CHAPTER V

RESULTS AND DISCUSSIONS

5.1 Characterization of the Catalyst

5.1.1 X-ray Diffraction Pattern

The X-ray diffraction patterns for the catalysts are shown in figure 5.1. The patterns of various catalysts prepared in this laboratory by quick method were almost the same as that of Mobil Oil Corporation [79]. This indicates that the metallosilicates also has the pentasil pore opening structure typical for the general metallosilicate catalysts, when compared the cation(Pt, Cu and Fe)-exchanged metallosilicate catalysts with the parent metallosilicates, the patterns of the cation-exchanged metallosilicate catalysts have the same crystalline structure, the pentasil pore-opening structure, as the parent metallosilicates. Consequently, the metal ion-exchange do not change structure of metallosilicates.

5.1.2 Specific Surface Area

BET surface areas of crystal are shown in figure 5.2. The surface area of all metal (Pt, Cu and Fe) ion-exchanged ZSM-5, Fe-silicates, and Cu-silicates were almost as large as that of parent H-form metallosilicates. This is consistent with the above-mentioned result that the XRD patterns of metal ion-exchanged H-form metallosilicates, Na-form ZSM-5, H-form ZSM-5, and NH_4-form ZSM-5 catalysts were almost the same as that of parent metallosilicates. The total surface area of catalyst was not affected by the metal loading on the catalyst.
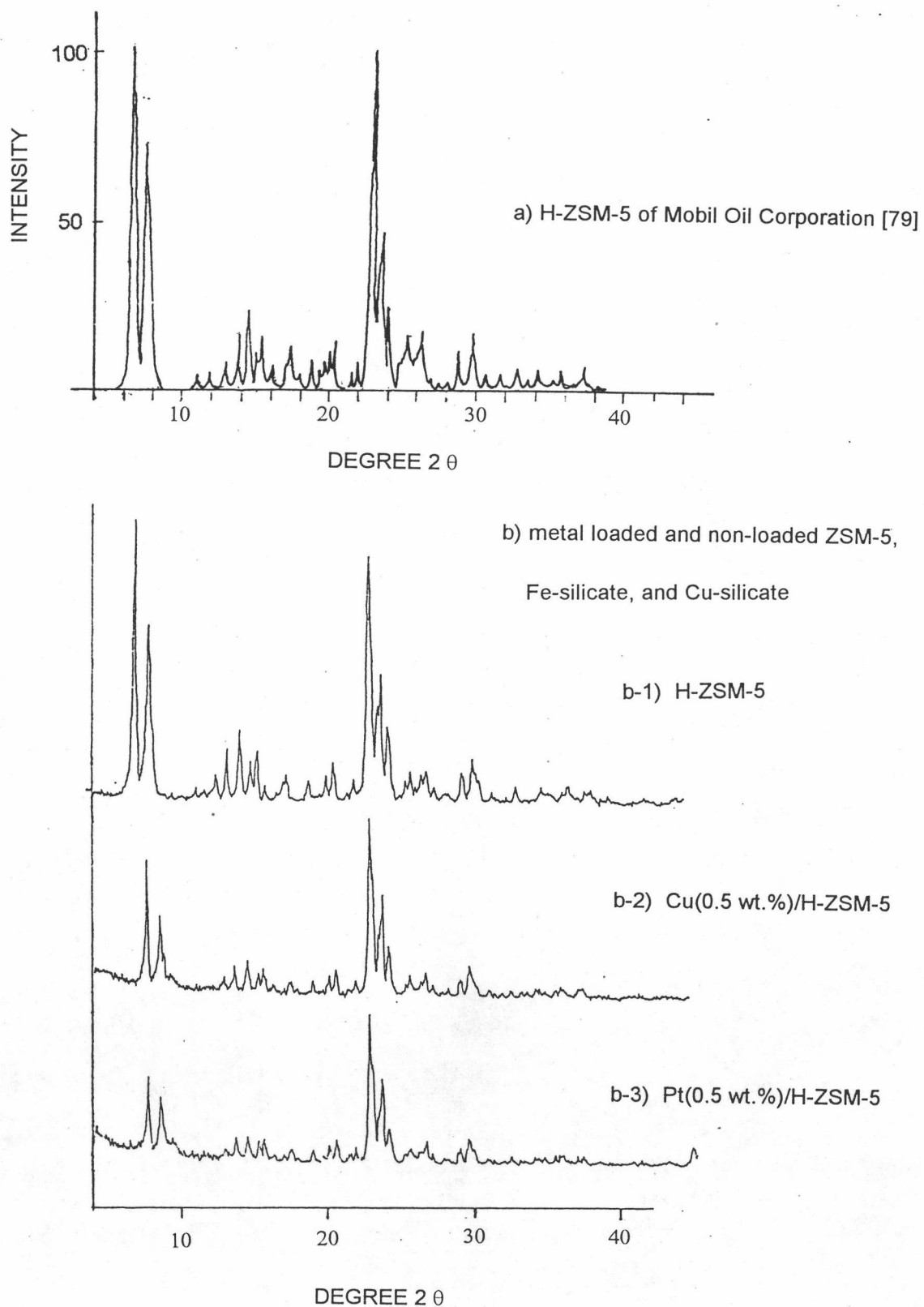
Figure 5.1 X-ray Diffration Patterns for

a) H-ZSM-5 of Mobil Oil Corporation [79]

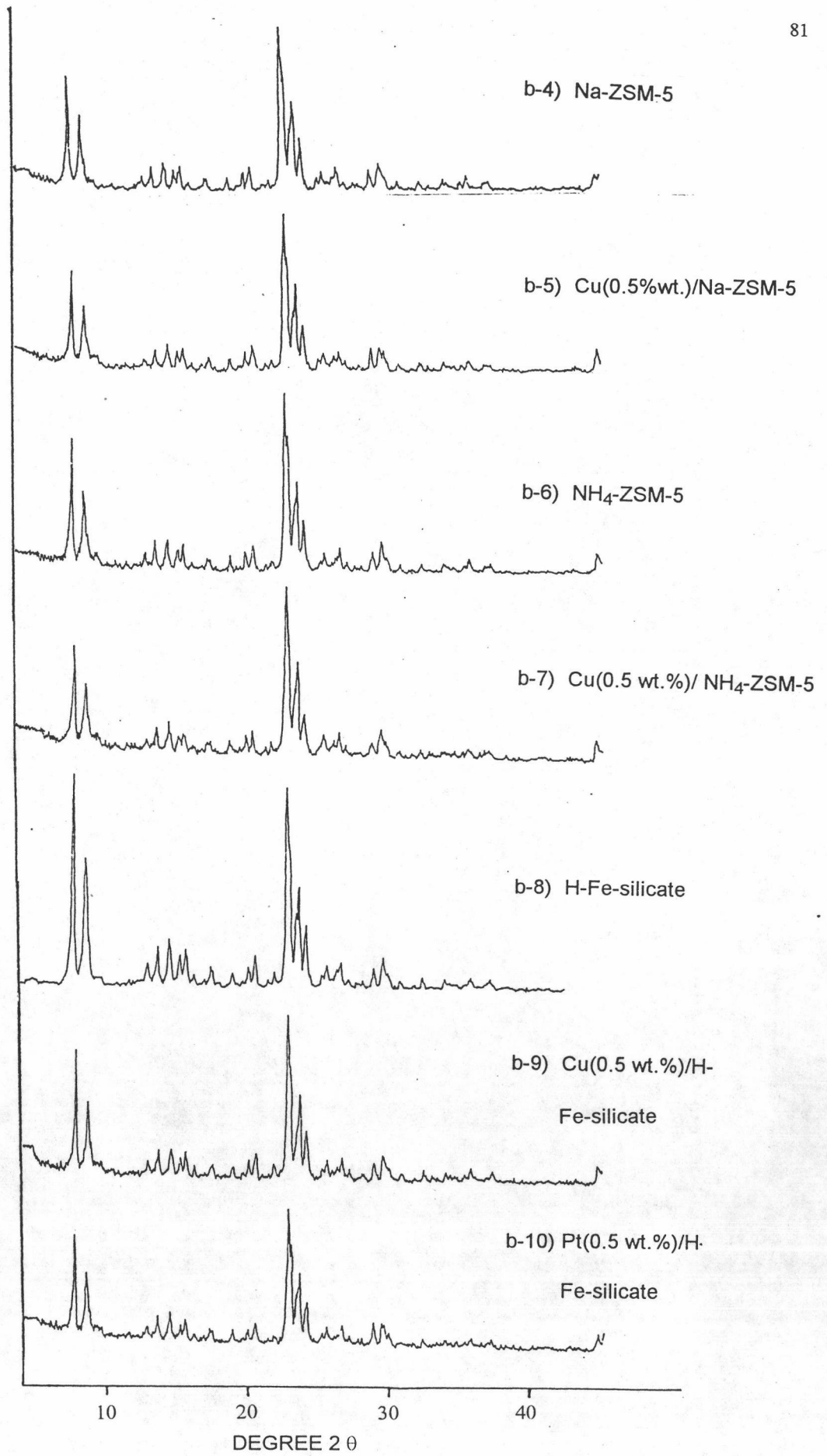b) metal loaded and non-loaded ZSM-5, Fe-silicate, and Cu-silicate

