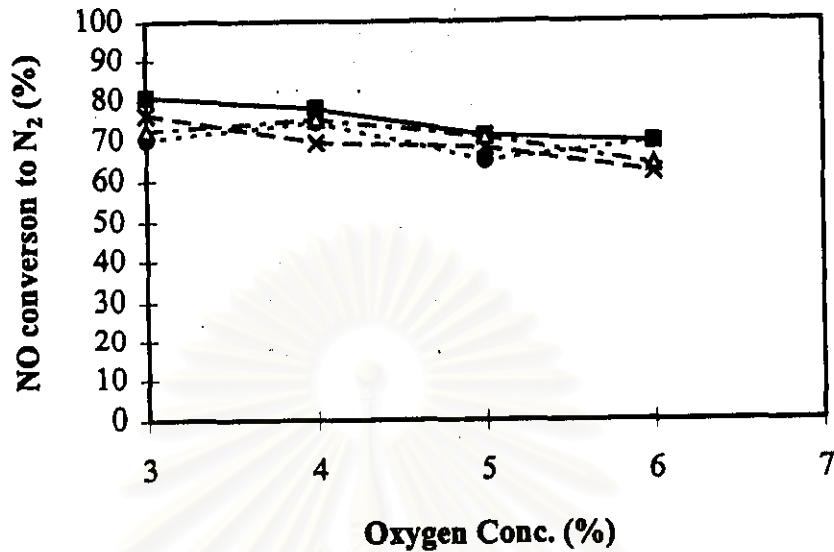


Figure 5.19 Effect of oxygen concentration on NO conversion to  $N_2$  over Cu/Na-ZSM-5 at 1000 ppm  $C_3H_8$ , 1000 ppm NO and He Bal., GHSV:  $12000\text{ h}^{-1}$  and at 350 °C ( .....●..... ), 400 °C ( .....■..... ), 450 °C ( .....△..... ) and 500 °C ( .....x..... ).

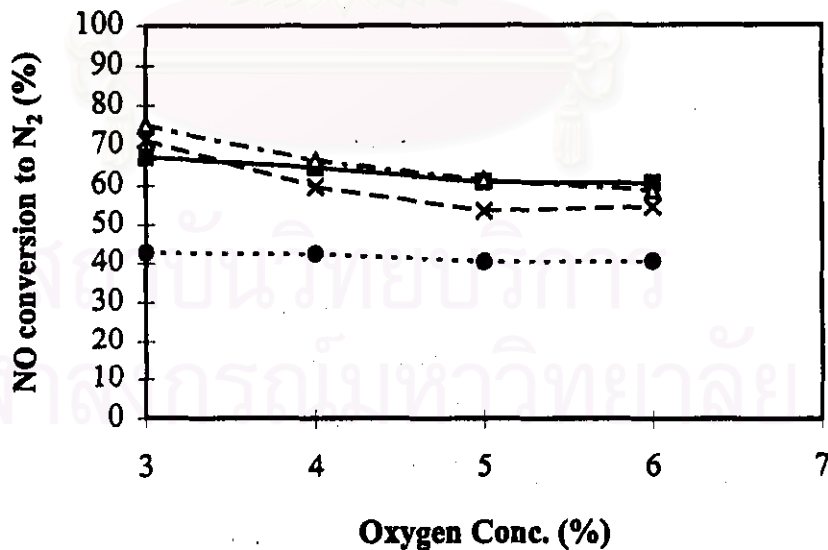


Figure 5.20 Effect of oxygen concentration on NO conversion to  $N_2$  over Cu/H-ZSM-5 at 1000 ppm  $C_3H_8$ , 1000 ppm NO and He Bal., GHSV:  $12000\text{ h}^{-1}$  and at 350 °C ( .....●..... ), 400 °C ( .....■..... ), 450 °C ( .....△..... ) and 500 °C ( .....x..... ).



The experiments in this section investigate the time characteristics of the appearance of reactant species as well as gas products when a specified feed gas is abruptly exchanged for another. The step change of  $\text{NO}$ ,  $\text{NO} + \text{O}_2$ ,  $\text{NO} + \text{C}_3\text{H}_8 + \text{O}_2$ , and  $\text{NO} + \text{C}_3\text{H}_8$  were studied. Na-ZSM-5, H-ZSM-5, Cu/Na-ZSM-5 and Cu/H-ZSM-5 catalysts were used in this study.

#### 5.4.1 Step Change of NO

The variation of NO absorbance with time during the switch from  $\text{N}_2$  to NO feed was studied. From the results in figures 5.21, 5.22 and 5.23, it is clear that Na-ZSM-5 and H-ZSM-5 are not active for the direct decomposition of NO because the transit time and trend of the NO response over both catalysts were similar to the one from a blank experiment. Also, only NO was observed for the Na-ZSM-5 and H-ZSM-5 systems. Apparently, NO does not adsorb on Na-ZSM-5 and H-ZSM-5 since there is no any transit time due to adsorption when NO was passed through the catalysts bed. The transit time in the blank experiment, Na-ZSM-5 experiment and H-ZSM-5 experiments are the same. Pirone et al.[134] also noticed that H-ZSM-5 has no catalytic activity for the decomposition of NO.

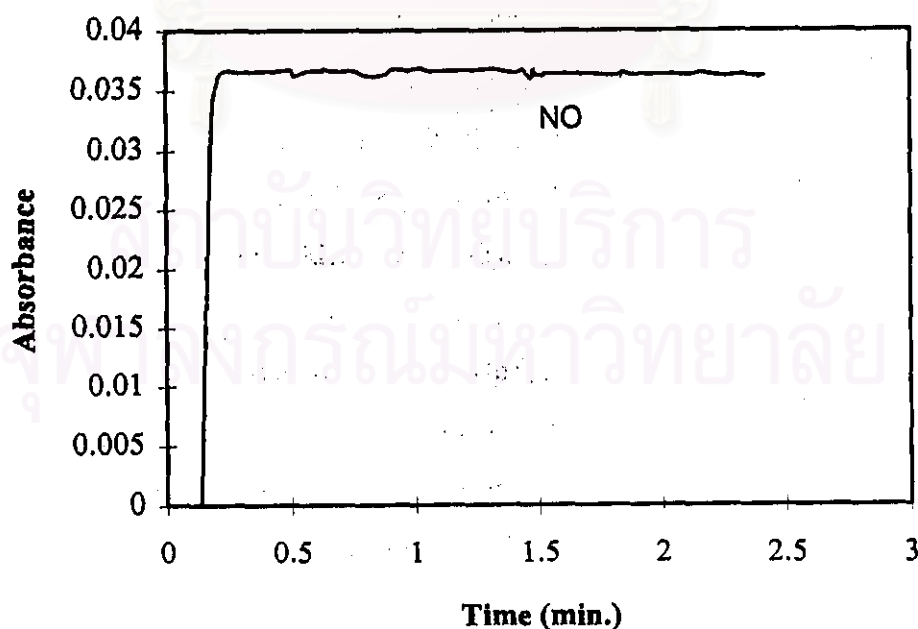


Figure. 5.21 Absorbance of gaseous species after switching from  $\text{N}_2$  to 1.2 % NO +  $\text{N}_2$  at 350 °C without catalyst

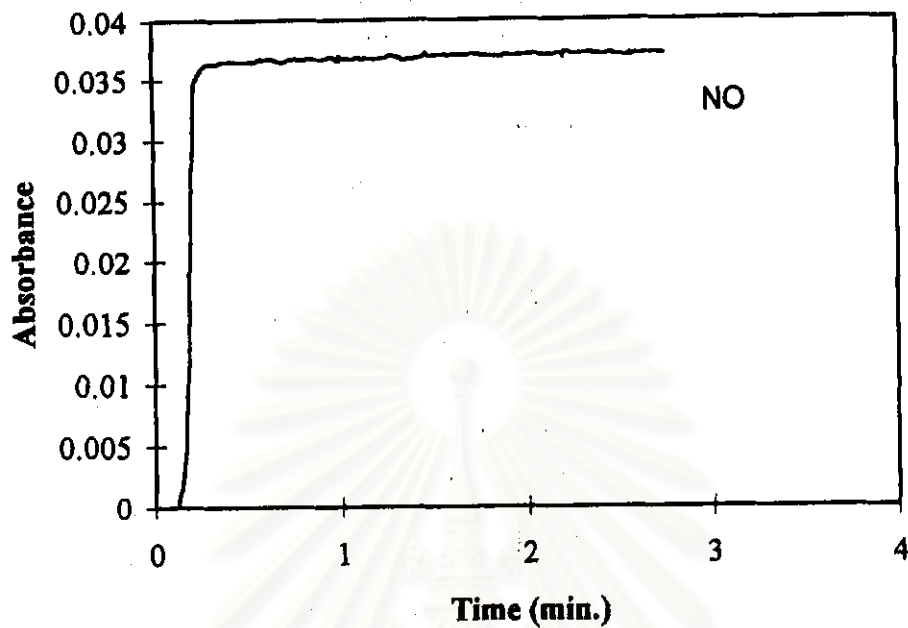


Figure. 5.22 Absorbance of gaseous species after switching from  $N_2$  to 1.2 % NO +  $N_2$  at 350 °C over Na-ZSM-5

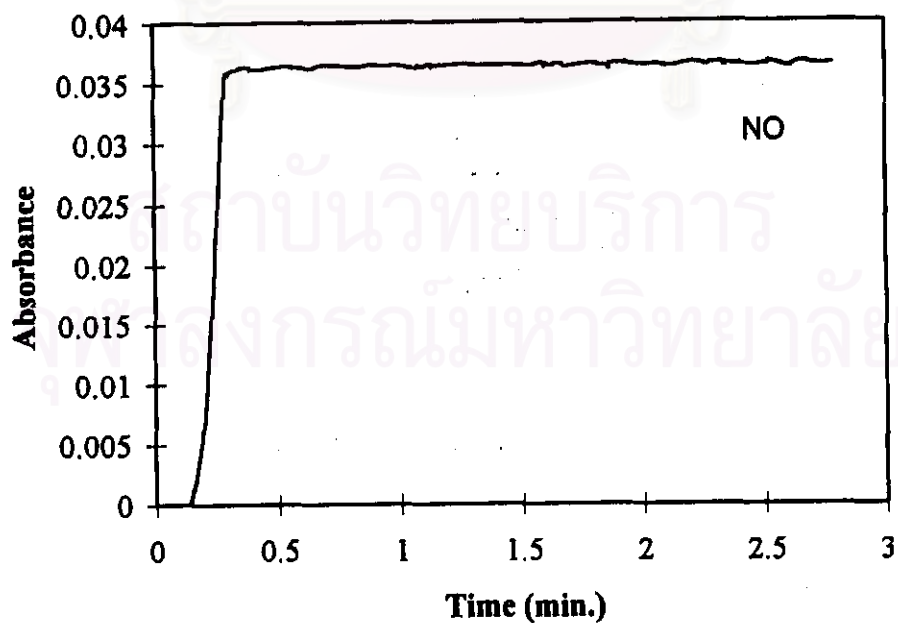


Figure. 5.23 Absorbance of gaseous species after switching from  $N_2$  to 1.2 % NO +  $N_2$  at 350 °C over H-ZSM-5

The results of the same experiments over Cu/Na-ZSM-5 and Cu/H-ZSM-5 at 350 °C are shown in figures 5.24 and 5.25, respectively. The transit time for Cu/Na-ZSM-5 and Cu/H-ZSM-5 system differed from the 0.2 minute for the experiment without catalyst (figure 5.21) which indicate the adsorption phenomena of reactant over Cu/ZSM-5. However, the signal of gas outlet of Cu/Na-ZSM-5 was first appear at ~1.2 min (figure 5.24) whereas the one of Cu/H-ZSM-5 was appeared at ~ 0.8 min. (figure 5.25). This may be result from the difference in gas adsorption capacity in these catalysts at 350 °C.

Unlike the results for Na-ZSM-5 and H-ZSM-5, NO<sub>2</sub> and N<sub>2</sub>O were observed in the reactions over both Cu/ZSM-5 zeolites. It has been known that Cu/ZSM-5 is the only catalyst which shows significant activity for NO decomposition although the activity is still not high enough for practical use[5, 123]. Although N<sub>2</sub> and O<sub>2</sub>, which are supposed to be the main products of NO decomposition, can not be measured due to the analyzer limitation, it was obvious that NO<sub>2</sub> and N<sub>2</sub>O are formed during the decomposition over Cu/ZSM-5. Pirone et al.[134] suggested that at a temperature below 300 °C, NO disproportionation to N<sub>2</sub>O and NO<sub>2</sub> would occur parallel with NO decomposition. Furthermore, Iwamoto et al.[122] mentioned that O<sub>2</sub> from the NO decomposition might further oxidize NO to produce NO<sub>2</sub>.

N<sub>2</sub>O overshoots after breakthrough and then gradually decreases to the steady state. By contrast, the NO<sub>2</sub> signals for both Cu catalysts increase slowly after breakthrough. These phenomena were also observed by Li and Hall [135] and Iwamoto et al.[13,122]. However, both figures 5.24 and 5.25 illustrate that Cu/H-ZSM-5 system produces more NO<sub>2</sub> whereas the Cu/Na-ZSM-5 system produces more N<sub>2</sub>O. These differences might contribute to the different performance of both catalysts in NO reduction, especially in absent oxygen system as discussed above.

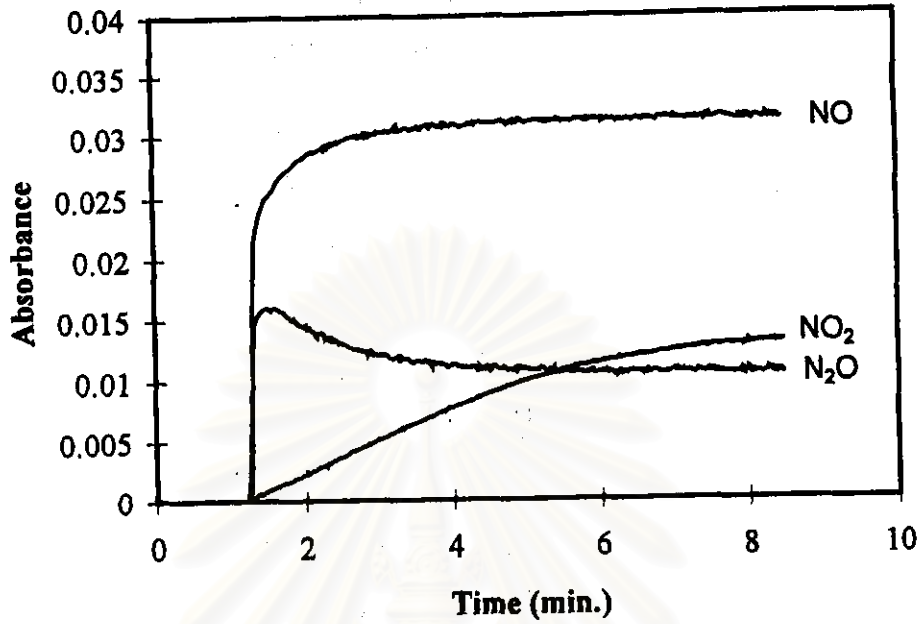


Figure. 5.24 Absorbance of gaseous species after switching from N<sub>2</sub> to 1.2 % NO + N<sub>2</sub> at 350 °C over Cu/Na-ZSM-5

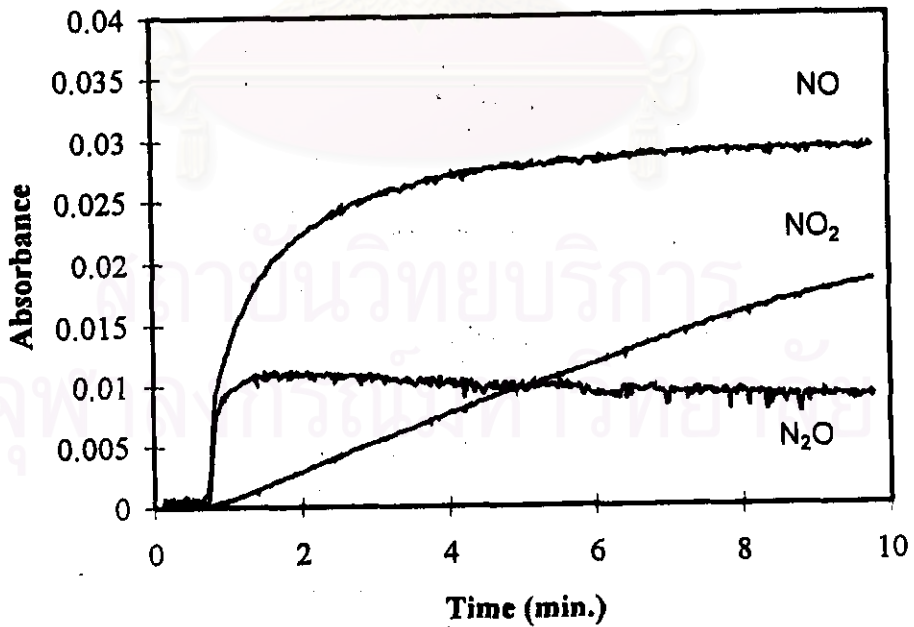


Figure. 5.25 Absorbance of gaseous species after switching from N<sub>2</sub> to 1.2 % NO + N<sub>2</sub> at 350 °C over Cu/H-ZSM-5

the response of  $N_2O$  signals were still much faster than that of  $NO_2$ . In addition, less  $N_2O$  was produced at this temperature over both Cu/ZSM-5 catalysts. The formation of  $N_2O$  as well as  $NO_2$  over both zeolites are not the same. The system on Cu/H-ZSM-5 produces less  $N_2O$  but more  $NO_2$  than Cu/Na-ZSM-5, similar to the measurements at 350 °C. The reactions at 400 °C over both Cu/ZSM-5 zeolites formed less  $NO_2$  than the reaction at 350 °C. However,  $NO_2$  signals of the runs at 400 °C reach steady state faster than the ones at 350 °C. Accordingly, at higher temperature, it is likely that the direct decomposition of NO is preferred rather than NO disproportionation which agree with the suggestions of Pirone et al.[134]. Although, thermodynamically,  $NO_2$  and  $N_2O$  would be less formed in higher temperature (see table 5.6), in Cu/ZSM-5 catalytic reaction, indeed, more  $NO_2$  and less  $N_2O$  formation with temperature increase observed in this study.

Figure 5.28 illustrates the disappearance of products after NO was suddenly removed from the system over Cu/H-ZSM-5 at 350 °C. Compared to the switching off of NO in the blank test (figure 5.21), there are significant lag times for each product over Cu/H-ZSM-5. Long tailing of  $NO_2$  signal was observed while  $N_2O$  is drops immediately.