b-4) Na-ZSM-5

b-5) Cu(0.5%wt.)/Na-ZSM-5

b-6) NH$_4$-ZSM-5

b-7) Cu(0.5 wt.%)/ NH$_4$-ZSM-5

b-8) H-Fe-silicate

b-9) Cu(0.5 wt.%)/H-Fe-silicate

b-10) Pt(0.5 wt.%)/H-Fe-silicate

DEGREE 2 θ

Figure 5.1 continued

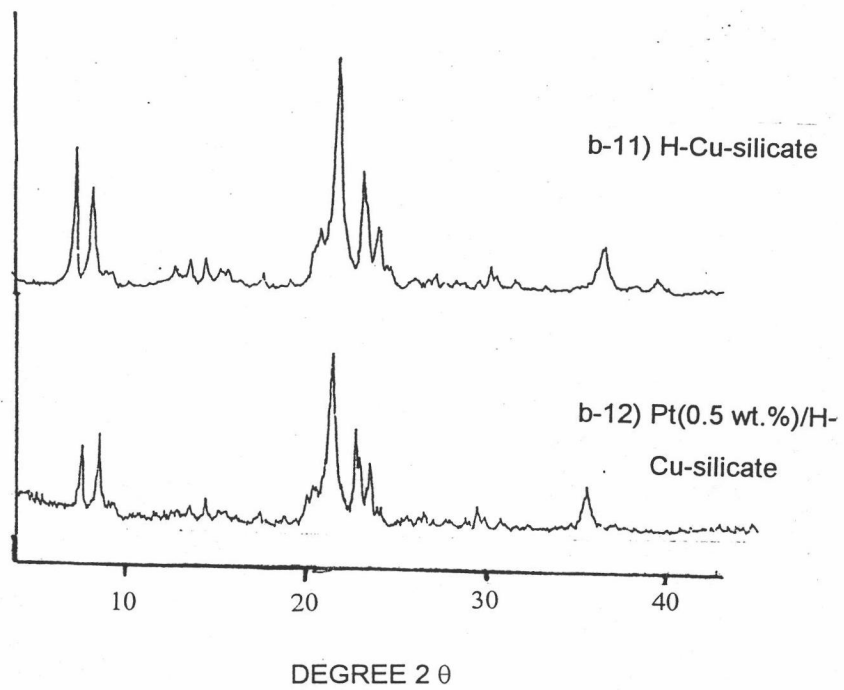b-11) H-Cu-silicate

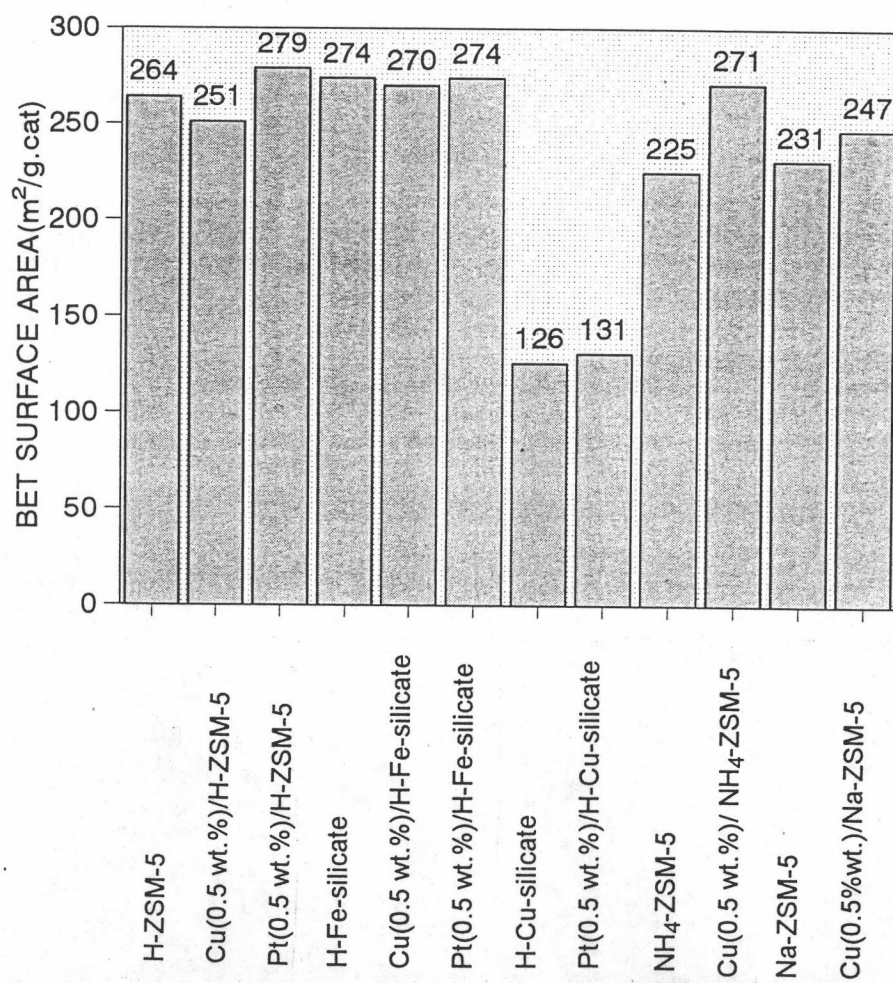b-12) Pt(0.5 wt.%)/H-Cu-silicate
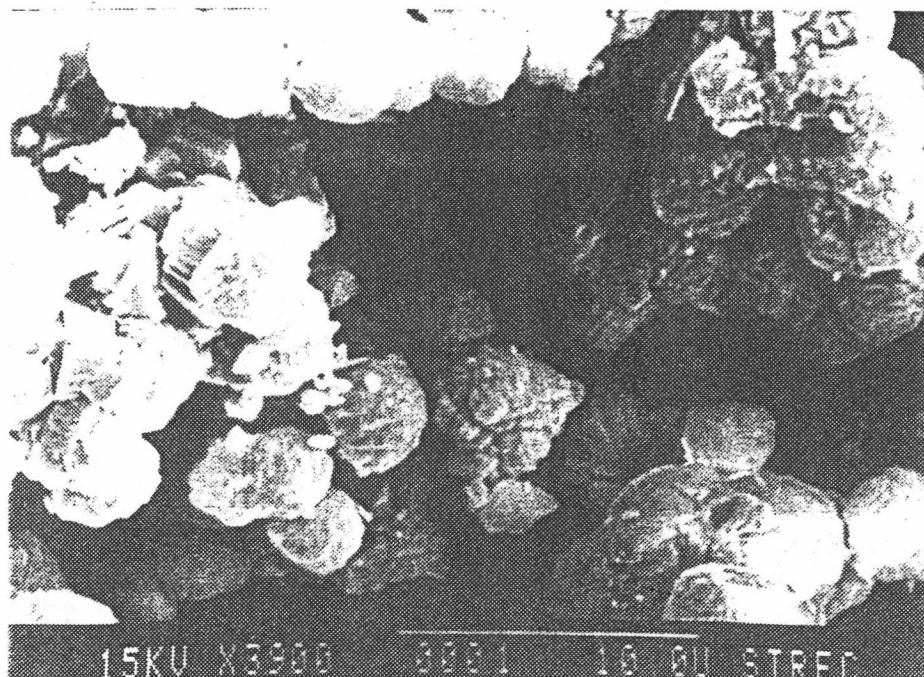
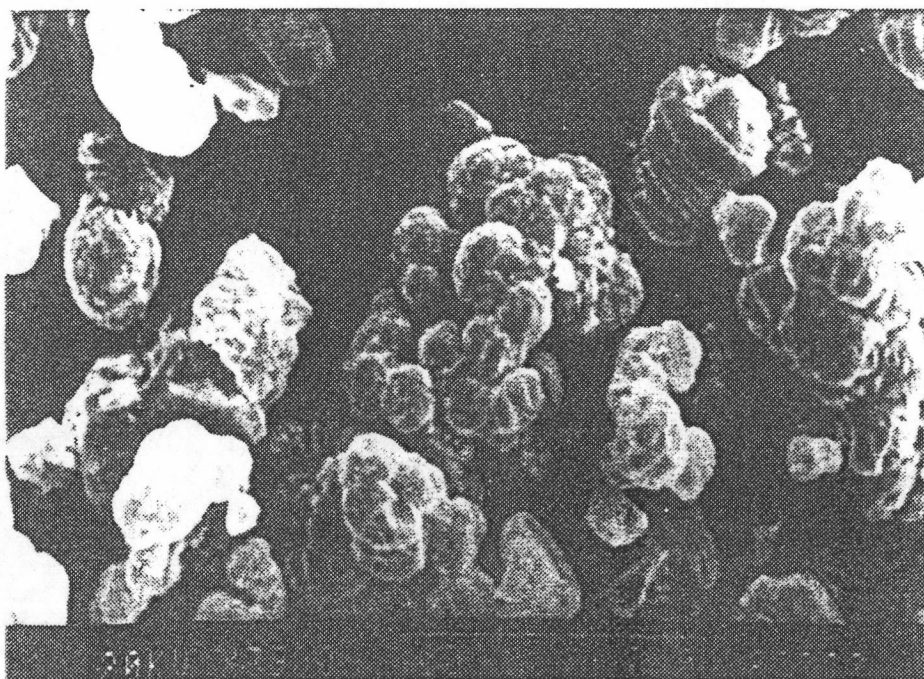DEGREE 2 θ

Figure 5.1 continued

Figure 5.2 BET surface areas of the catalysts.

a) H-ZSM-5

b) Cu(0.5 wt.%)/H-ZSM-5
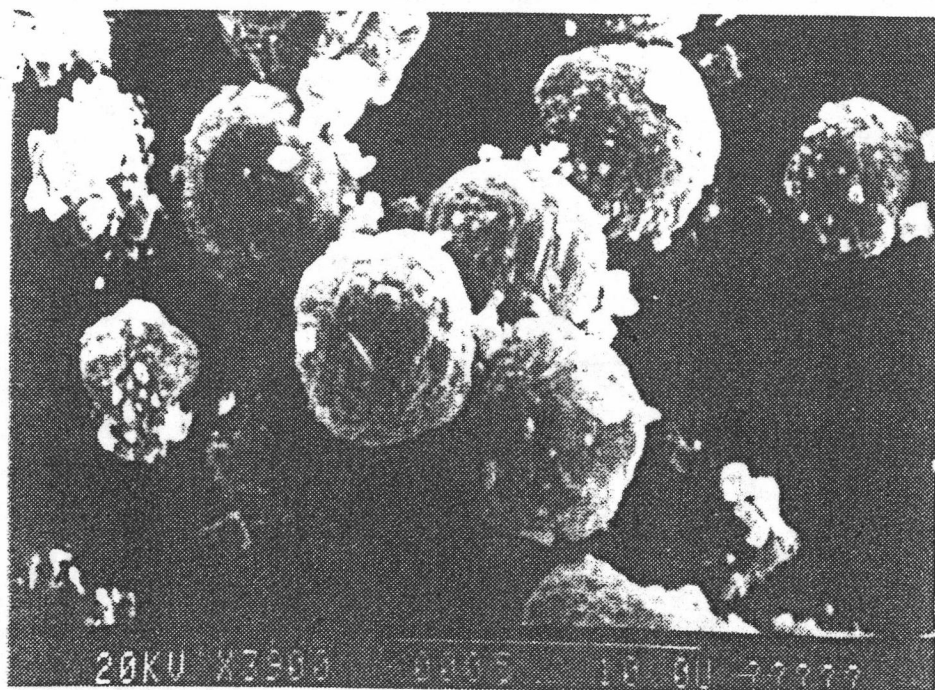
Figure 5.3 SEM photographs of metal loaded and non-loaded ZSM-5, Fe-silicate, and Cu-

silicate

c) Pt(0.5 wt.%)/H-ZSM-5

d) Na-ZSM-5

Figure 5.3 continued
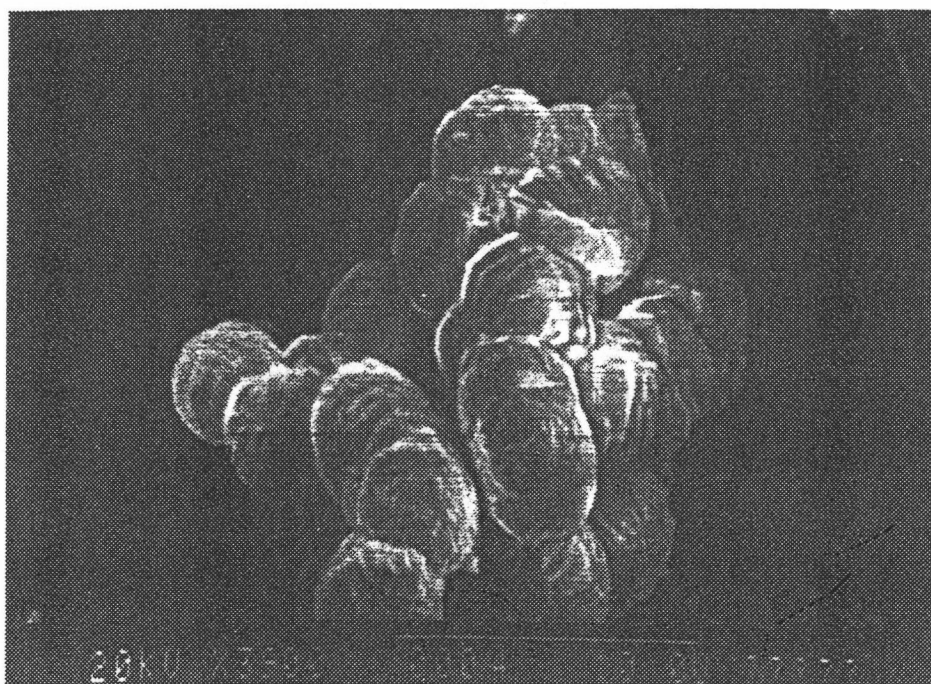
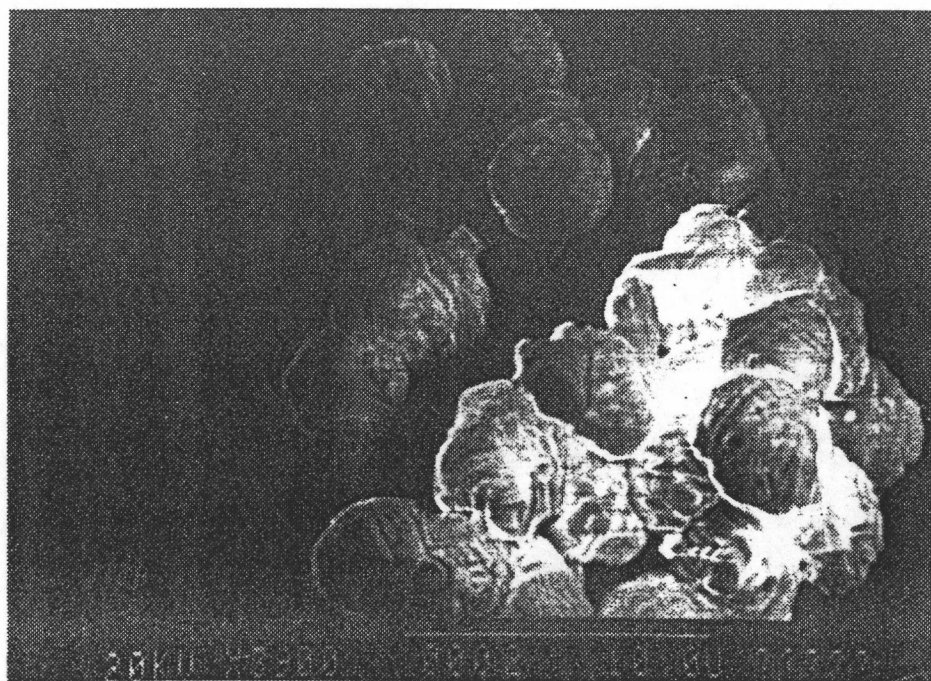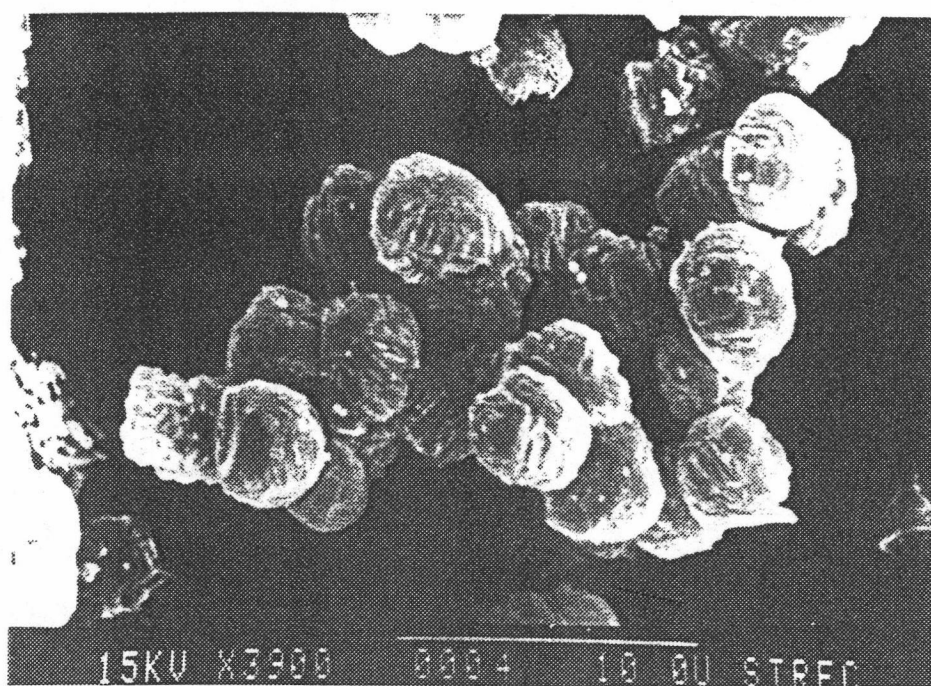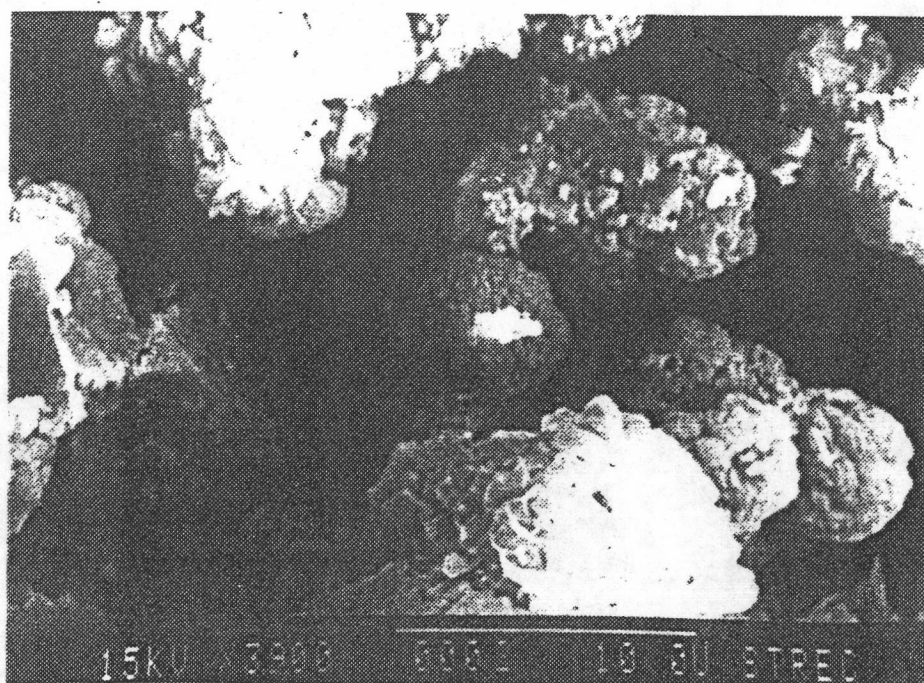e) Cu(0.5%wt.)/Na-ZSM-5