#### 5.4.2 Step Change of $NO + O_2$

Figures 5.29 and 5.30 show the results of step change from the inert gas to a gas mixture of 0.5 % NO + 12%  $O_2$  as well as the step back to inert again. The results indicate that NO can be oxidized in the gas phase and preferably occurs at a low temperature. The rate of this homogeneous reaction is reduced as the temperature increases because the reverse reaction becomes more important (figures 5.29 and 5.30). The equilibrium constants of NO oxidation shown in table 5.6 also support the blank tests. The occurrence of a homogeneous reaction was demonstrated by Chajar et al.[50].

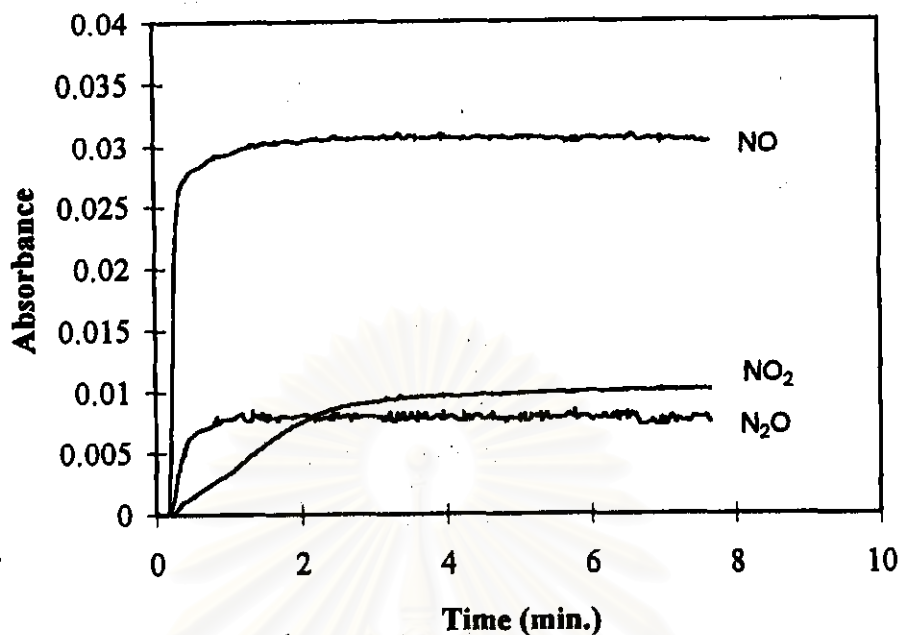


Figure. 5.26 Absorbance of gaseous species after switching from N<sub>2</sub> to 1.2 % NO + N<sub>2</sub> at 400 °C over Cu/Na-ZSM-5

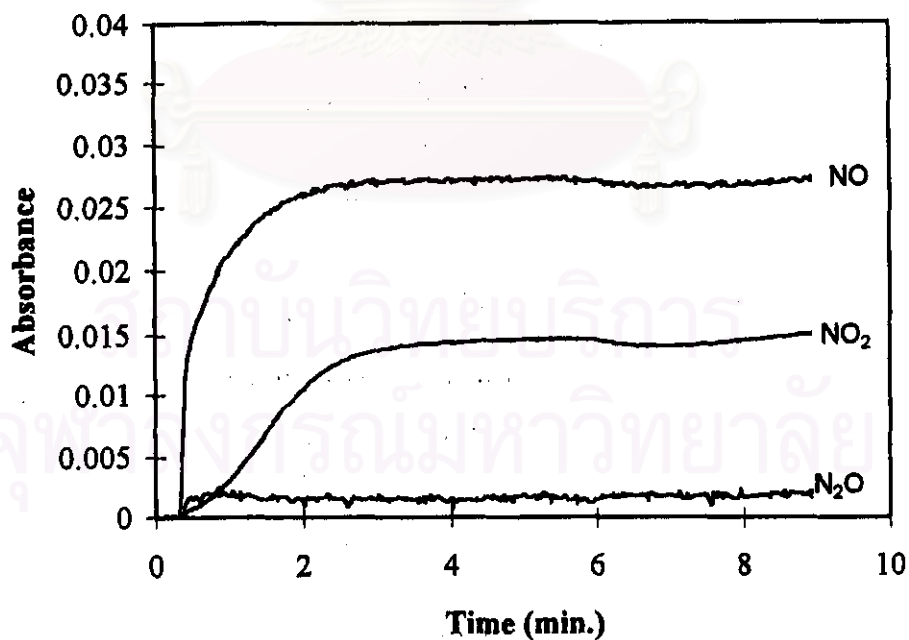


Figure. 5.27 Absorbance of gaseous species after switching from N<sub>2</sub> to 1.2 % NO + N<sub>2</sub> at 400 °C over Cu/H-ZSM-5.

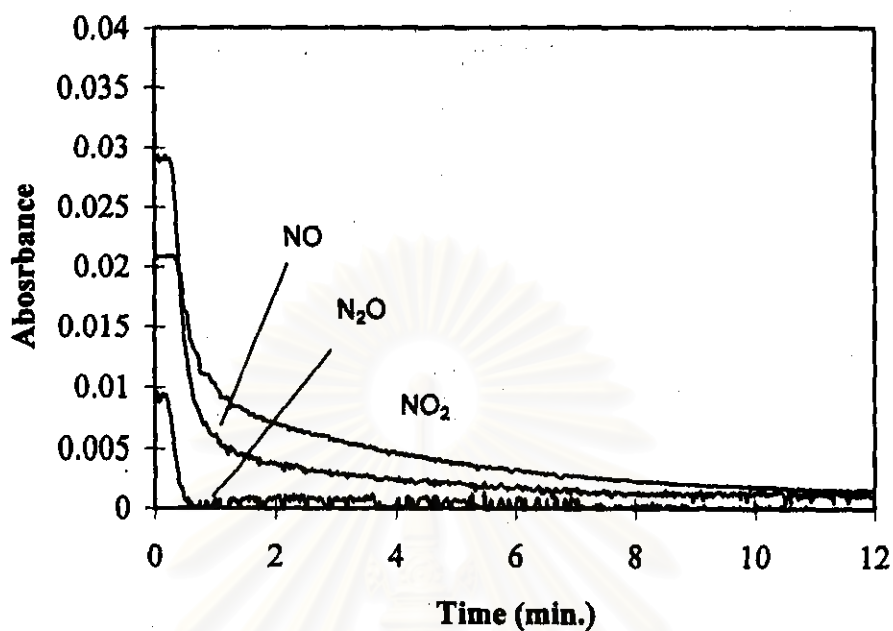


Figure. 5.28. Absorbance of gaseous species after switching from 1.2 % NO + N<sub>2</sub> to N<sub>2</sub> at 350 °C over Cu/H-ZSM-5.

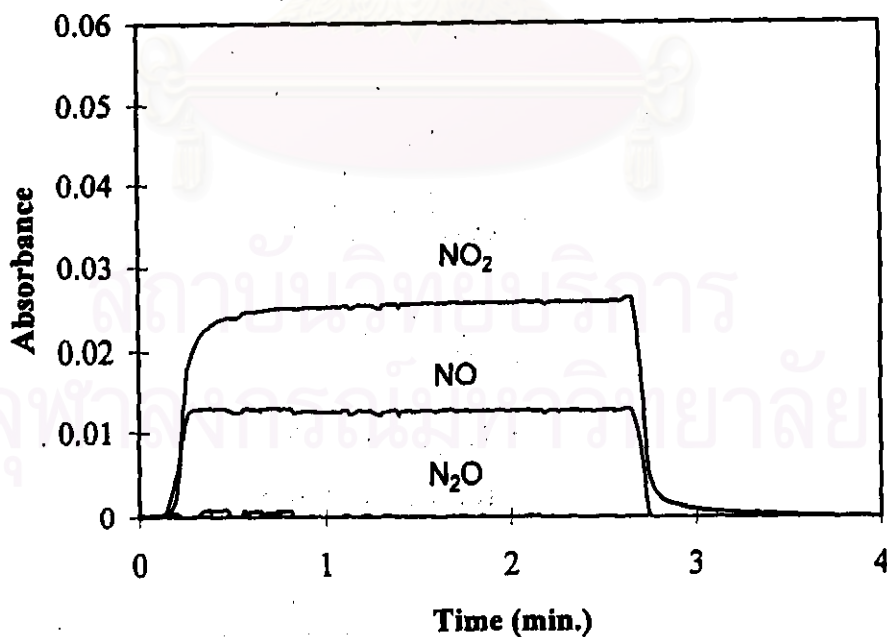


Figure. 5.29 Absorbance of gaseous species after switching from N<sub>2</sub> to 0.5 % NO + 12 % O<sub>2</sub> + N<sub>2</sub> and switch back to N<sub>2</sub> again after 2.5 minutes at room temperature without catalyst