f) NH$_4$-ZSM-5
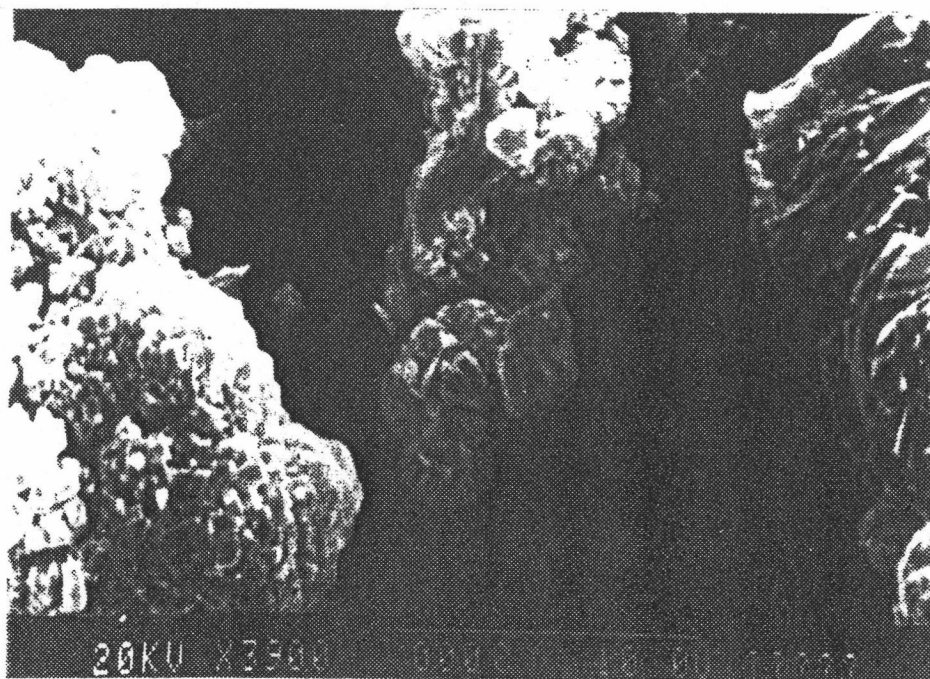
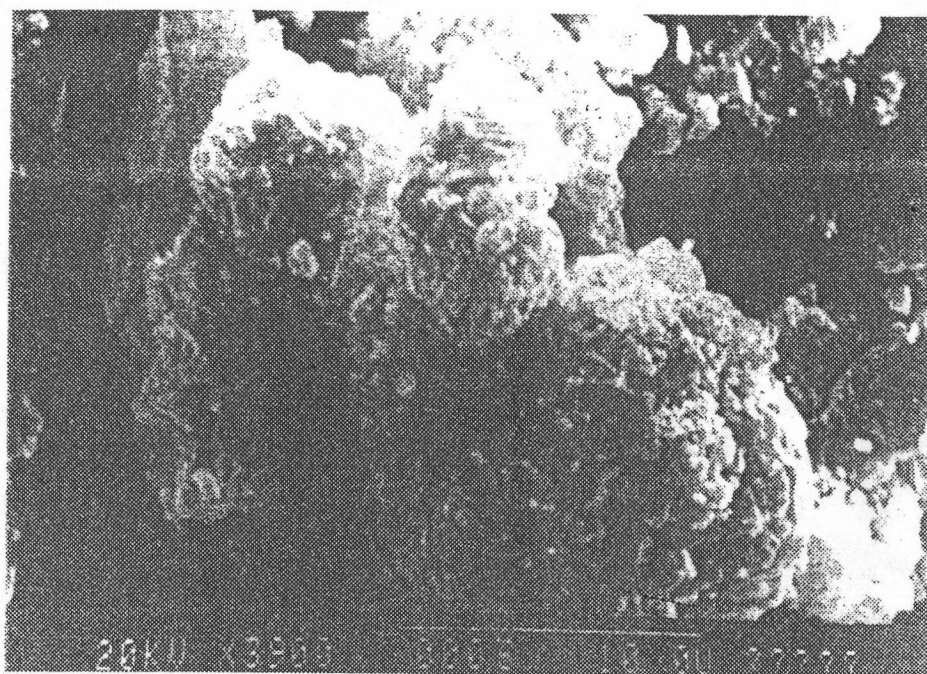Figure 5.3 continued

g) Cu(0.5 wt.%)/ NH$_4$-ZSM-5
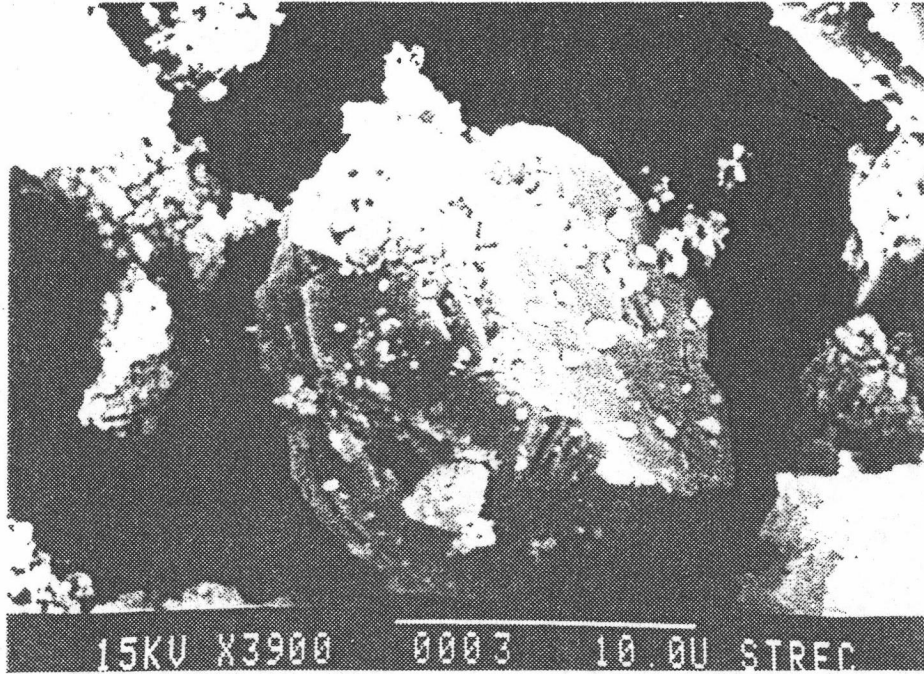

h) H-Fe-silicate

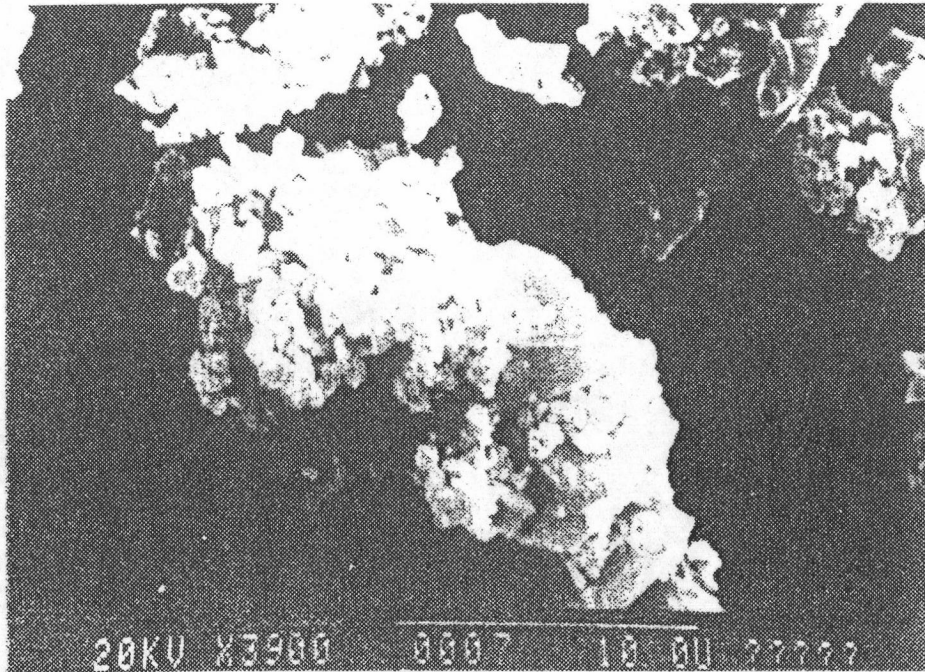Figure 5.3 continued

i) Cu(0.5 wt.%)/H-Fe-silicate

j) Pt(0.5 wt.%)/H-Fe-silicate

Figure 5.3 continued

k) H-Cu-silicate

l) Pt(0.5 wt.%)/H-Cu-silicate

Figure 5.3 continued
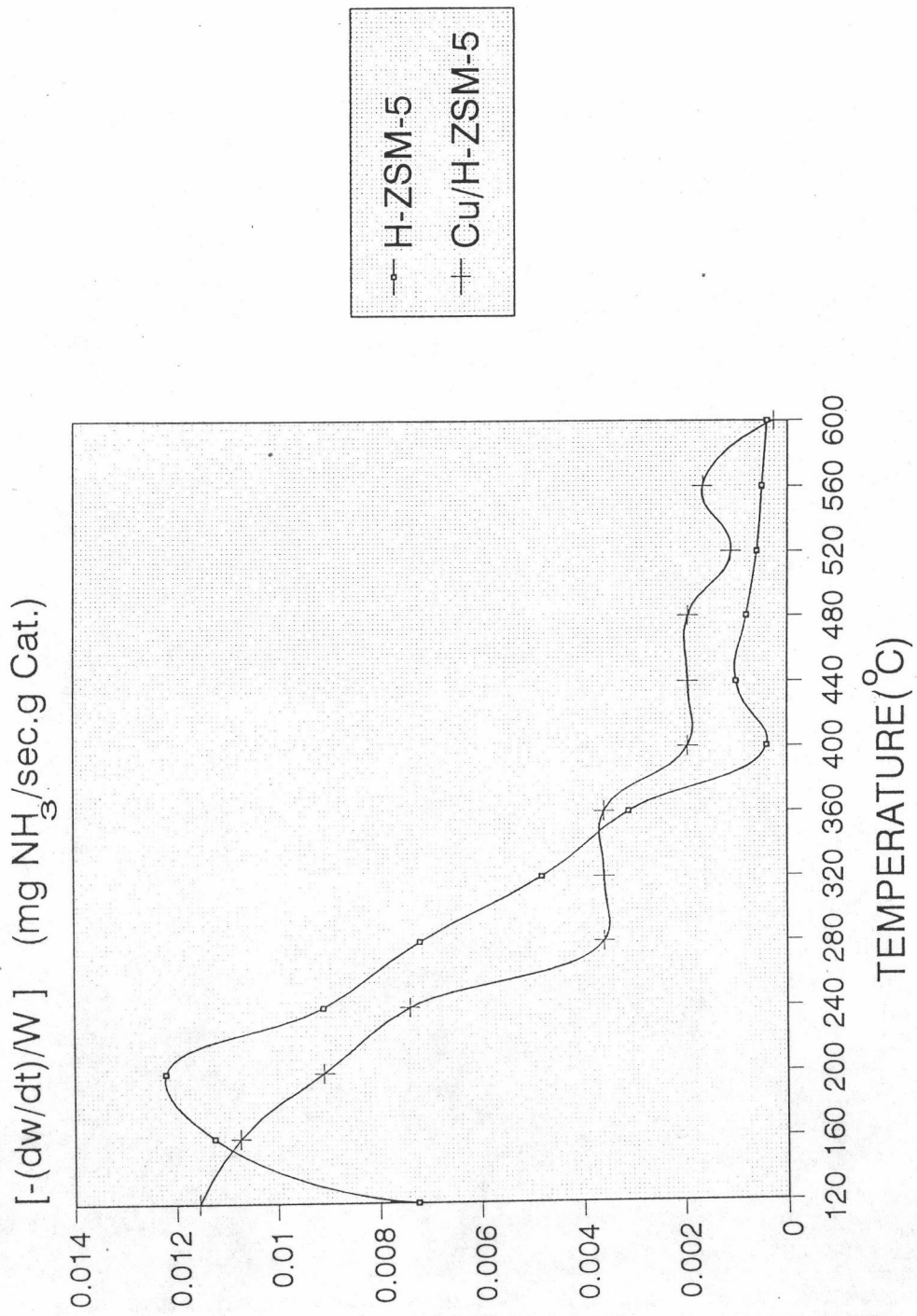
Figure 5.4 TPD profile of desorbed NH_3 form H-ZSM-5, and Cu/H-ZSM-5.

5.1.3 Morphology

Figure 5.3 shows the photographs of the scanning electron microscope of the morphology of the metal loaded and non-loaded(Pt, Cu and Fe) catalysts were identical with the parent H-form, Na-form and NH_4-form ZSM-5, and H-form metallosilicates and conformed to their characteristics of catalysts on 5.1 and 5.2.

5.1.4 Acidity

Figure 5.4 shows the TPD profile of desorbed NH_3 from Cu loaded and non-loaded catalysts. The profile of H-ZSM-5 is composed of two peaks, i.e., a high temperature peak of strong acid sites and a low temperature peak of weak acid sites [80-83]. The separation of high temperature and low temperature peaks was made at 300 ºC. For strong acid sites, the amount of the acid site of Cu loading on H-ZSM-5 were lower than the parent H-ZSM-5 catalyst, weak acid sites were higher than the parent H-ZSM-5 catalyst. This indicates that the strong acid sites from the parent H-ZSM-5 catalyst were decreased by the copper loading on H-ZSM-5 and catalyst.

5.2 Effect of Cation-exchange of H-ZSM-5 ,H-Fe-silicate, and H-Cu-silicate using Copper and Platinum on Selective Reduction of NO by propane in Oxidizing Atmosphere.

The experimental results of propane oxidation by the present catalysts are summarized in table 5.1 and 5.2 along with those of selective reduction of NO by propane. Table 5.3 shows the amount of platinum contents on various catalysts which were measured by ICPS method. The data from the table indicates that the platinum contents of platinum ion-exchanged zeolite and metallosilicates which were prepared by using ratio of Pt/ catalyst

= 0.005. The amount of copper contents on various catalysts which were measured by AAS method, as shown in table 5.4. The data from the table shows the amount of copper contents of copper ion-exchanged zeolite and metallosilicates which were prepared by using ratio of Cu/catalyst = 0.005.

Table 5.1 Catalytic activities for the oxidation of propane .

No.	Catalyst	Conversion of C_3H_8 to CO, CO_2 (%)													
		150 °C			200 °C			250 °C			300 °C			350 °C		
		CO	CO_2	C_3H_8	CO	CO_2	C_3H_8	CO	CO_2	C_3H_8	CO	CO_2	C_3H_8	CO	CO_2	C_3H_8
1	H-ZSM-5	0	3.96	3.96	0.84	6.61	7.46	4.54	9.46	13.99	7.74	13.29	21.03	0.2	45.55	45.75
2	Cu/HZSM-5	0	0	0	0.13	4.13	4.25	3.79	8.94	12.73	12.1	14.02	26.13	22.06	28.18	50.24
3	Pt/H-ZSM-5	0	3.7	3.7	0	24.4	24.4	0	65.07	65.07	0	100	100	0	100	100
4	H-Fe-silicate	0	10.81	10.81	0.84	7.58	8.42	22.34	31.6	53.94	51.31	37.74	89.05	16.27	80.33	96.6
5	Cu/Fe-silicate	0	4.93	4.93	0.96	13.01	13.98	15.16	29.81	44.97	38.64	50.81	89.45	1.2	100	100
6	Pt/H-Fe-silicate	0	13.84	13.48	0	21.55	21.55	0	67.25	67.25	0	100	100	0	100	100
7	H-Cu-silicate	0	0	0	0	0	0	0	1.96	1.96	0	3.97	3.97	0	7.04	7.04
8	Pt/H-Cu-silicate	0	3.96	3.96	0.84	6.61	7.46	4.54	9.46	13.99	7.74	13.29	21.03	0.2	45.55	45.75

table 5.1 continued

No.	Catalyst	400 °C			450 °C			500 °C			550 °C			600 °C		
		CO	CO_2	C_3H_8	CO	CO_2	C_3H_8	CO	CO_2	C_3H_8	CO	CO_2	C_3H_8	CO	CO_2	C_3H_8
1	H-ZSM-5	0.52	64.99	65.51	0	79.48	79.48	0	91.4	91.4	0	100	100	0	100	100
2	Cu/HZSM-5	31.66	32.86	64.52	15.14	56.59	71.73	3.15	76.6	79.75	0	100	100	0	100	100
3	Pt/H-ZSM-5	0	100	100	0	100	100	0	100	100	0	100	100	0	100	100
4	H-Fe-silicate	4.44	95.56	100	0	100	100	0	100	100	0	100	100	0	100	100
5	Cu/Fe-silicate	0	100	100	0	100	100	0	100	100	0	100	100	0	100	100
6	Pt/H-Fe-silicate	0	100	100	0	100	100	0	100	100	0	100	100	0	100	100
7	H-Cu-silicate	0	13.95	13.95	0	24.09	24.09	0	49.72	49.72	0	100	100	0	100	100
8	Pt/H-Cu-silicate	0.52	64.99	65.51	0	79.48	79.48	0	91.4	91.4	0	100	100	0	100	100

Table 5.2 Catalytic activities for the selective reduction of NO by propane.

No.	Catalyst	Conversion of NO to N_2 (%)								
		150 °C	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C	500 °C	550 °C	600 °C
1	H-ZSM-5	8.21	14.06	48.18	91.11	84.65	83.89	76.9	68.85	9.88	9.5
2	Cu/HZSM-5	0	7.3	38.45	52.97	72.11	68.01	61.32	61.02	31.08	5.62
3	Pt/H-ZSM-5	10.18	12.92	18.09	15.88	12.23	10.11	13.53	3.88	2.58	3.5
4	H-Fe-silicate	0	20.37	83.29	99.22	42.4	25.38	14.67	13.07	15.58	8.43
5	Cu/Fe-silicate	0	23.56	67.71	81.31	48.03	22.27	13.6	11.78	10.56	8.43
6	Pt/H-Fe-silicate	15.12	17.4	29.86	21.43	6	2.74	3.34	2.36	4.86	5.78
7	H-Cu-silicate	3.8	0	1.82	2.28	1.06	3.04	8.05	10.64	9.88	3.12
8	Pt/H-Cu-silicate	10.18	12.92	18.09	15.88	12.23	10.11	13.53	3.88	2.58	3.5

Table 5.3 The platinum contents of various catalysts which were measured by
          ICPS method.

Catalyst sample	Platinum salt used (0.5 wt. %)	Metal containing method	Platinum contents (Ion-exchanged Pt (wt.%))
Pt/H-ZSM-5	$Pt(NH_3)_4Cl_2 \cdot H_2O$	ion-exchanged	0.3583
Pt/H-Fe-silicate	$Pt(NH_3)_4Cl_2 \cdot H_2O$	ion-exchanged	0.4485
Pt/H-Cu-silicate	$Pt(NH_3)_4Cl_2 \cdot H_2O$	ion-exchanged	0.2149

Table 5.4 The metal contents of various catalysts which were measured by AAS method.

Catalyst sample	Metal salt used	Metal containing method	Metal contents (Ion-exchange metal) (wt.%))
Cu/H-ZSM-5	$Cu(NO_3)_2 \cdot 3H_2O$	ion-exchanged	Cu = 0.0135
Cu/H-Fe-silicate	$Cu(NO_3)_2 \cdot 3H_2O$	ion-exchanged	Cu = 0.0075
H-Cu-silicate	$Cu(NO_3)_2 \cdot 3H_2O$	incorporated	Cu = 0.295
H-Fe-silicate	$Fe(NO_3)_3 \cdot 9H_2O$	incorporated	Fe = 3.350
Fe/H-ZSM-5	$Fe(NO_3)_3 \cdot 9H_2O$	ion-exchanged	Fe = 0.1440

Table 5.3 shows the amount of platinum contents on various catalysts which was measured by ICPS method. The data from the table represents the platinum contents of platinum ion-exchanged zeolite and metallosilicates which was prepared by using ratio of Pt/catalyst = 0.005.

5.2.1 Effect of Cation-exchange of H-ZSM-5 Using Copper and Platinum on Selective Reductive NO by propane in Oxidizing Atmosphere.

H-ZSM-5, Cu/H-ZSM-5, and Pt/H-ZSM-5 showed catalytic activities for oxidation of propane to CO and CO_2 as shown in table 5.1, and for propane conversion shown in figure 5.6. The conversion propane to CO_x almost 100% at 550 ºC for H-ZSM-5 and Cu/H-ZSM-5, at 350 ºC for Pt/H-ZSM-5. The catalytic activities in NO conversion are shown in figure 5.5.

Figure 5.5 Temperature Dependence of NO Conversion on various Cation-exchanged H-

ZSM-5 Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 % O_2, and balanced He,

GHSV = 4000 h^{-1}.

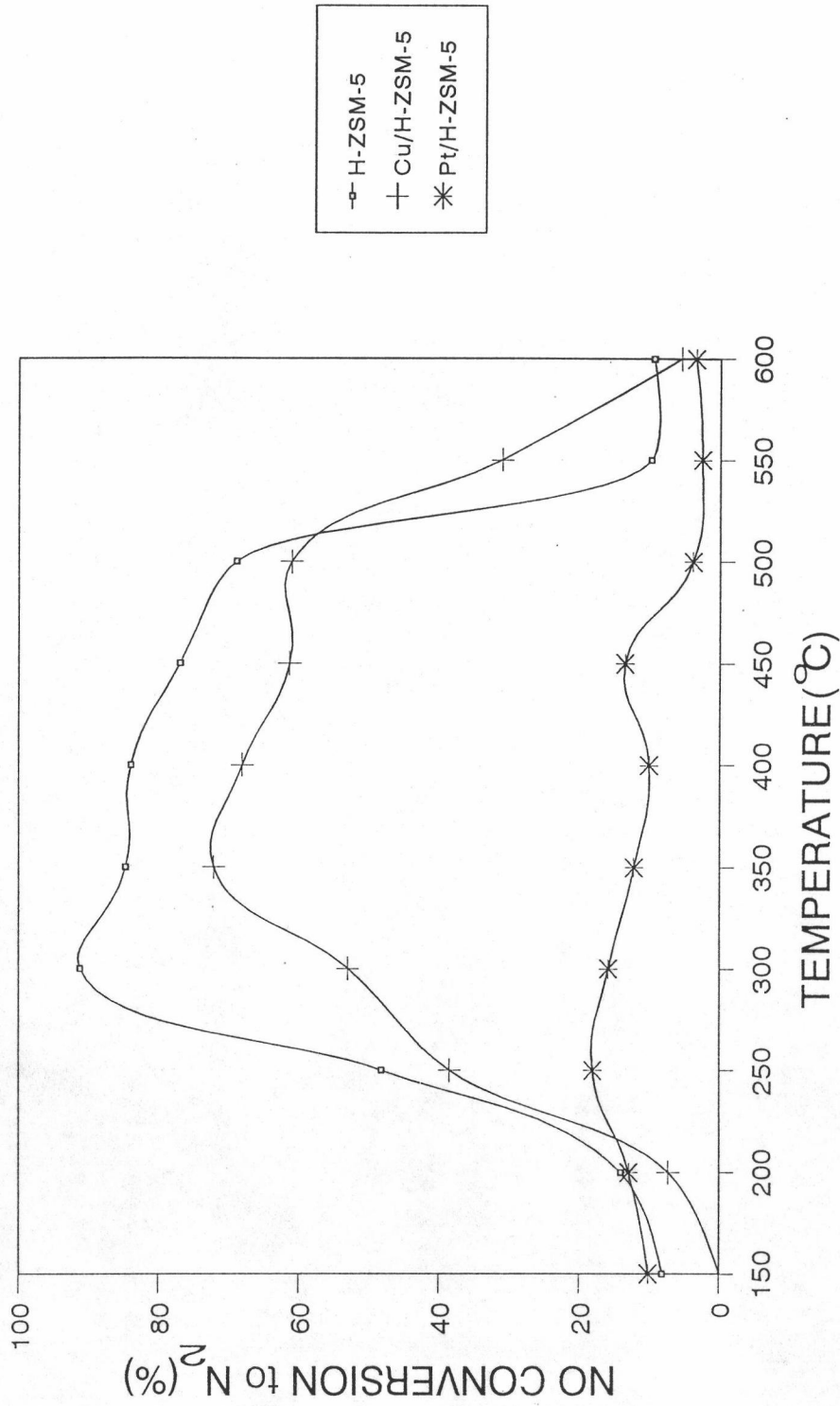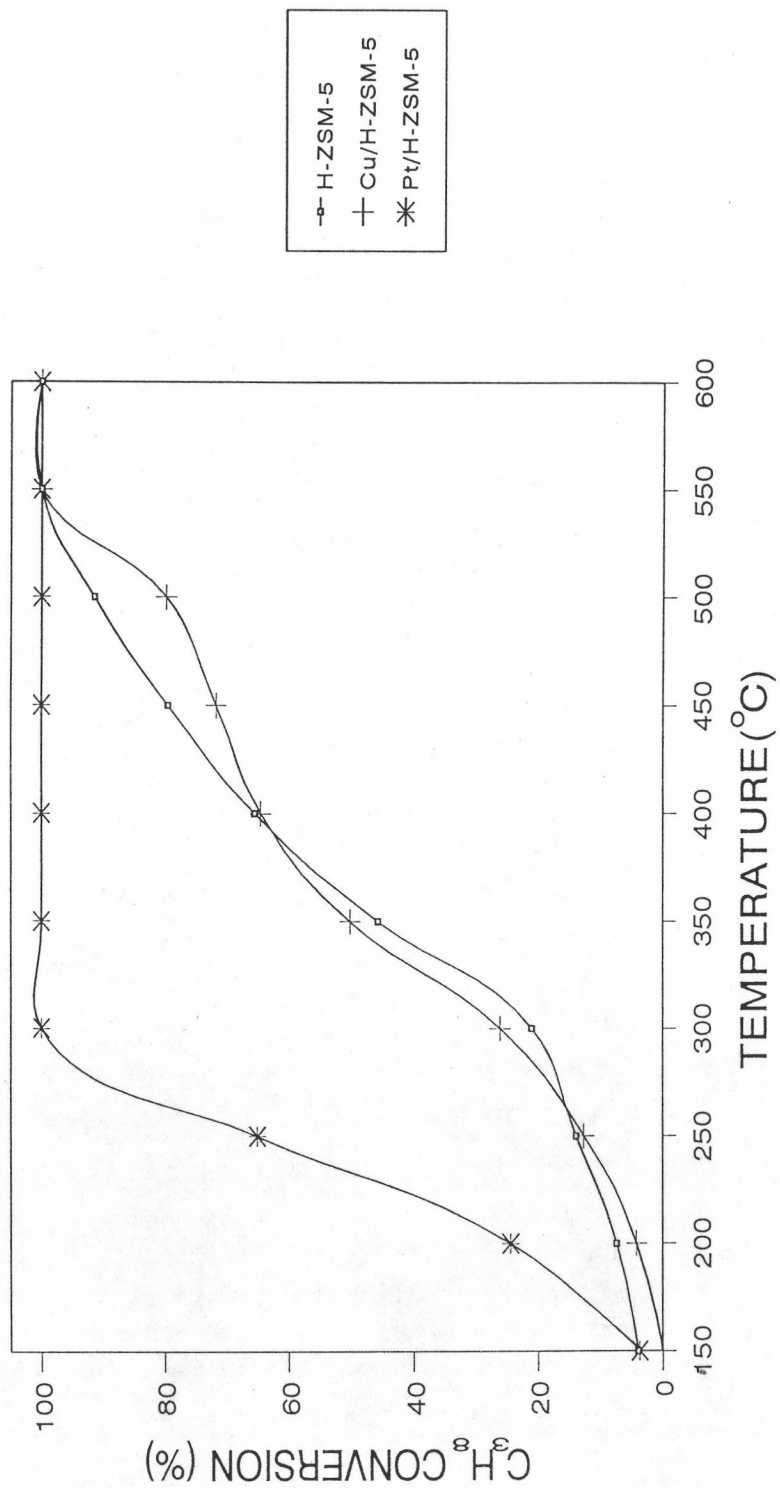Figure 5.6 Temperature Dependence of Propane Conversion on various Cation-exchanged

H-ZSM-5 Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced He,

GHSV = 4000 h^{-1}.