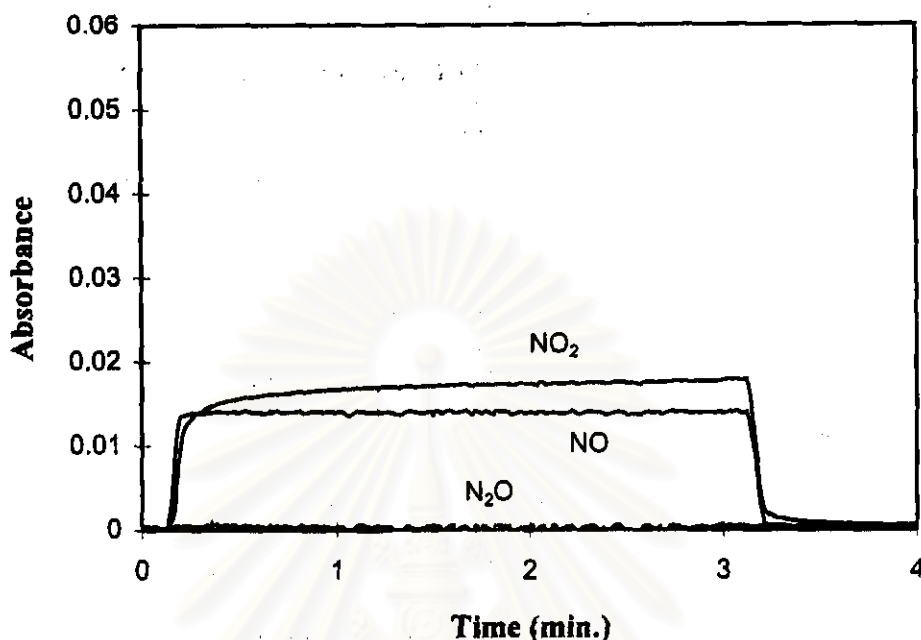


Figure. 5.30 Absorbance of gaseous species after switching from  $N_2$  to 0.5 % NO + 12 %  $O_2$  +  $N_2$  and switch back to  $N_2$  again after 3 minutes at 350 °C without catalyst

The response for Na-ZSM-5 catalyst shown in figure 5.31 is similar with the blank test shown in figures 5.29 and 5.30. This indicates the activity of Na-ZSM-5 in the oxidation of NO to  $NO_2$  is negligible. The formation of  $NO_2$  in the reaction over H-ZSM-5, shown in figure 5.32, is quite similar to that over Cu/H-ZSM-5 and Cu/Na-ZSM-5 shown in figures 5.33 and 5.34. Surprisingly, the lag times of the appearance of  $NO_x$  with the Cu catalysts are much longer than with H-ZSM-5.  $NO_x$  signals in the experiment over H-ZSM-5 appears about half a minute whereas, in the Cu/ZSM-5 experiments,  $NO_x$  was first detected around 4 minutes after switching. This indicates the high  $NO_2$  adsorption capacity of Cu/ZSM-5 comparing to H-ZSM-5.

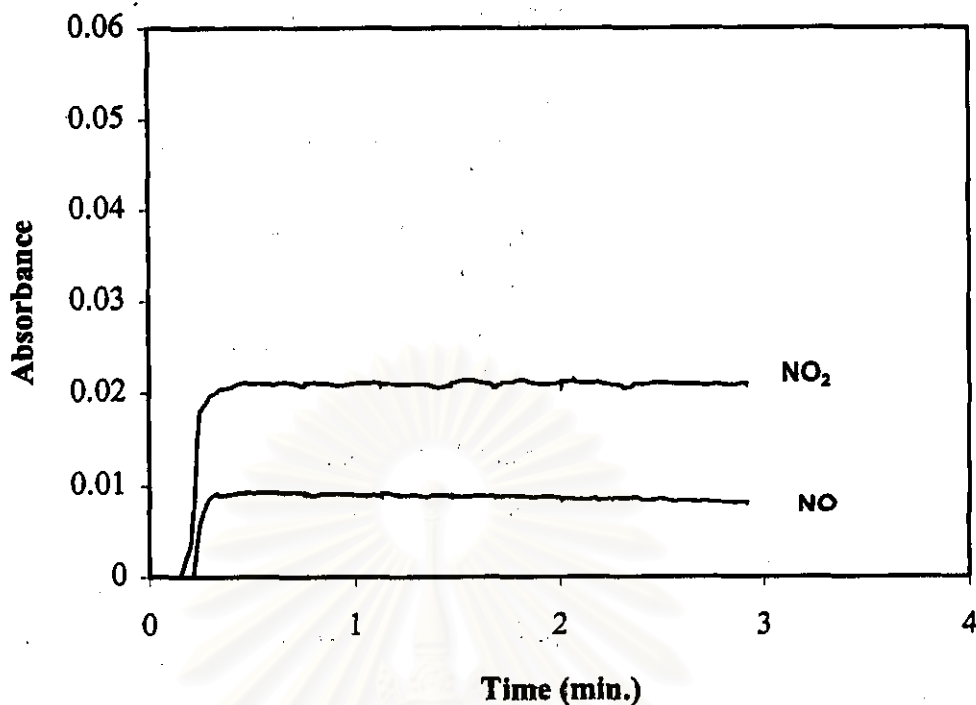


Figure 5.31 Absorbance of gaseous species after switching from N<sub>2</sub> to 0.5 % NO + 12 % O<sub>2</sub> + N<sub>2</sub> at 350 °C over Na-ZSM-5.

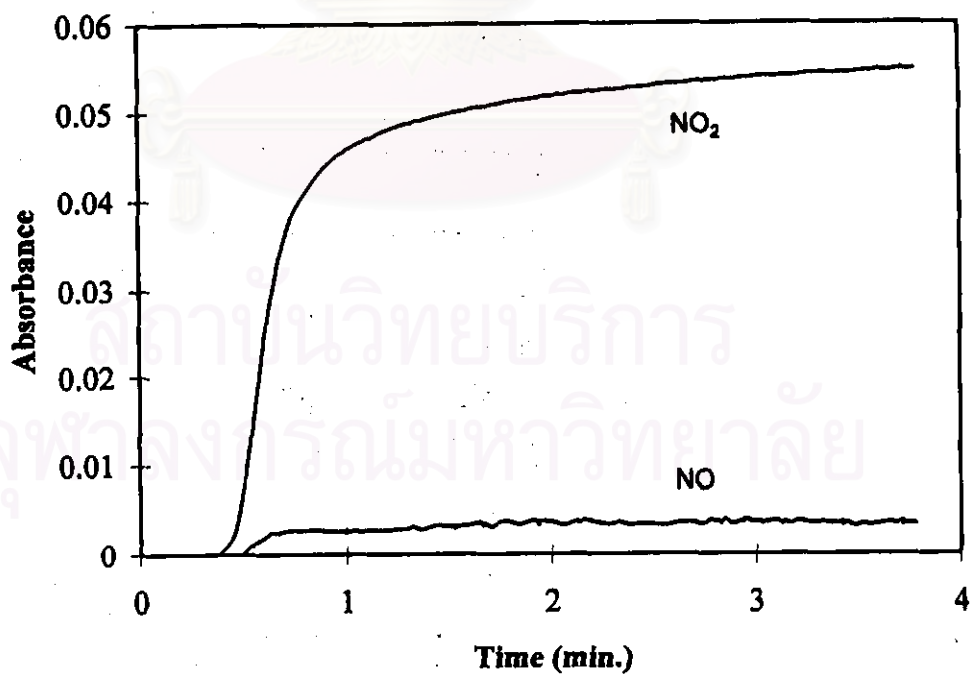


Figure 5.32 Absorbance of gaseous species after switching from N<sub>2</sub> to 0.5 % NO + 12 % O<sub>2</sub> + N<sub>2</sub> 350 °C over H-ZSM-5.

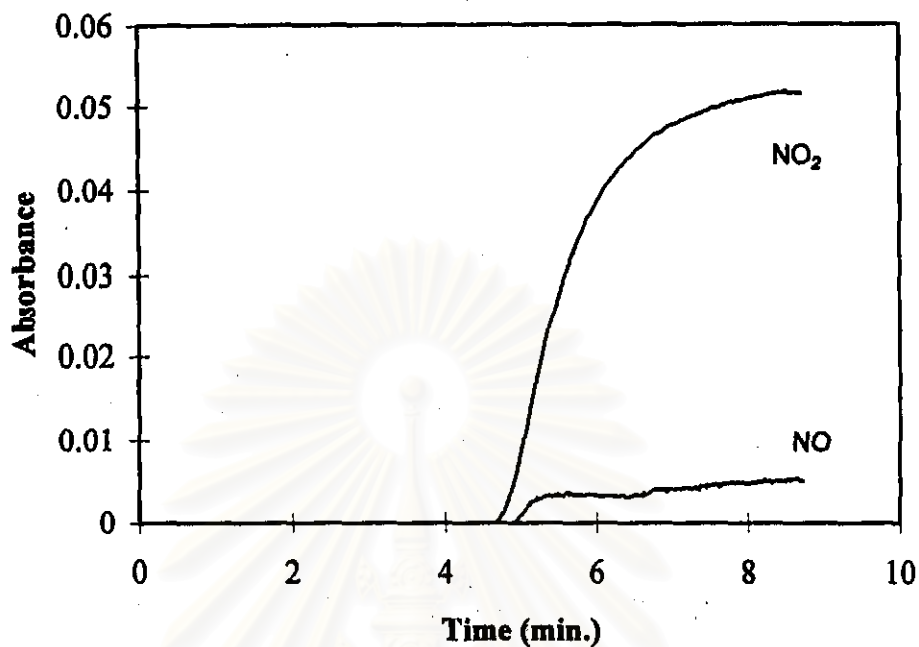


Figure. 5.33 Absorbance of gaseous species after switching from N<sub>2</sub> to 0.5 % NO + 12 % O<sub>2</sub> + N<sub>2</sub> 350 °C over Cu/Na-ZSM-5.