H-ZSM-5 catalyst showed the highest activity in NO conversion. The order of activity for NO reduction at 300 ºC was as follows, H-ZSM-5 > Cu/H-ZSM-5 > Pt/H-ZSM-5.

5.2.2 Effect of Cation-exchange of H-Fe-silicates Using Copper and Platinum on Selective Reduction NO by Propane in Oxidizing Atmosphere.

Effect of temperature on the conversion of NO to N_2 and propane to CO and CO_2 conversion by protonated Fe-silicate, Cu/H-Fe-silicate, and Pt/H-Fe-silicate, respectively are shown in figure 5.7 - 5.8. H-Fe-silicate and Cu/H-Fe-silicate exhibited activities for both NO conversion and propane combustion at above 150 ºC, and attained their maximum NO conversion, 99.3% at 300 ºC and 81.3% at 300 ºC, respectively. The catalytic activity for NO conversion of Pt/H-Fe-silicate showed at 150-600 ºC and achieved maximum conversion 29.9% at 250 ºC. The peaks of NO conversions on H-Fe-silicate, and Cu/H-Fe-silicate were higher than Pt/H-Fe-silicate. The propane combustion on H-Fe-silicate and Cu/H-Fe-silicate began to increase above 150 ºC and reached to constant level(100%) at 350 ºC. As for Pt/H-Fe-silicate, propane combustion activity was highest; at 300 ºC conversion and attained the constant level(100%).

5.2.3 Effect of Cation-exchange of H-Cu-silicate Using Platinum on Selective Reduction of NO by Propane in Oxidizing Atmosphere.

The temperature dependence of NO conversion and propane combustion on H-Cu-silicate and Pt/H-Cu-silicate are shown in figure 5.9 and 5.10, respectively. The NO conversion on H-Cu-silicate was higher compared with that on Pt/H-Cu-silicate. On the other hand, the catalytic activity for propane combustion on Pt/H-Cu-silicate was higher.

Figure 5.7 Temperature Dependence of NO Conversion on various Cation-exchenged H-Fe-silicate Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced He, GHSV = 4000 h^{-1}.

Figure 5.8 Temperature Dependence of Propane Conversion on various Cation-exchanged

H-Fe-silicate Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 % O_2, and balanced
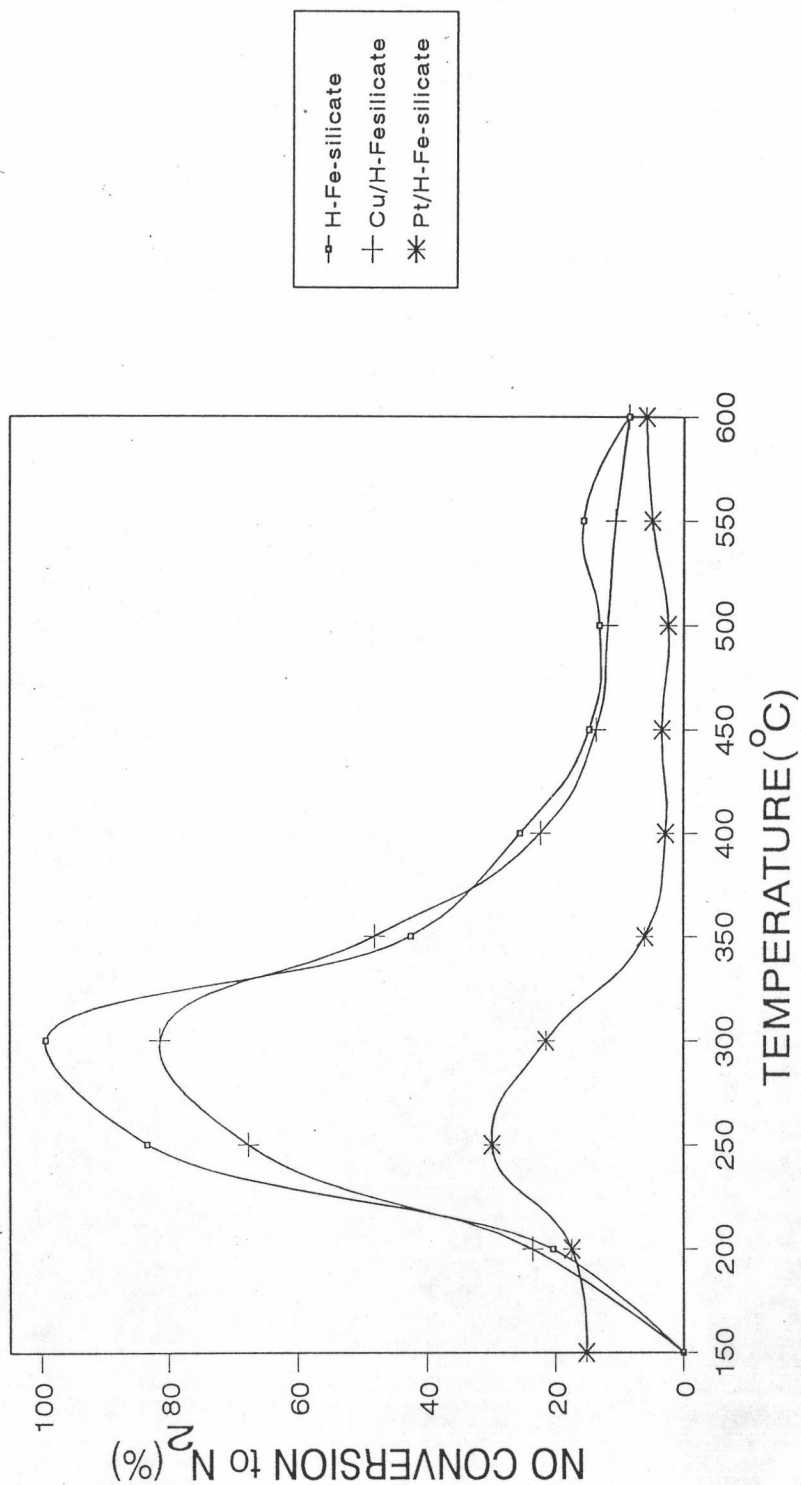
He, GHSV = 4000 h^{-1}.

Figure 5.9 Temperature Dependence of NO Conversion on various Cation-exchenged H-Cu-silicate Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced He, GHSV = 4000 h^{-1}.
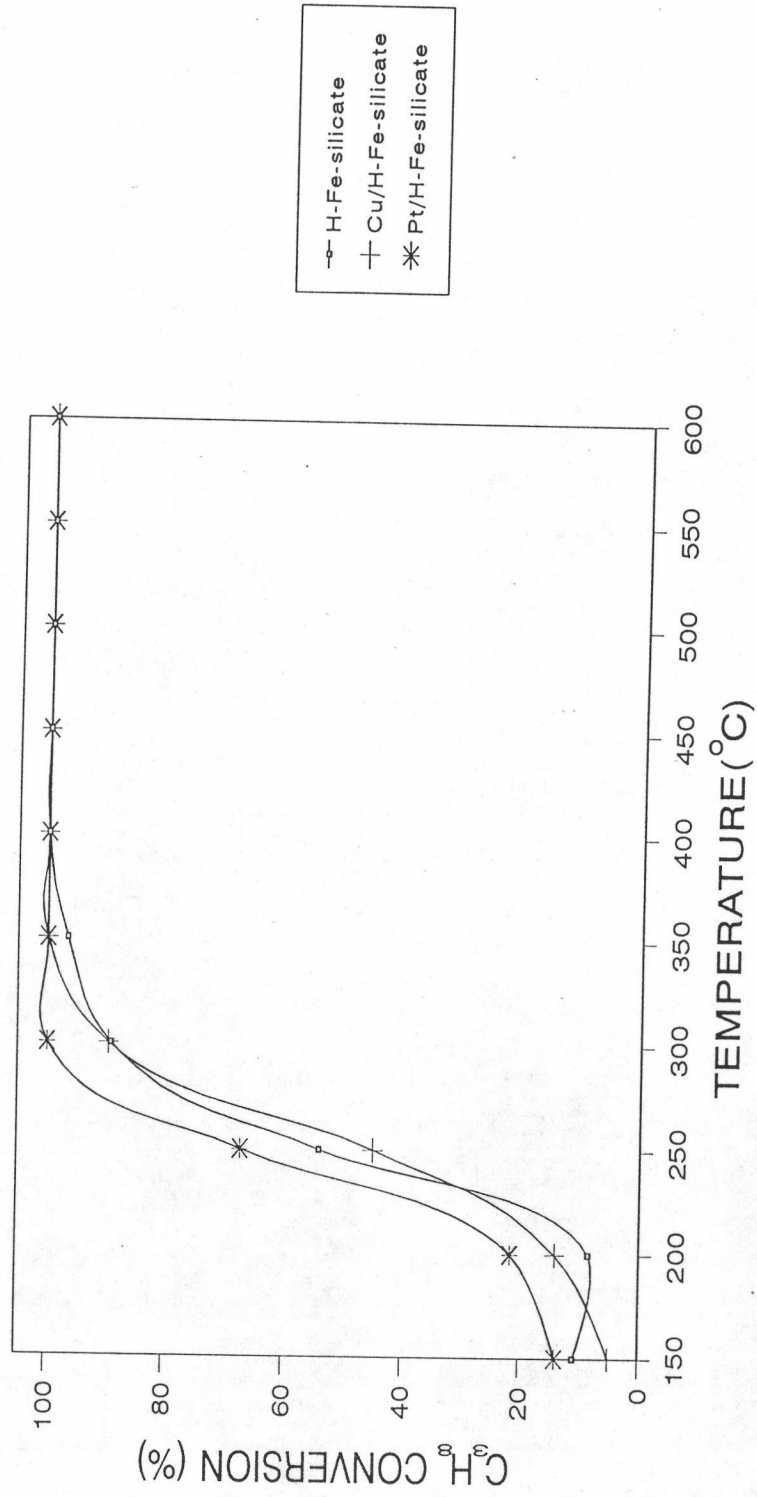
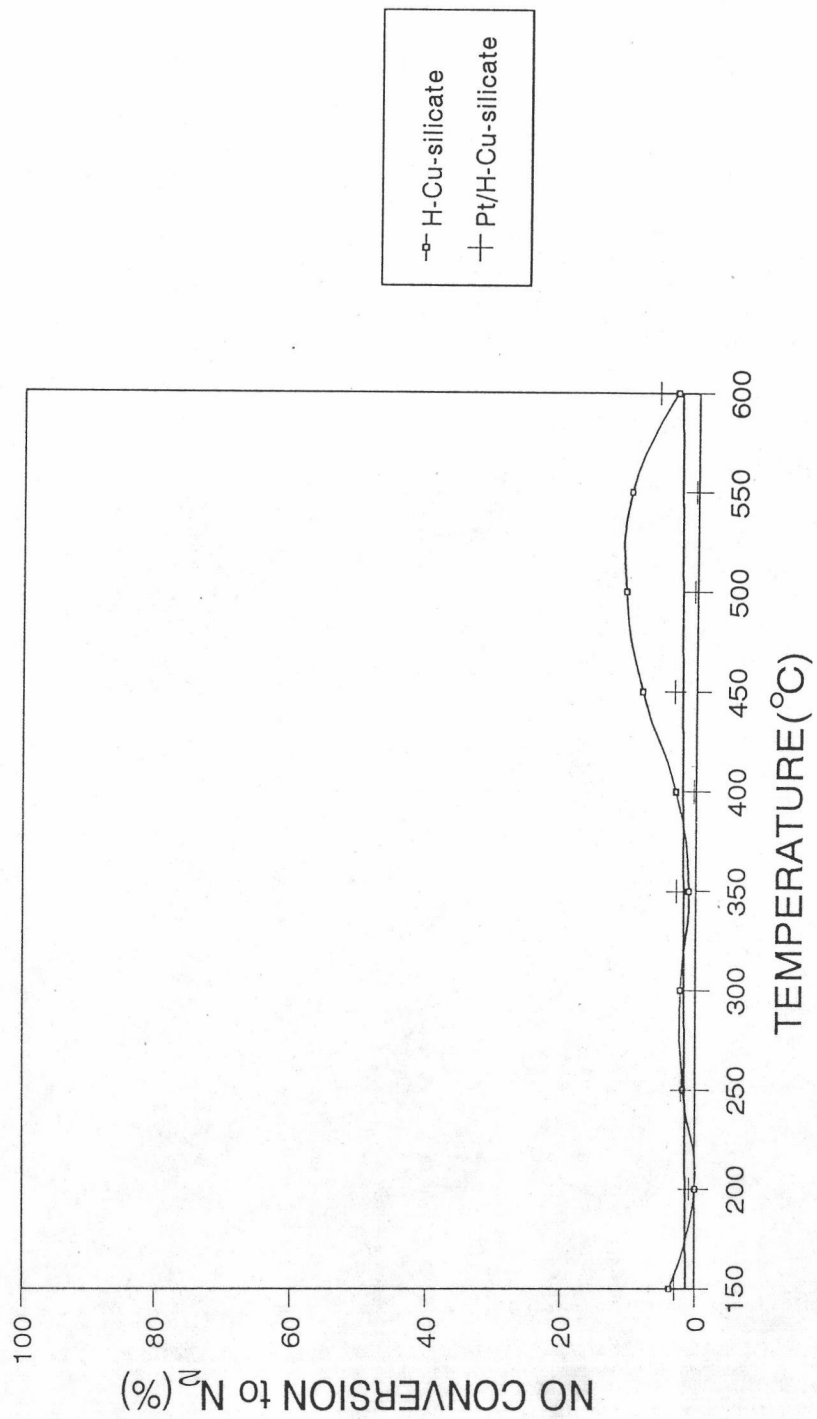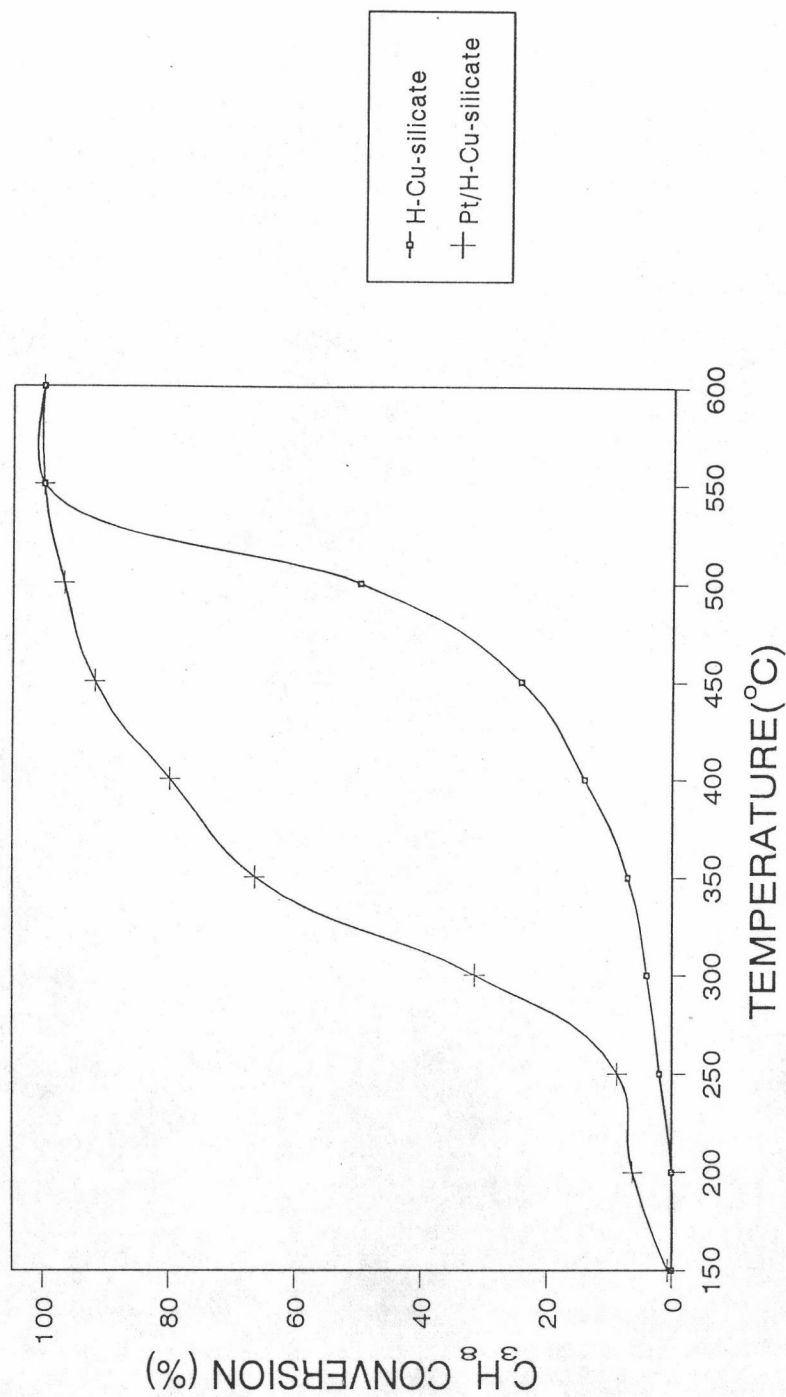Figure 5.10 Temperature Dependence of Propane Conversion on various Cation-exchanged
H-Cu-silicate Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced
He, GHSV = 4000 h^{-1}.