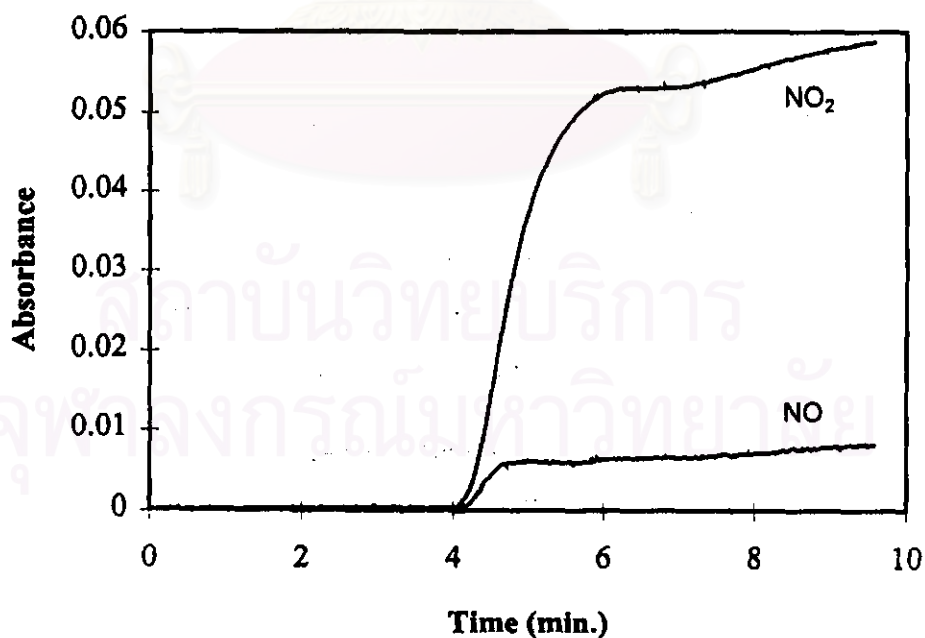


Figure. 5.34 Absorbance of gaseous species after switching from N<sub>2</sub> to 0.5 % NO + 12 % O<sub>2</sub> + N<sub>2</sub> 350 °C over Cu/H-ZSM-5.

The delay in the appearance of NO in figures 5.33 and 5.34 may be explained by the rapid oxidation of NO to NO<sub>2</sub> in the presence of O<sub>2</sub> in feed. NO<sub>2</sub> appear only when the catalyst is saturated with NO<sub>2</sub>. This condition interfered with NO oxidation allowing the appearance of some NO in the product gas. In addition, the lag of about 4 minutes in figures 5.33 and 5.34 compared to about 1 minute in figures 5.24 and 5.25 is due to the different concentration of NO in feed between the NO tests and NO + O<sub>2</sub> tests. It is 1.2 % in the former and 0.5 % in the latter.

The slow rise in NO<sub>2</sub> in figures 5.24 and 5.25 appears to be due to strong adsorption of NO<sub>2</sub> on the copper. Differences between the results in figures 5.24. and 5.25 and the ones in figures 5.33 and 5.34 probably reflect reduction of the copper catalyst by NO when O<sub>2</sub> is not present in the feed.

Neither Na-ZSM-5 nor H-ZSM-5 is active in NO decomposition, but, for the oxidation of NO by O<sub>2</sub>, Na-ZSM-5 is not active whereas H-ZSM-5 is quite active. Catalytic sites in H-ZSM-5 are not active for feeds having only NO but active for feeds having NO and O<sub>2</sub>. Perhaps the active site in H-ZSM-5 does not adsorb NO but preferably adsorbs O<sub>2</sub> instead. In NO oxidation over H-ZSM-5, NO<sub>2</sub> is produced by reaction between adsorbed oxygen and NO in the gas phase. Pirone et al.[134] also noticed that H-ZSM-5 does not adsorb NO. However, the study of Halasz et al. [136] does not correspond with our results. They mentioned the important role of the Brønsted acid site in the adsorption of NO and its participation in the oxidation of NO to NO<sub>2</sub>. The surface character of their catalysts may be different. Not only the Brønsted site in H-ZSM-5 but also the Lewis acid site, which is generated by dehydroxylation of two adjacent Brønsted acids is possibly involved in the catalytic process. Quantities of Brønsted acid site and Lewis acid site depend on the treatment of a catalyst[137,138]. Significant amount of Lewis acid sites has been found in H-ZSM-5 [137]. A Lewis acid site may involve in the adsorption of oxygen and the oxidation of NO rather than the Brønsted acid site. A mechanism proposed in literature [3] proposed that oxygen is adsorbed on Lewis acid site(Z<sup>+</sup>O<sup>-</sup>) before interacting with NO gas to produce NO<sub>2</sub>. Unlike H-ZSM-5, the oxidation of NO over Cu/H-ZSM-5

might occur either via (1) a surface reaction between adsorbed species or (2) a reaction between adsorbed species and gas phase species. NO might be adsorbed either on  $\text{Cu}^{2+}\text{O}^{-1}$  [38] or on  $\text{Cu}^+$  [139] to initiate the decomposition. This makes Cu/ZSM-5 more active than H-ZSM-5 for NO decomposition.

The performances of Cu/Na-ZSM-5 and Cu/H-ZSM-5 in the NO oxidation were quite similar although, at steady state, the  $\text{NO}_2$  signal in Cu/H-ZSM-5 is slightly higher. Because of high activities of both Cu/ZSM-5 catalysts, obvious difference of their catalysts was not observed.

#### 5.4.3 Step change of $\text{NO} + \text{C}_3\text{H}_8$

Absorbance of gases with time on stream shown in figures 5.35 and 5.36 were obtained from experiments without oxygen in the feed gas over Cu/Na-ZSM-5 and Cu/H-ZSM-5 zeolites. After switching from  $\text{N}_2$  to  $\text{C}_3\text{H}_8$ , formation of  $\text{CO}_2$  in the first few minutes after a step change comes from the reaction between  $\text{C}_3\text{H}_8$  and residual adsorbed oxygen in the catalyst and/or extralattice oxygen (ELO) which come from cation hydration during catalyst preparation as mentioned by Valyon and Hall [75,76]. Therefore, when oxygen in the surface was exhausted, the signal of  $\text{CO}_2$  disappeared. After  $\text{CO}_2$  formation ended, the response of propane signal in the reactor outlet gradually increased until reaching a constant level after about 10 minutes. This could be the result from the chromatographic effect of the light hydrocarbon over Cu/ZSM-5 [53, 55]. This effect is likely due to competitive adsorption of  $\text{CO}_2$  and light hydrocarbon over the catalysts. However, the  $\text{C}_3\text{H}_8$  signal at steady state measured with Cu/Na-ZSM-5 was higher than the one from Cu/H-ZSM-5. This implies that Cu/H-ZSM-5 adsorbs more hydrocarbon than Cu/Na-ZSM-5. Perhaps this is attributable to acid sites remaining in Cu/H-ZSM-5 since it was known that the Brønsted sites are active for the dehydrogenation and cracking processes [77]. Both these processes require hydrocarbon adsorption.

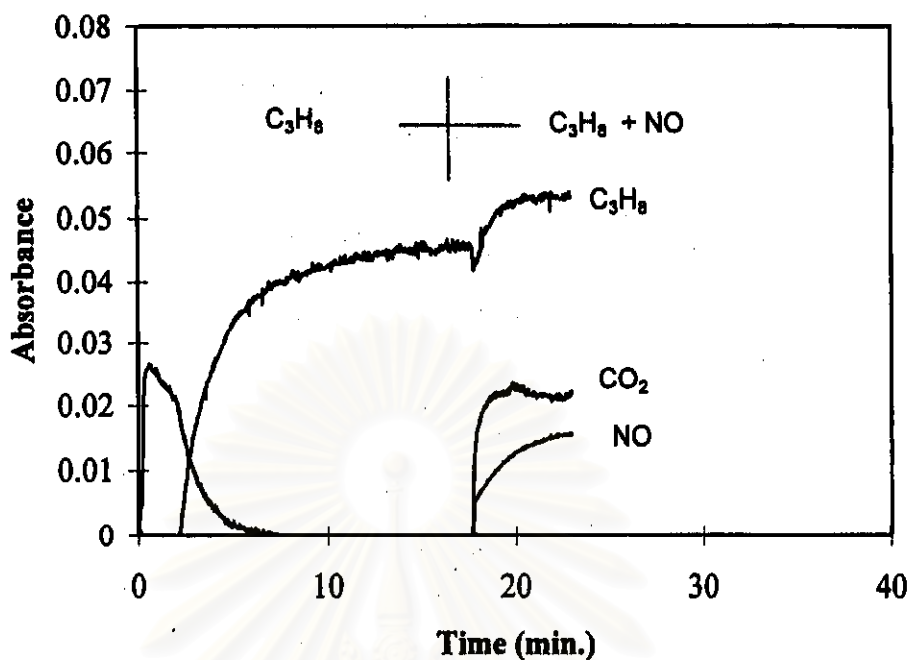


Figure. 5.35 Absorbance of gaseous species after switching from N<sub>2</sub> to 0.4 % C<sub>3</sub>H<sub>8</sub> and then 0.5 % NO was added at time = 16 minutes at 400 °C over Cu/Na-ZSM-5.