From these results, it is shown that H-form metallosilicates show activity and selective reduction of NO with propane, even in the presence of excess oxygen. The activities of NO reduction are in order of H-form > Cu/H-form > Pt/H-form in the wide range of temperature(150-600 °C). The orders of activities of propane conversion are as follows, Pt/H-form > H-form ~ Cu/H-form catalysts, respectively.

The conversions of NO on H-form and Cu/H-form are higher than on Pt/H-form metallosilicates. By contrast, the conversion level of propane was lower on H-form and Cu/H-form than on Pt/H-form metallosilicates. Propane was completely consumed on Pt/H-form above lower temperature because of the high ability of this catalyst for oxidation of propane. The high activity of oxidation would rather limit the reaction of NO to N_2 in the presence of excess oxygen [84]. The ability of H-form and Cu/H-form catalysts for the oxidation of propane was moderate by comparison with that of Pt/H-form catalysts. Therefore, the high efficiency was attained for the reaction of propane with NO. It has been reported that Pt is more active in low temperature oxidation of hydrocarbons [85]. Comparison of maximum conversion of NO, the catalytic activity of H-form is greater than that of copper ion-exchanged H-form metallosilicate. It would be caused by double calcination of Cu/H-form catalysts at 540 °C in a procedure of catalyst preparation. The amount of copper content in this study was expressed on the basis of weight as shown in table 5.4. This suggests that the decrease in the catalytic activity on Cu/H-form for NO reduction compared with H-form resulted form the destruction of the crystal structure and low amount of copper content in Cu/H-form metallosilicate.
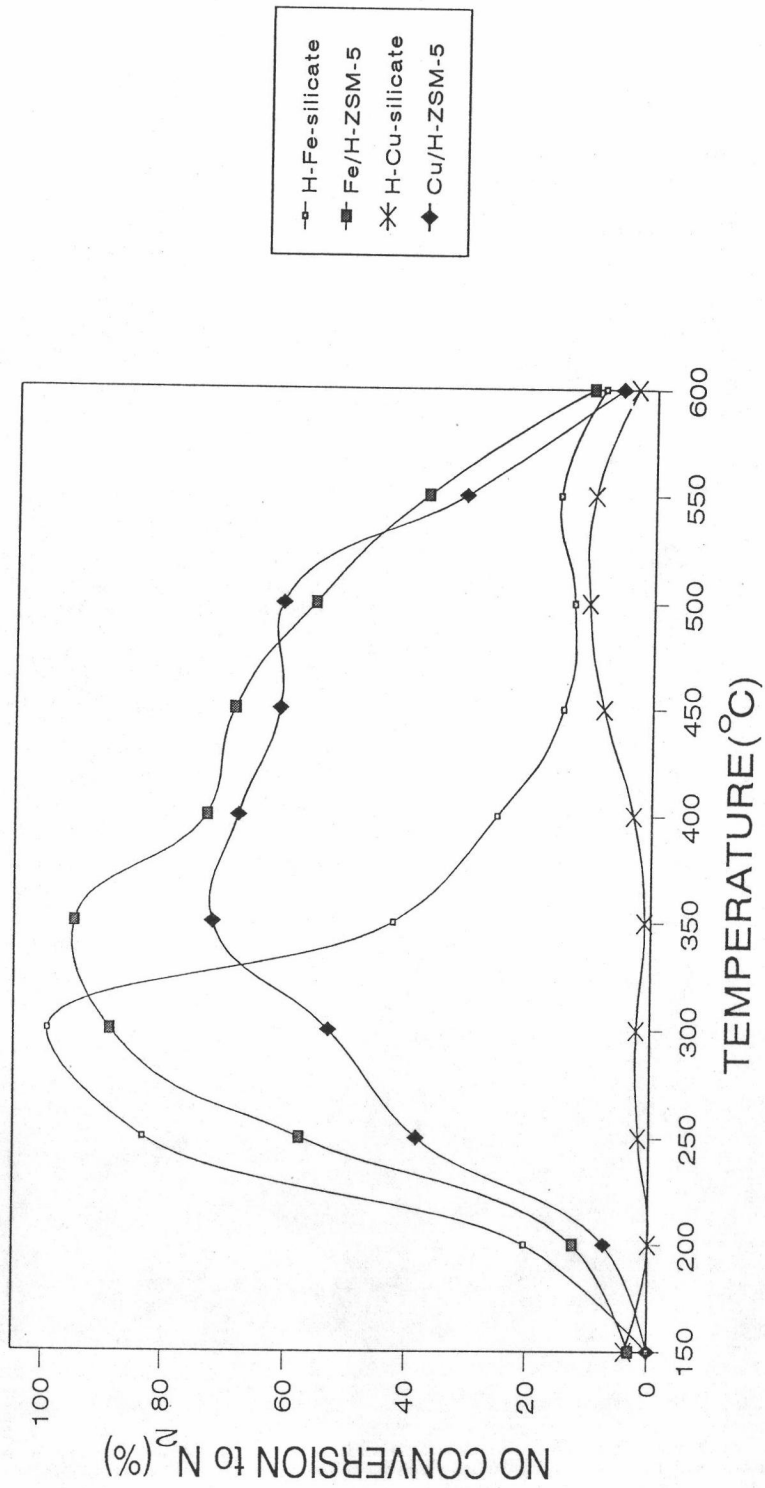
Figure 5.11 Temperature Dependence of NO Conversion on various Cu containing Catalysts.

1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced He, GHSV = 4000 h^{-1}.

5.2.4 Comparison of the catalytic activity for NO reduction on metal -ion-exchanged H-ZSM-5 and metal incorporated MFI-type silicate.

Figure 5.11 shows catalytic activities for NO reduction on H-Cu-silicate, Cu/H-ZSM-5, H-Fe-silicate, and Fe/H-ZSM-5 catalysts. The amount of metal contents of these catalysts are shown in table 5.4. Cu/H-ZSM-5 was more active for the reduction of NO than H-Cu-silicate in the temperature range 150-600 ^{o}C. The conversion NO on H-Fe-silicate increased sharply with increasing temperature and reached a maximum at 300 ^{o}C and drastically decreased at around 300-600 ^{o}C. It is found that the NO conversion on H-Fe-silicate is higher than that of Fe/H-ZSM-5 below 300 ^{o}C. From these results, it is shown that Fe/H-ZSM-5 shows high stability for this reaction at high temperature, and that H-Fe-silicate and Cu/H-ZSM-5 shows high activity for reduction of NO with propane, even in the presence of excess oxygen to compare with H-Cu-silicate. In conclusion, the catalytic activity for NO reduction on metal-ion-exchanged H-ZSM-5 has been selected to be the suitable catalyst for the reduction of NO in an oxidizing atmosphere.

5.3 Comparison of Activities among H-ZSM-5, Cu/H-ZSM-5, Na-ZSM-5,and Cu/Na-ZSM-5 Catalysts for Selective Reduction of NO by Propane in Oxidizing Atmosphere.

Table 5.5 and 5.6 summarizes the catalytic activities for the oxidation of propane and reduction of nitric oxide on various catalysts, respectively. The amount of copper content is summarized in table 5.7.

As showing in figure 5.12, the orders of activities for NO conversion of various catalysts are as follows, expressed as the name of catalyst ;

Cu/Na-ZSM-5 > H-ZSM-5 > Cu/H-ZSM-5 > Na-ZSM-5
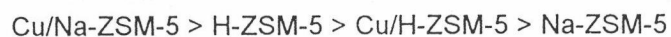
, respectively The range of reaction temperature was observed at above 250-500 ºC. Figure 5.13 shows the propane conversion of these catalysts. The order of activity for C_3H_8 conversion of these catalysts is Cu/Na-ZSM-5 > H-ZSM-5 ~ Cu/H-ZSM-5 > Na-ZSM-5. The range of temperature was observed above 250-500 ºC.

It is note that Cu/Na-ZSM-5 catalyst the most active selective reduction of NO by propane in the presence of excess oxygen at the temperature 300 ºC and it is the most active oxidation of propane at temperature 350 ºC among the catalysts shown in figure 5.12 and 5.13, respectively. The dependency of activities of Cu/Na-ZSM-5 catalyst at reaction temperature on the exchange level of copper compared with Na-ZSM-5(without copper content), as shown in figure 5.12 and 5.13. The activity increased with the increment in the copper content. On the other hand, the conversion into N_2 on Cu/H-ZSM-5 decreased with the presence of copper content in H-ZSM-5, as shown in figure 5.12. Table 5.7 shows the copper content in copper ion-exchanged ZSM-5 catalysts.

From the results described above, it can be suggested that copper content(Cu = 0.1007 wt.%) in Na-ZSM-5 structure plays an important role in the selective reduction of nitric oxide over Cu/Na-ZSM-5 catalyst. On the contrary, the activity was not enhanced by copper content in H-ZSM-5 (Cu = 0.0135 wt.%) and the activity of the reduction of nitric oxide to nitrogen decreased by Cu/H-ZSM-5 catalyst. This suggests that the decrease in the catalytic activity for NO reduction resulted from the destruction of crystal structure and low copper content in Cu/H-ZSM-5, and effect of Cu/Na-ZSM-5 catalyst on the component of copper will be study in section 5.9.

TABLE 5.5. Catalytic activities for the oxidation of propane .

No.	Catalyst	Conversion of C_3H_8 to CO, CO_2 (%)														
		150 ^{0}C			200 ^{0}C			250 ^{0}C			300 ^{0}C			350 ^{0}C		
		CO	CO_2	C_3H_8	CO	CO_2	C_3H_8	CO	CO_2	C_3H_8	CO	CO_2	C_3H_8	CO	CO_2	C_3H_8
1	H-ZSM-5	0	3.96	3.96	0.84	6.61	7.46	4.54	9.46	13.99	7.74	13.29	21.03	0.2	45.55	45.75
2	Cu/HZSM-5	0	0	0	0.13	4.13	4.25	3.79	8.94	12.73	12.1	14.02	26.13	22.06	28.18	50.24
3	Na-ZSM-5	0	2.31	2.31	0	5.52	5.52	0.49	0.36	0.85	1.3	1.42	2.73	2.15	4.86	7.01
4	Cu/Na-ZSM-5	0	0.52	0.52	0	10.4	10.4	0	21.07	21.07	0	81.7	81.7	0	100	100

table 5.5 continued

No.	Catalyst	Conversion of C_3H_8 to CO, CO_2 (%)														
		400 ^{0}C			450 ^{0}C			500 ^{0}C			550 ^{0}C			600 ^{0}C		
		CO	CO_2	C_3H_8	CO	CO_2	C_3H_8	CO	CO_2	C_3H_8	CO	CO_2	C_3H_8	CO	CO_2	C_3H_8
1	H-ZSM-5	0.52	64.99	65.51	0	79.48	79.48	0	91.4	91.4	0	100	100	0	100	100
2	Cu/HZSM-5	31.66	32.86	64.52	15.14	56.59	71.73	3.15	76.6	79.75	0	100	100	0	100	100
3	Na-ZSM-5	1.89	19.56	21.45	1.62	24.43	26.06	9.04	58.13	67.17	2.19	97.81	100	1.52	98.48	100
4	Cu/Na-ZSM-5	0	100	100	0	100	100	0	100	100	0	100	100	0	100	100

TABLE 5.6 Catalytic activities for the selective reduction of NO by propane.

No.	Catalyst	Conversion of NO to N_2 (%)									
		150^{0}C	200^{0}C	250^{0}C	300^{0}C	350^{0}C	400^{0}C	450^{0}C	500^{0}C	550^{0}C	600^{0}C
1	H-ZSM-5	8.21	14.06	48.18	91.11	84.65	83.89	76.9	68.85	9.88	9.5
2	Cu/HZSM-5	0	7.3	38.45	52.97	72.11	68.01	61.32	61.02	31.08	5.62
3	Na-ZSM-5	3.5	12.61	9.35	29.26	28.72	29.64	33.21	53.73	8.28	4.64
4	Cu/Na-ZSM-5	0	0	42.71	100	97.72	96.13	88.98	99.47	6.46	13.3

Table 5.7 The copper contents of various catalysts which were measured by AAS method.

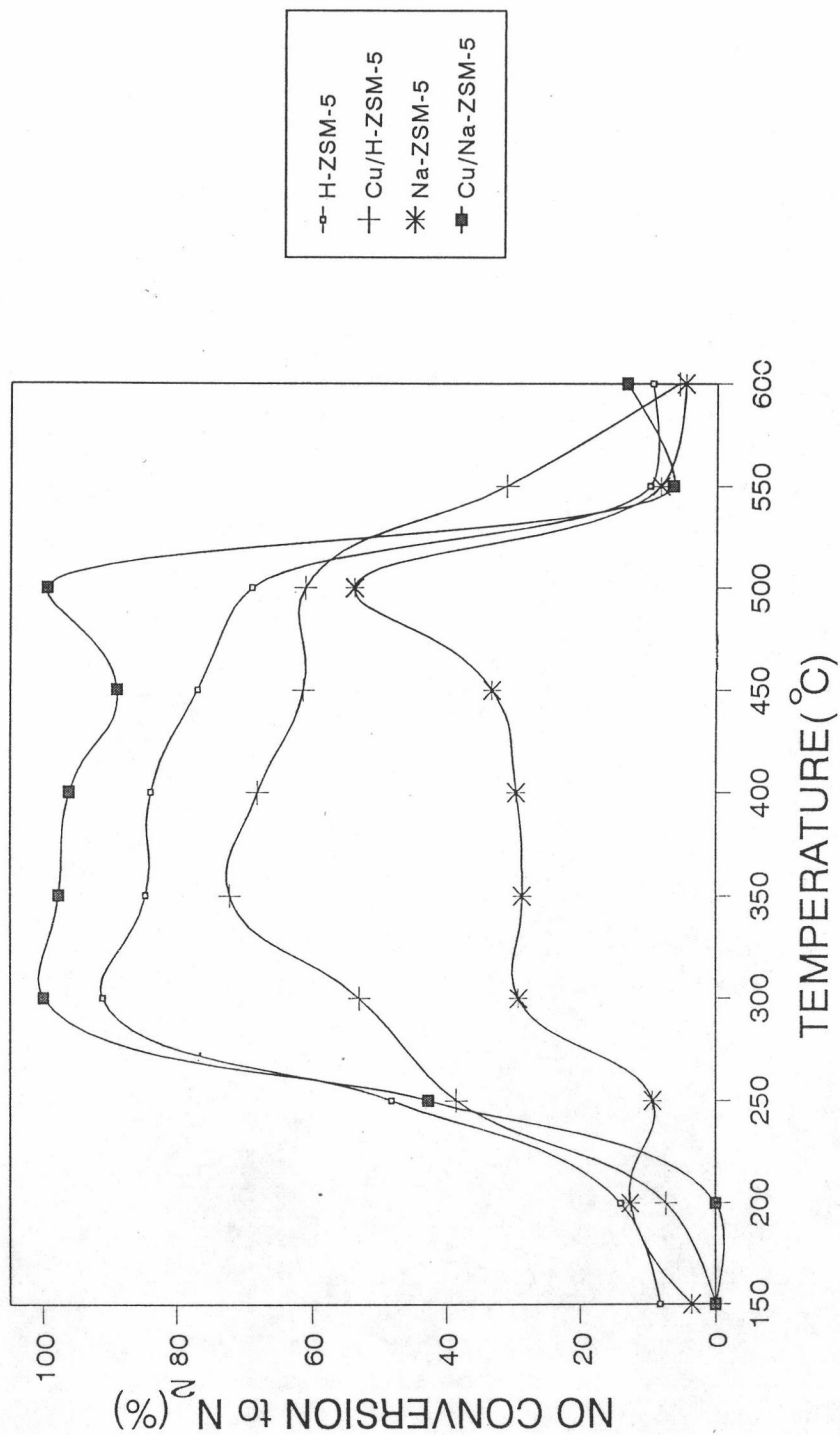| Catalyst sample	Copper salt used(0.5wt.%)	Copper contents (Ion-exchange Cu (wt.%))
Cu/H-ZSM-5	$Cu(NO_3)_2 \cdot 3H_2O$	0.0135
Cu/Na-ZSM-5	$Cu(NO_3)_2 \cdot 3H_2O$	0.1007

Figure 5.12 Temperature Dependence of NO Conversion on various forms of ZSM-5 and Cu

Ion-exchanged ZSM-5 Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and

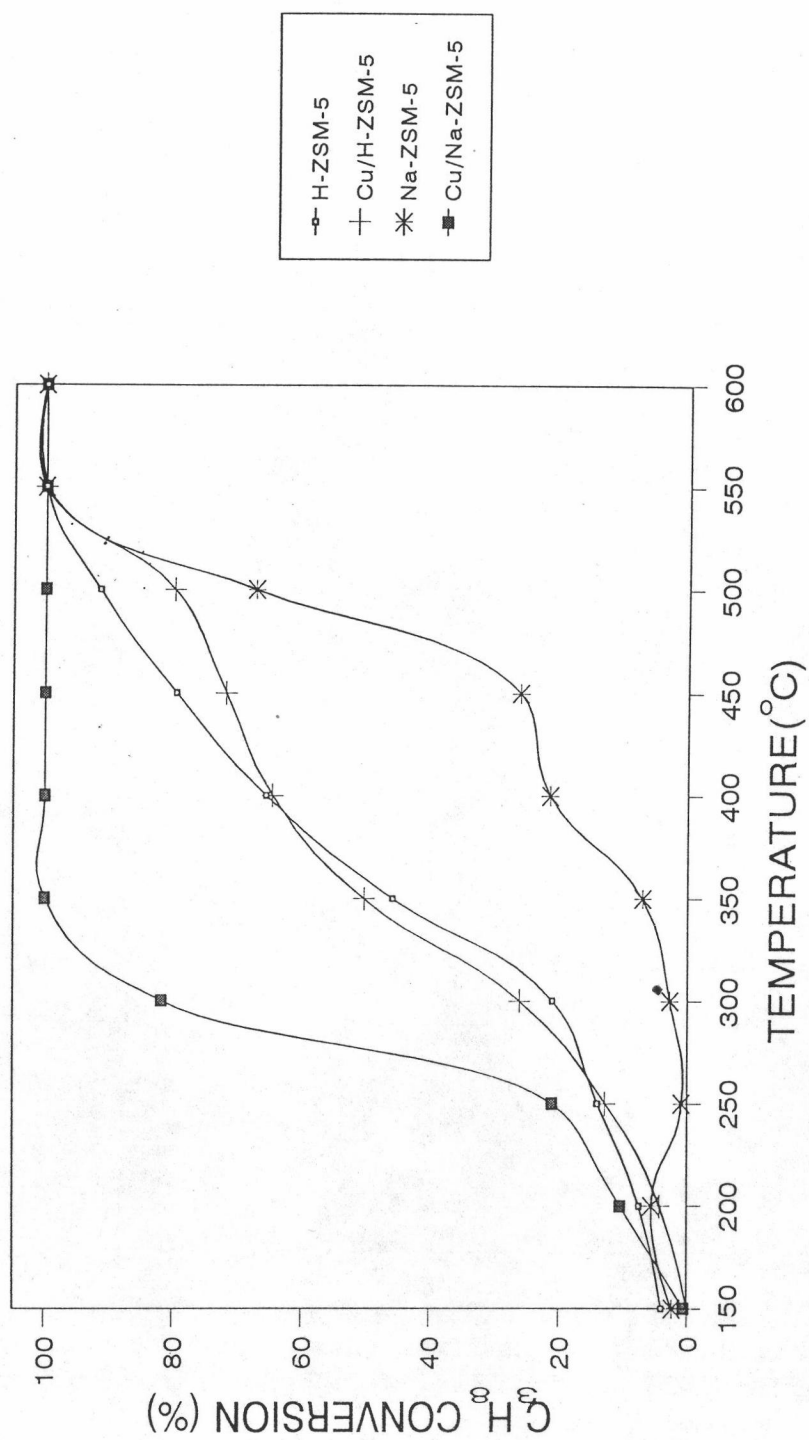balanced He, GHSV = 4000 h^{-1}.

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Figure 5.13 Temperature Dependence of Propane Conversion on various forms of ZSM-5

and Cu ion-exchanged ZSM-5 Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 %

O_2, and balanced He, GHSV = 4000 h^{-1}.

5.4 Effect of Copper Salts of Copper on Catalytic Activity of Copper Ion-exchanged Na-ZSM-5 Catalysts for the Selective Reduction of NO by Propane in the Presence of Oxygen.

The results of NO to N_2 conversion and C_3H_8 conversion are shown in figure 5.14 and 5.15, respectively, as a function of the reaction temperature for Cu/Na-ZSM-5 which were ion-exchanged with 0.5 wt.% of copper using $CuCl_2 \cdot 2H_2O$ (Cu/NaZ1), CuCl (Cu/NaZ2), $CuSO4 \cdot 5H_2O$ (Cu/NaZ3), $Cu(CH_3COO)_2 \cdot H_2O$ (Cu/NaZ4), and $Cu(NO_3)_2 \cdot 3H_2O$ (Cu/NaZ5), respectively.

Cu/NaZ1, Cu/NaZ3, and Cu/NaZ4 exhibited the activity for their NO conversion and propane oxidation at above 150 ºC and attained their NO conversion 100% at 350 ºC and their maximum conversion 100% at 400 ºC.

As for Cu/NaZ2, the NO conversion reached 100% at 500 ºC and the propane conversion reached 100% at 550 ºC.

The 100% conversion of NO on Cu/NaZ5 is attained at 300 ºC and the propane conversion 100% at 350 ºC.

The copper contents are summarized in table 8. The amounts of copper contents are 0.0744, 0.0458, 0.0769, 0.0782, and 0.1007 with Cu/NaZ1, Cu/NaZ2, Cu/NaZ3, Cu/NaZ4, and Cu/NaZ5, respectively. It remarks that al catalysts have high copper contents except Cu/NaZ2.