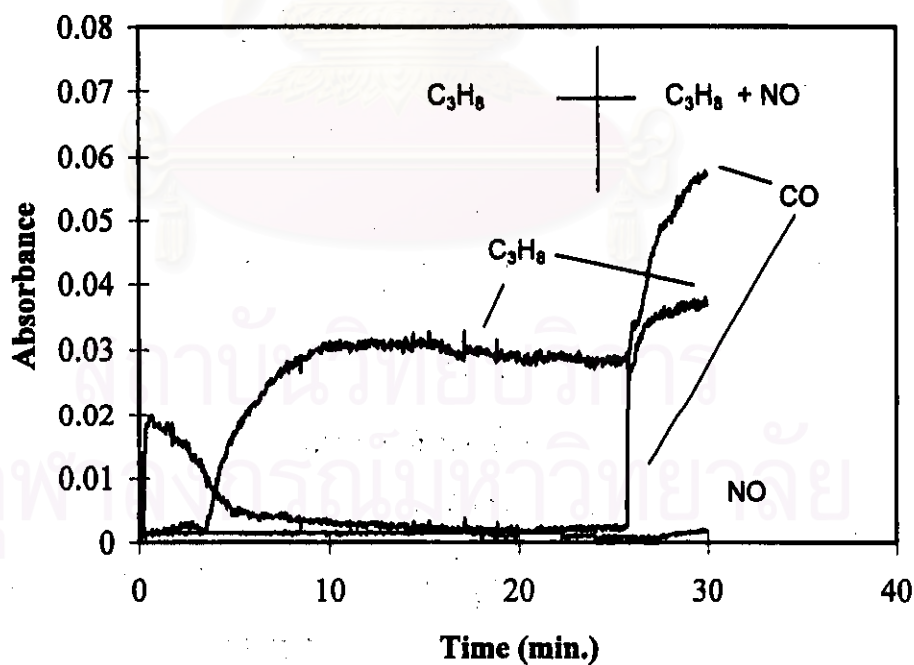


Figure. 5.36 Absorbance of gaseous species after switching from N<sub>2</sub> to 0.4 % C<sub>3</sub>H<sub>8</sub> and then 0.5 % NO was added at time = 24 minutes at 400 °C over Cu/H-ZSM-5.



After NO was added to the catalyst bed (at 16 min. in figure 5.35 and 24 min. in figure 5.36), the NO substantial reduction and CO<sub>2</sub> formation appears after an adsorption lag. NO conversion and CO<sub>2</sub> production of Cu/H-ZSM-5 experiment were higher than of Cu/Na-ZSM-5. Moreover, this result are in accord with the result of steady state reactions in section 5.2. This section showed that Cu/H-ZSM-5 was more active for NO reduction at 400 °C than Cu/Na-ZSM-5 and also gives more CO<sub>2</sub> and the Cu/Na-ZSM-5 system. The signal of C<sub>3</sub>H<sub>8</sub> in the experiment over both catalysts is enhanced after addition of NO because NO competes for sites pre-adsorbed hydrocarbon. This causes some hydrocarbon to desorb and creates a new hydrocarbon of adsorption – desorption equilibrium. Hoost et al.[140] noticed that propane adsorption decrease in the presence of NO<sub>x</sub>. During NO reduction by propane in the absence of oxygen in this study, CO, N<sub>2</sub>O, and NO<sub>2</sub> were not observed.

The first step of the reaction after introduction of NO would be the decomposition of NO[54]. Oxygen generated will react further to form NO<sub>2</sub> or to oxidize propane. The NO<sub>2</sub> formed would be further reduced by propane to form CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>. NO<sub>2</sub> has been considered as the key intermediate of SCR of NO by hydrocarbon because it is more easily reduced by hydrocarbon than NO[35, 46-51]. NO decomposition, Cu/H-ZSM-5 produces more NO<sub>2</sub> than Cu/Na-ZSM-5 (figures 5.24 and 5.25). In the same way, with propane in the feed, more NO<sub>2</sub> might be formed and thus lead to a higher rate of CO<sub>2</sub> formation over the Cu/H-ZSM-5 catalyst.

#### 5.4.4 Step change of NO + C<sub>3</sub>H<sub>8</sub> + O<sub>2</sub>

When the gas stream is changed from N<sub>2</sub> to a mixture of C<sub>3</sub>H<sub>8</sub> and O<sub>2</sub>, only CO<sub>2</sub> is observed. These measurements are shown in figure 5.37 to 5.41. Signals for C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub> are seen for Na-ZSM-5 and H-ZSM-5 (figures 5.38 and 5.39). Although with the blank test, hardly any CO<sub>2</sub> is produced. These indicate the low activity of Na-ZSM-5 and H-ZSM-5 in propane combustion. However, this is substantial CO<sub>2</sub> produced over H-ZSM-5 while much less CO<sub>2</sub> forms over Na-ZSM-5.

In comparison, only CO<sub>2</sub> is observed for Cu/Na-ZSM-5 and Cu/H-ZSM-5 (figures 5.40 and 5.41). Propane is completely oxidized over both Cu/ZSM-5 catalysts. The different performance between Cu/H-ZSM-5 and H-ZSM-5 may be the result of



the existence of copper ion in the catalysts. Copper sites seems to be more active in combustion than the more prevalent acid sites on H-ZSM-5. A low activity of acid sites in hydrocarbon oxidation was reported by Sasaki et al.[46]. On the other hand, copper in zeolite is known to be active in hydrocarbon oxidation[141, 142]. The increase and decrease of the  $C_3H_8$  signals before approaching a constant observed in the experiments with  $C_3H_8 + O_2$  over Na-ZSM-5 and H-ZSM-5 is possibly due to the fluctuation of gas flow during switching rather than adsorption behavior.

When NO is suddenly added into the feed,  $CO_2$  formation rises rapidly and then gradually drops until a steady state is reached. This overshooting could be observed over all catalyst systems studied in this experiment. It suggests that sites active for NO reduction store  $CO_2$ . This  $CO_2$  is released when NO is added to the feed and competes with  $CO_2$  for these sites. Overshoot, however, contradicts the transient result of Centi et al.[65]. Their study observed a drop in the  $CO_2$  signal but an overshoot of the  $C_3H_8$  and NO signals when NO was fed into  $O_2 + C_3H_8$  flow. Difference in observations probably can be attributed to different a gas composition and the amount of catalyst used. Centi's work fed a quite a high concentration of NO(1.2 % NO ). Our study used 1.2 g. of catalyst while they used 0.3 g. The explanation of  $CO_2$  overshoot in this study could be the competitive adsorption between Cu/Na-ZSM-5 and Cu/H-ZSM-5. The appearance of NO forces  $CO_2$  on catalyst surface desorbs and a new balance of adsorption rates will be reached.  $NO_2$  was observed only in the experiment over Na-ZSM-5. NO and  $C_3H_8$  were not detected in the experiment over Cu/H-ZSM-5 and Cu/Na-ZSM-5. In the H-ZSM-5 experiment, after NO was added into the system,  $C_3H_8$  conversion increased enormously and a NO signal was not observed. This observation indicates that NO reduction proceeds readily over the H-ZSM-5 samples. NO reduction, however, is not able to account for the drop in  $C_3H_8$  concentration leaving the reactor or for the large increase in  $CO_2$  formation.

Even though the responses cannot be converted to concentrations because the IR signals were not calibrated, figure 5.39 can be analyzed by noting that the IR response at the low concentrations used will be proportional to concentration. Stoichiometry considerations that 3 moles of  $CO_2$  are formed per a mole of  $C_3H_8$

combusted mean that total oxidation of propane by  $O_2$  over the H-ZSM-5 sample must be promoted by the presence of NO in the reactor feed. Only this assumption can account for the response after NO introduction shown in figure 5.39. H-ZSM-5 is very active for NO oxidation by  $O_2$  (see figure 5.32). Thus, we speculate that NO oxidation proceeds through



With  $C_3H_8$  present the reactive O(ad) on the surface, results in combustion. This is in addition to  $O_2$  oxidation of the  $C_3H_8$  that probably occurs at a different surface site. The promotion of hydrocarbon oxidation by  $O_2$  is the presence of NO appears to be a new observation for zeolite catalysts.

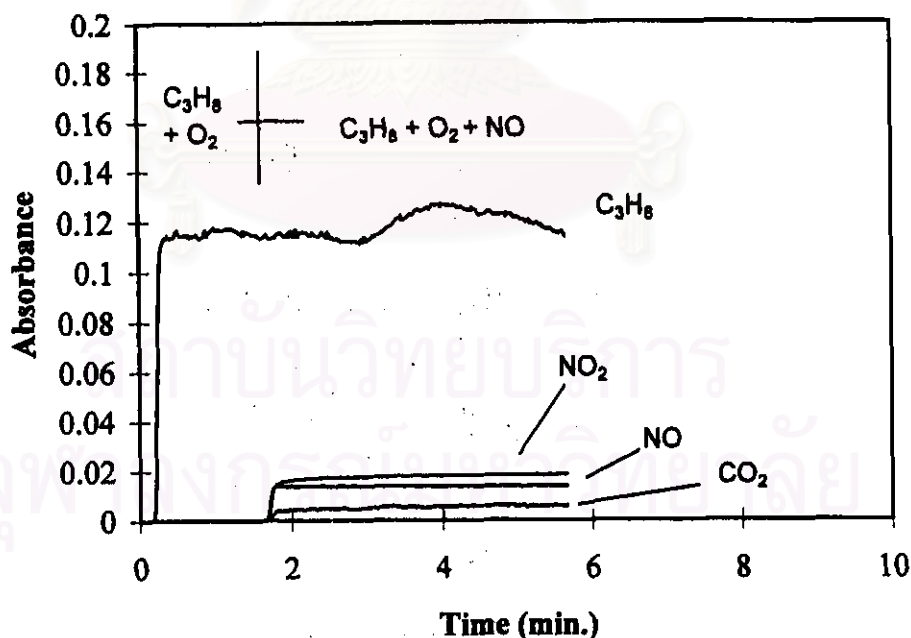


Figure. 5.37 Absorbance of gaseous species after switching from  $N_2$  to 0.4 %  $C_3H_8$  + 12 %  $O_2$  and then 0.5 % NO was added at time = 1.5 minutes at 350 °C without catalyst

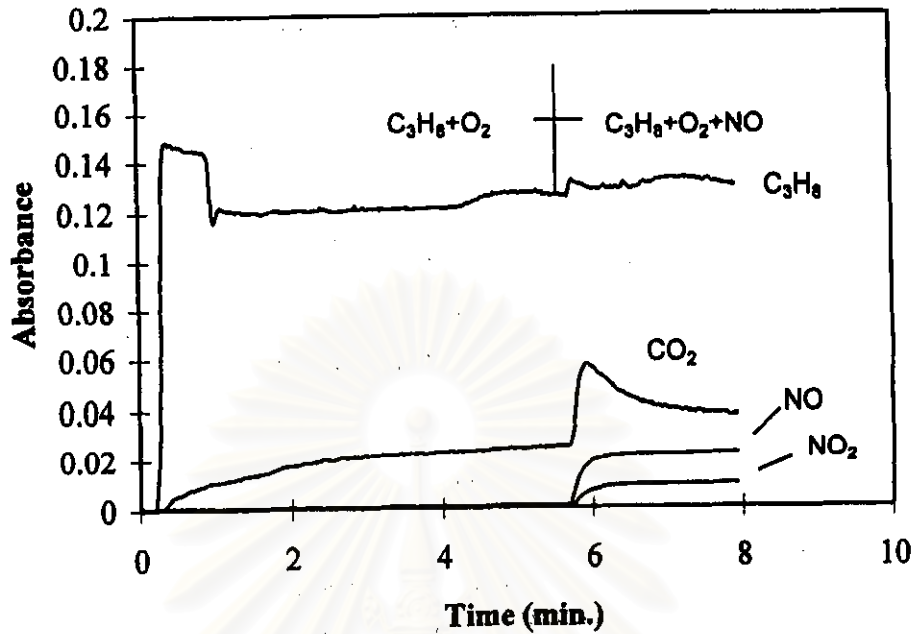


Figure. 5.38 Absorbance of gaseous species after switching from  $N_2$  to 0.4 %  $C_3H_8$  + 12 %  $O_2$  and then 0.5 %  $NO$  was added at time = 5.5 minutes at 350 °C over Na-ZSM-5

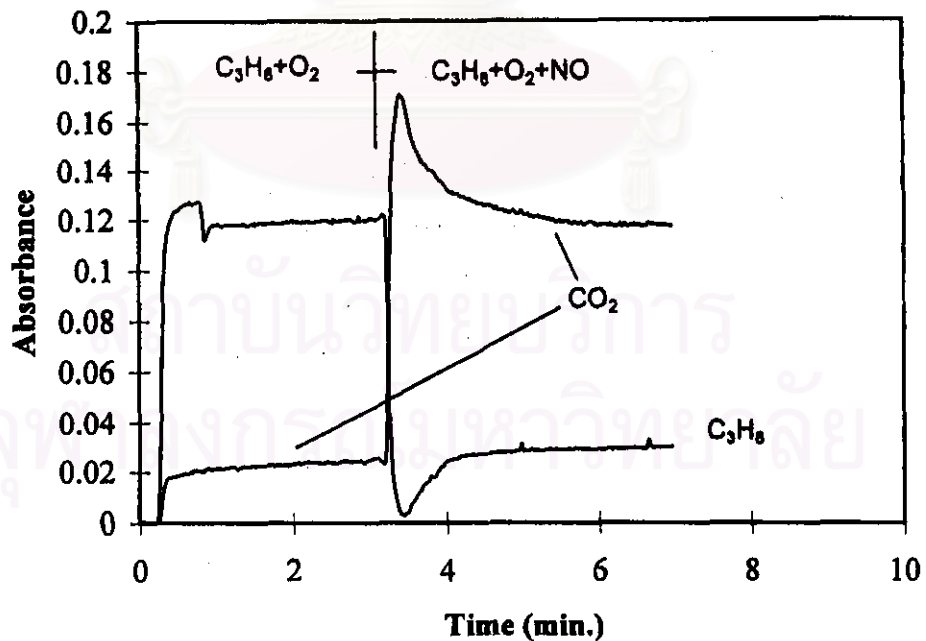


Figure. 5.39 Absorbance of gaseous species after switching from  $N_2$  to 0.4 %  $C_3H_8$  + 12 %  $O_2$  and then 0.5 %  $NO$  was added at time = 3.0 minutes at 350 °C over H-ZSM-5

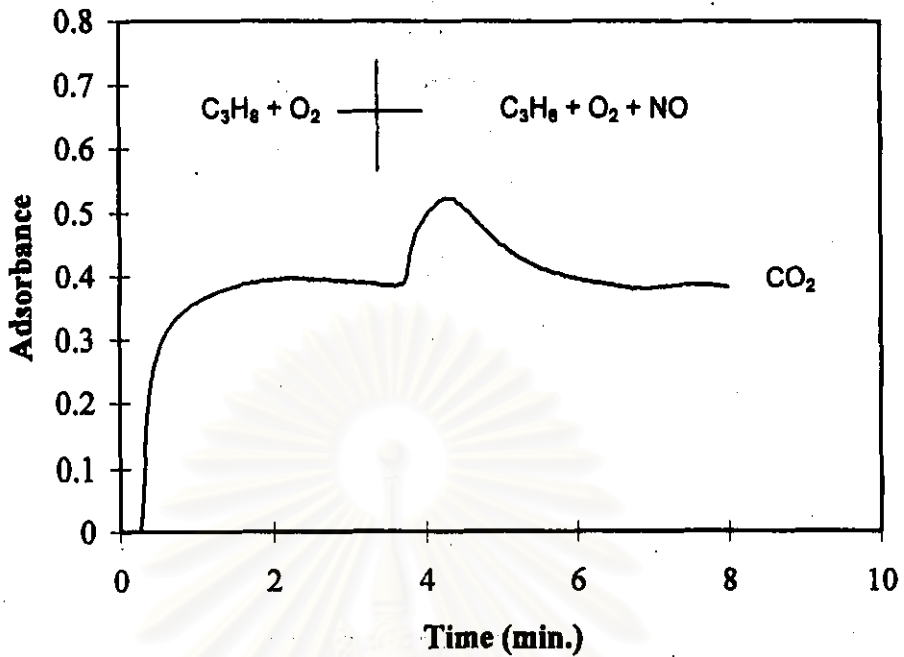


Figure. 5.40 Absorbance of gaseous species after switching from N<sub>2</sub> to 0.4 % C<sub>3</sub>H<sub>8</sub> + 12 % O<sub>2</sub> and then 0.5 % NO was added at time = 5.5 minutes at 350 °C over Cu/Na-ZSM-5

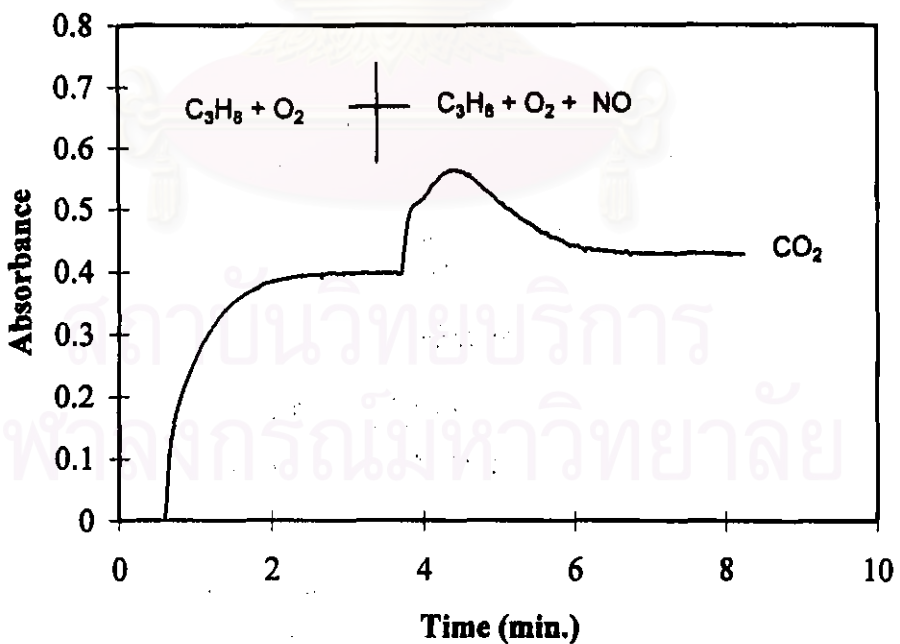


Figure. 5.41 Absorbance of gaseous species after switching from N<sub>2</sub> to 0.4 % C<sub>3</sub>H<sub>8</sub> + 12 % O<sub>2</sub> and then 0.5 % NO was added at time = 5.5 minutes at 350 °C over Cu/H-ZSM-5

The above results suggest no difference of apparent activity between Cu/Na-ZSM-5 and Cu/H-ZSM-5 for NO reduction with propane in excess oxygen as well as for NO oxidation. However, Cu/Na-ZSM-5 was found to be slightly more active than Cu/H-ZSM-5 in NO reduction in excess oxygen under steady state. This might be because of different conditions. These transient experiments used very low GHSV ( $\sim 2000 \text{ h}^{-1}$ ) compared with the steady state measurements in the previous section which used at GHSV  $\sim 12000 \text{ h}^{-1}$ . Also, in this experiments, NO reductions was complete over both Cu/H-ZSM-5 and Cu/Na-ZSM-5. Thus, any difference of both catalysts could not be seen.

On the contrary, the reaction are much slower with absence of oxygen. Cu/H-ZSM-5 was more active than Cu/Na-ZSM-5 for the NO reduction with propane in the absence of oxygen in both cases of  $\text{CO}_2$  production and NO consumption. Moreover, in the test with only NO in feed, Cu/H-ZSM-5 produced more  $\text{NO}_2$  but less  $\text{N}_2\text{O}$ .

The systems with and without hydrocarbon in the feed show the same result. There is no difference in activity between both catalysts in the  $\text{NO} + \text{C}_3\text{H}_8 + \text{O}_2$  system and the  $\text{NO} + \text{O}_2$  system. On the other hand, Cu/H-ZSM-5 appears to be more active in the NO reduction with propane in the absence of oxygen and in NO decomposition. This suggests that cations remaining in the zeolites is not involved in hydrocarbon activation or any mechanism of hydrocarbon interaction and coke formation.

From the NO decomposition result, Cu/H-ZSM-5 produces more  $\text{NO}_2$  than Cu/Na-ZSM-5 does.  $\text{NO}_2$  is one of the species which has been proposed to be a key intermediate of the SCR of NO by hydrocarbon[35, 46 - 51]. Thus, in the absence of oxygen reaction, Cu/H-ZSM-5 produces more  $\text{NO}_2$  and, subsequently, NO is more reduced by propane.

From the CO adsorption result in section 5.1, Cu/H-ZSM-5 has higher  $\text{Cu}^{1+}/\text{Cu}^{2+}$  ratio than Cu/Na-ZSM-5. There have been many reports mentioning about the role of  $\text{Cu}^{1+}$  active site for NO decomposition involving redox cyclic[70, 81, 83, 131] whereas  $\text{Cu}^{2+}$  has been proposed as an active site for NO reduction by hydrocarbon[3, 57, 133]. Since Cu/Na-ZSM-5 has more  $\text{Cu}^{2+}$  than Cu/H-ZSM-5, Cu/Na-ZSM-5 would be more active than Cu/H-ZSM-5 for the NO reduction with

propane in the presence of oxygen. This could be clearly seen in high GHSV tests. For the NO reduction in absence of oxygen, due to lack of oxygen, the first step of the reaction would be the NO direct decomposition to form O<sub>2</sub> and N<sub>2</sub>. Since Cu/H-ZSM-5 has more Cu<sup>1+</sup>, which is active for NO decomposition, than Cu/Na-ZSM-5, Cu/H-ZSM-5 would be more active than Cu/Na-ZSM-5 for NO decomposition. Therefore, the O<sub>2</sub> production, which would be the limitation step of NO reduction in the absence of oxygen, is more taken place in Cu/H-ZSM-5 system. Moreover, Cu/H-ZSM-5 system produces more NO<sub>2</sub> than Cu/Na-ZSM-5 because Cu/H-ZSM-5 has proton acidic sites which are active for NO oxidation whereas Cu/Na-ZSM-5 does not or has less. Cu<sup>1+</sup> may also participate in this reaction. Because Cu/H-ZSM-5 system produces more oxygen and NO<sub>2</sub>, This catalyst is more active in NO reduction in the absence of oxygen.

## **5.5 Characterization of Catalysts after Reaction Tests**

### **5.5.1 Coke formation**

Cu/H-ZSM-5 and Cu/Na-ZSM-5 used in the transient experiment of N<sub>2</sub> to NO + C<sub>3</sub>H<sub>8</sub> in the feed were tested to determine the coke deposition by Temperature-Programmed Oxidation(TPO) and the results are shown in figure 5.42. Only one peak of TPO curve was observed in the Cu/ZSM-5 zeolites. This is an outstanding character of these catalysts which differs from the typical catalysts for dehydrogenation. These always exhibit coke deposition. This TPO shape was also observed in the work of L.d'Iri[143]. Amount of carbonaceous deposited on Cu/Na-ZSM-5 was 0.065 % carbon/g. of cat. and on Cu/H-ZSM-5 it was 0.060 % carbon/g. of cat. Size and shape of TPO peaks as depicted in figure 5.42 of both catalysts are quite similar. Since both the amount and activity of coke formed over both catalysts surfaces are almost the same, it appears that the residual cations are not relevant to the coke formation and thus hydrocarbon activation.



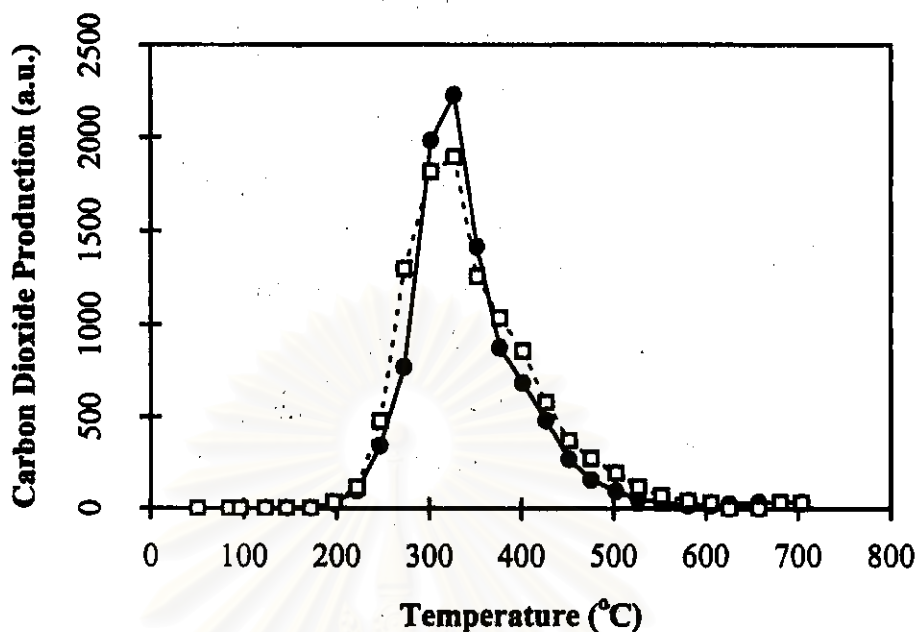


Figure 5.41 Temperature programmed oxidation of Cu/Na-ZSM-5 (—●—) and Cu/H-ZSM-5 (---□---) after pretreating with NO + C<sub>3</sub>H<sub>8</sub> at 400 °C for 1 hr.

### 5.5.2 Dealumination

Another explanation of the zeolite differences observed in our study is different extents of formation of Lewis acid sites through dealumination of the zeolite. This possibility was examined by carefully measuring alumina content of our zeolite samples. Figure 5.43 shows Al-NMR pattern of H-ZSM-5 and Cu/H-ZSM-5. Only one peak at around 50 ppm was observed in all samples. This peak is assigned to tetrahedral aluminum. The intensity of the peak was not reduced in spent catalysts. This indicates that the dealumination did not occur in this study. This is confirmed by Torre-A breu[92]. The dealumination of H-ZSM-5 and Cu/ZSM-5 was observed only in severely steamed samples[88, 93]. Therefore, the dealumination of catalyst is not involved in the different activities observed among the zeolites in this study.



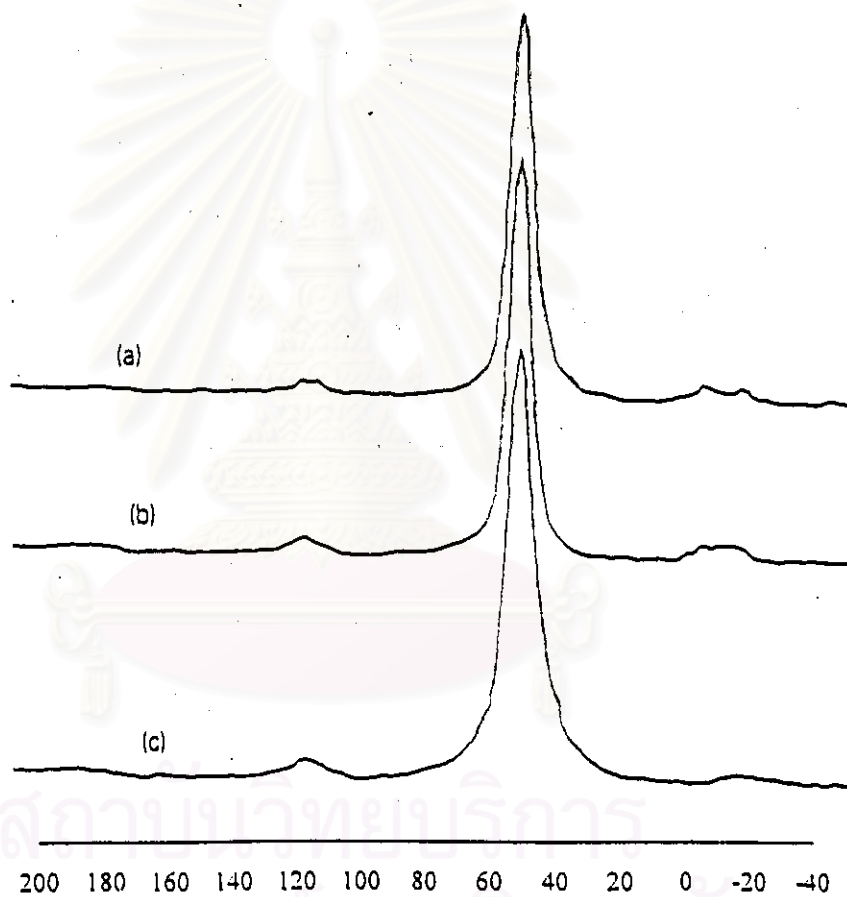


Figure 5.43 Al – NMR spectra of (a) H-ZSM-5, (b) spent H-ZSM-5 and (c) spent Cu/H-ZSM-5