From these results, it is shown that Cu/NaZ5 catalyst is the most active for the selective reduction of NO and oxidation of propane in an oxidizing atmosphere. The abilities
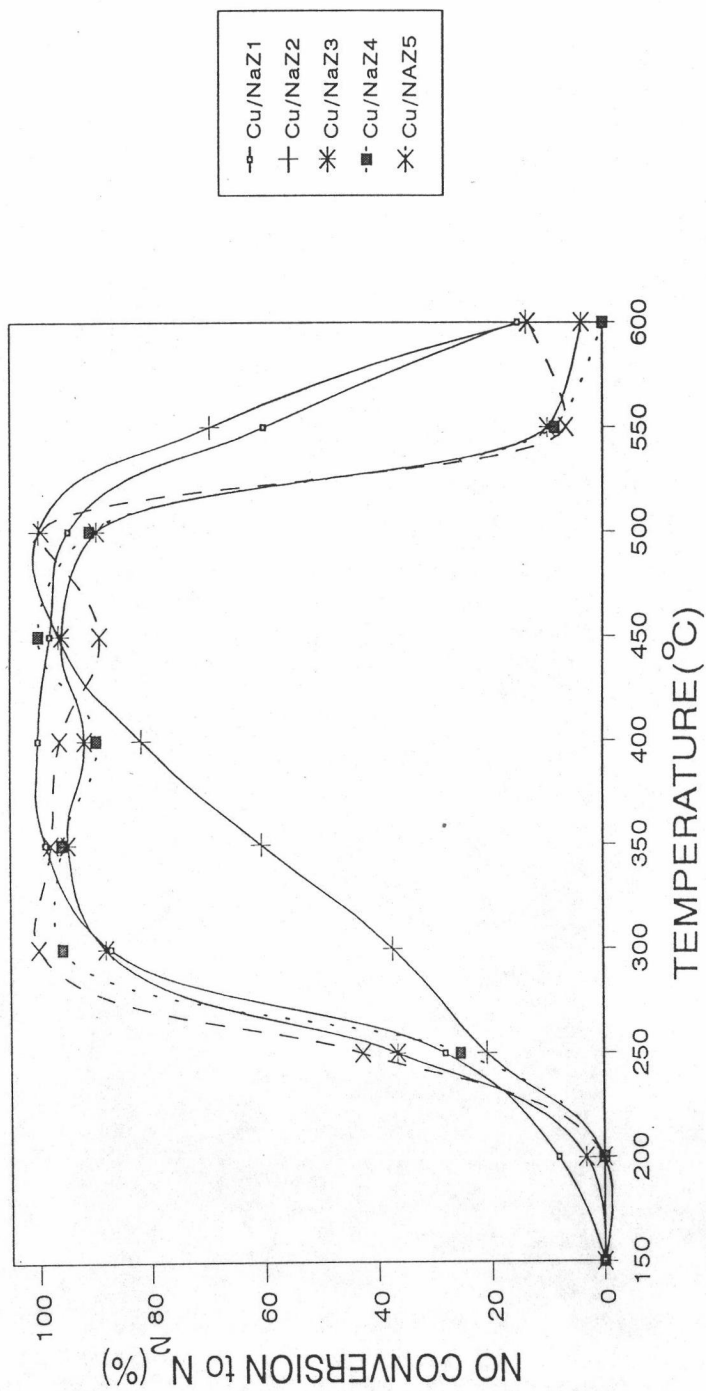
Figure 5.14 Temperature Dependence of NO Conversion on various Cu ion-exchanged

Na-ZSM-5 Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced
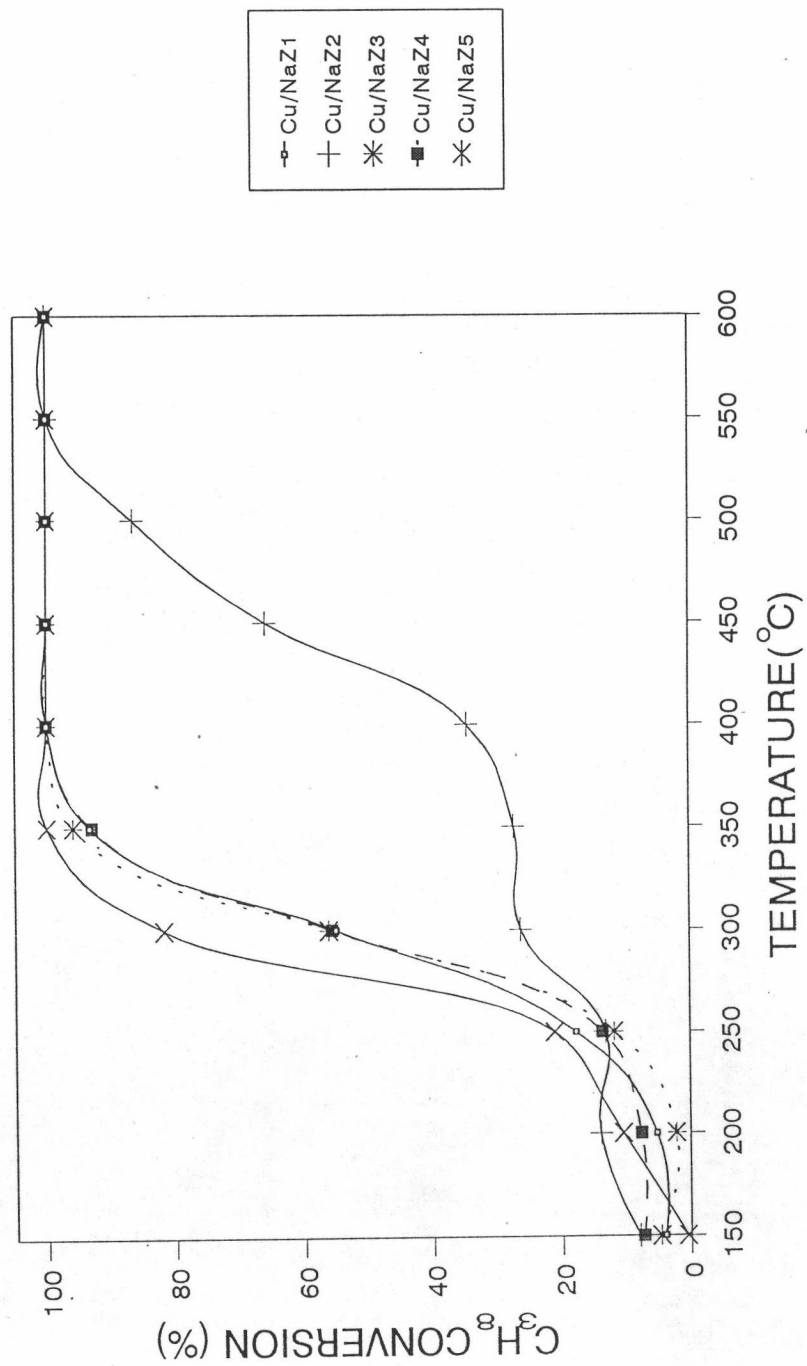
He, GHSV = 4000 h^{-1}.

Figure 5.15 Temperature Dependence of Propane Conversion on various Cu ion-exchanged

Na-ZSM-5 Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced

He, GHSV = 4000 h^{-1}.

of Cu/NaZ1, Cu/NaZ3, and Cu/NaZ4 catalysts for the oxidation of propane and reduction of NO were moderate Although Cu/NaZ2 shows relatively high activity above 450 °C and 550 °C for NO conversion and propane combustion, respectively, Its activity was poor below this temperature. The activity of Cu/NaZ2 was lower than other catalysts because it is active at high temperature. The activity increased with the increase of copper content in ZSM-5 structure. The amount of copper content of Cu/NaZ2 is lowest among these catalysts listed in table 5.8. The ability of catalytic activity was defined that the high efficiency was attained for the lower reaction temperature. The low amount of copper content of Cu/NaZ2 was due to the low ability of copper ion-exchange. Cu/NaZ2 was prepared by the ion-exchange of sodium form ZSM-5 using aqueous solution of CuCl in 1M HCl at room temperature for 12 h, followed calcination at 540 °C. The difference in copper ion-exchange of sodium form ZSM-5 between Cu/NaZ2 and the other catalysts are that CuCl salt is insoluble in water but CuCl is dissolved in HCl acid. Therefore, aqueous solutions of copper salts give difference of pH of aqueous solution.

It was suggested as mentioned above that acid or base property of copper salt solution affected for amount of copper content of copper ion-exchanged Na-ZSM-5 catalysts. Further studies are required to understand the effect of acid on copper content by copper ion-exchange method. It is concluded in this study that the difference of copper salts (anion) can not effectively increase copper content by copper ion-exchange method.

Table 5.8   Effect of copper salt on the on the ion-exchange copper of the resulting Cu/Na-ZSM-5, Cu/H-ZSM-5, and Cu/NH$_4$-ZSM-5, ion-exchange room temperature, Cu/catalyst = 0.005.

Catalysts	Copper salt used (0.5 wt.%)	ZSM-5 form	Copper content(wt.%)
Cu/NaZ1	CuCl$_2$·2H$_2$O	Na-ZSM-5	0.0744
Cu/NaZ2	CuCl	Na-ZSM-5	0.0458
Cu/NaZ3	CuSO$_4$·5H$_2$O	Na-ZSM-5	0.0769
Cu/NaZ4	Cu(CH$_3$COO)$_2$·H$_2$O	Na-ZSM-5	0.0782
Cu/NaZ5	Cu(NO$_3$)$_2$·3H$_2$O	Na-ZSM-5	0.1007
Cu/H-ZSM-5	Cu(NO$_3$)$_2$·3H$_2$O	H-ZSM-5	0.0135
Cu/NH$_4$-ZSM-5	Cu(NO$_3$)$_2$·3H$_2$O	NH$_4$-ZSM-5	0.0706

Cu/NaZ2 was prepared by using copper ion-exchange with CuCl in 1 M HCl. The copper contents of various catalysts were measured by AAS.

Table 5.8 shows the amount of copper contents on Cu/ZSM-5 catalysts which were measured by AAS method. The data from the table indicate the copper contents of Cu/NaZ1- 4 catalysts which were ion-exchanged with various copper salt and Cu/NaZ5- 7 catalysts with aqueous solution of Cu(NO$_3$)$_2$·3H$_2$O.

5.5 Effect of Addition of Acid on the Ion-exchange Copper of the Resulting Cu/H-ZSM-5 and Cu/Na-ZSM-5.

In the previous section, it is found that Na-ZSM-5 catalyst exchanged with CuCl salt aqueous solution(Cu/NaZ2) is the lowest active for the selective reduction of NO and oxidation of propane among the catalysts which were prepared by using Na-ZSM-5

exchanged with other copper salts aqueous solutions, as shown in table 5.8. The amount of copper content of Cu/NaZ2 is low, (0.0458 wt.%), as shown in table 5.9. From these results, it was expected that addition of 1 M HCl in copper aqueous solution affected on the amount of copper content of catalyst. In order to confirm the difference amount of copper content in catalysts using various copper salts exchanged with Na-ZSM-5 and addition of the same amount of HCl acid, the amount of copper contents of Cu/Na-ZSM-5 catalysts by using $CuSO_4.5H_2O$ and $CuCl_2.2H_2O$ salts with the same amount of HCl acid (for Cu/NaZ2 used) were measured by AAS. As shown in table 5.9, Cu/Na-ZSM-5 (Na-ZSM-5 + $CuCl_2 2H_2O$ + 1.0 ml of 1 HCl), Cu/Na-ZSM-5 (Na-ZSM-5 + $CuSO_4 5H_2O$ + 1.0 ml of 1 HCl), Cu/NaZ1(Na-ZSM-5 + $CuCl_2 2H_2O$), Cu/NaZ3 (Na-ZSM-5+ $CuSO_4 5H_2O$), Cu/H-ZSM-5 (H-ZSM-5 + CuCl +1.0 ml of 1 HCl), and Cu/H-ZSM-5 (H-ZSM-5 +$CuCl_2 2H_2O$ + 1.0 ml of 1 HCl) attained their amounts of copper contents, 0.0490, 0.0404, 0.0744, 0.0769, 0.0020, and 0.0015 wt.%, respectively.

As a result, it is observed that Cu/H-ZSM-5 and Cu/Na-ZSM-5 catalysts using various copper salts with the same amount of HCl acid for ion-exchange have the same amount of copper contents in their structures. It is concluded in this study that, the amount of copper contents in Cu/Na-ZSM-5 and Cu/H-ZSM-5 depended on amount of acid (pH of ion-exchange solution) and type of parent zeolites. By contrast, difference of copper salts does not show such effects for the increase of level of copper ion-exchange.

Table 5.9 Effect of addition of acid on the ion-exchange copper of the resulting Cu/H-ZSM-5 and Cu/Na-ZSM-5.

Copper salt used (0.5 wt.%)	ZSM-5 form	Addition of 1 M HCl (ml)	Copper content (wt.%)
CuCl	Na-ZSM-5	1.0	0.0458
CuCl$_2$·2H$_2$O	Na-ZSM-5	1.0	0.0490
CuSO$_4$·5H$_2$O	Na-ZSM-5	1.0	0.0404
CuCl$_2$·2H$_2$O	Na-ZSM-5	0	0.0769
CuSO$_4$·5H$_2$O	Na-ZSM-5	0	0.0744
CuCl	H-ZSM-5	1.0	0.0020
CuCl$_2$·2H$_2$O	H-ZSM-5	1.0	0.0015

The copper contents of various catalysts were measured by AAS methods.

5.6 Effect of Addition of Acidic and Basic Solutions on the Ion-exchanged Copper of the Resulting Cu/H-ZSM-5,Cu/NH$_4$-ZSM-5, and Cu/Na-ZSM-5.

From the previous section, it is observed that amount of copper content of Cu/Na-ZSM-5 is greater than that of Cu/H-ZSM-5 by the same condition of preparation. Parent zeolites and acid - base property of solution using in ion-exchange affected amount of copper content in structure of zeolites.

Table 5.10 shows the effect of addition of acidic and basic solution. The correlations between the amount of copper content of copper ion-exchanged various form ZSM-5 catalysts and that the pH of copper ion-exchange solution are shown in figure 5.16. The various forms of ZSM-5 such as H-ZSM-5, NH$_4$-ZSM-5, and Na-ZSM-5 were ion-exchanged

with in an aqueous copper nitrate solution through addition of acidic and basic solution according to adjusting pH of mother solution.

Cu/H-ZSM-5 catalysts were prepared by the ion-exchange of H-ZSM-5 using aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ through adjusting pH by addition of 10% vol. of NH_4OH. The pH was varied at 4.0, 5.0, 7.0, 8.0, and 10.0. Copper contents of catalyst were analyzed by AAS. The amount of copper content increased with increasing the pH of mother solutions.

Cu/NH_4-ZSM-5 catalysts were prepared by the ion-exchange of ammonium form ZSM-5 using an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ and adjusting the pH of mother solution by addition of 1 M of HNO_3 and 10% vol. of NH_4OH. The pH was varied at 3.0, 4.0, 5.1, 6.2, 8.2, and 10. The catalysts had predominant amount of copper content at around pH 6.0 -7.0 and copper ion-exchange levelled constant at pH 8.0 - 10.0.

Cu/Na-ZSM-5 catalysts were prepared by the ion-exchange of the sodium form ZSM-5 zeolite using an aqueous solution of copper nitrate and varying the pH of mother solution by addition of 1 M HNO_3 and 10% vol. of NH_4OH. The variety of the pH was attained at 4.0, 5.0, 7.0, 8.0, 9.0, and 10. The amount of copper content increased with the increase of pH from 4.0 - 10.0.

The comparison of copper ion-exchange ability of various form ZSM-5 zeolites are as follows, Na-ZSM-5 > NH_4-ZSM-5 > H-ZSM-5. In conclusion, Na-ZSM-5 and NH_4-ZSM-5 have been to be the suitable parent zeolite for copper ion-exchanged ZSM-5 catalyst preparation. In this regard, it is found that the ZSM-5 zeolites with increasing loading of copper ions could be prepared through the addition of basic compounds.
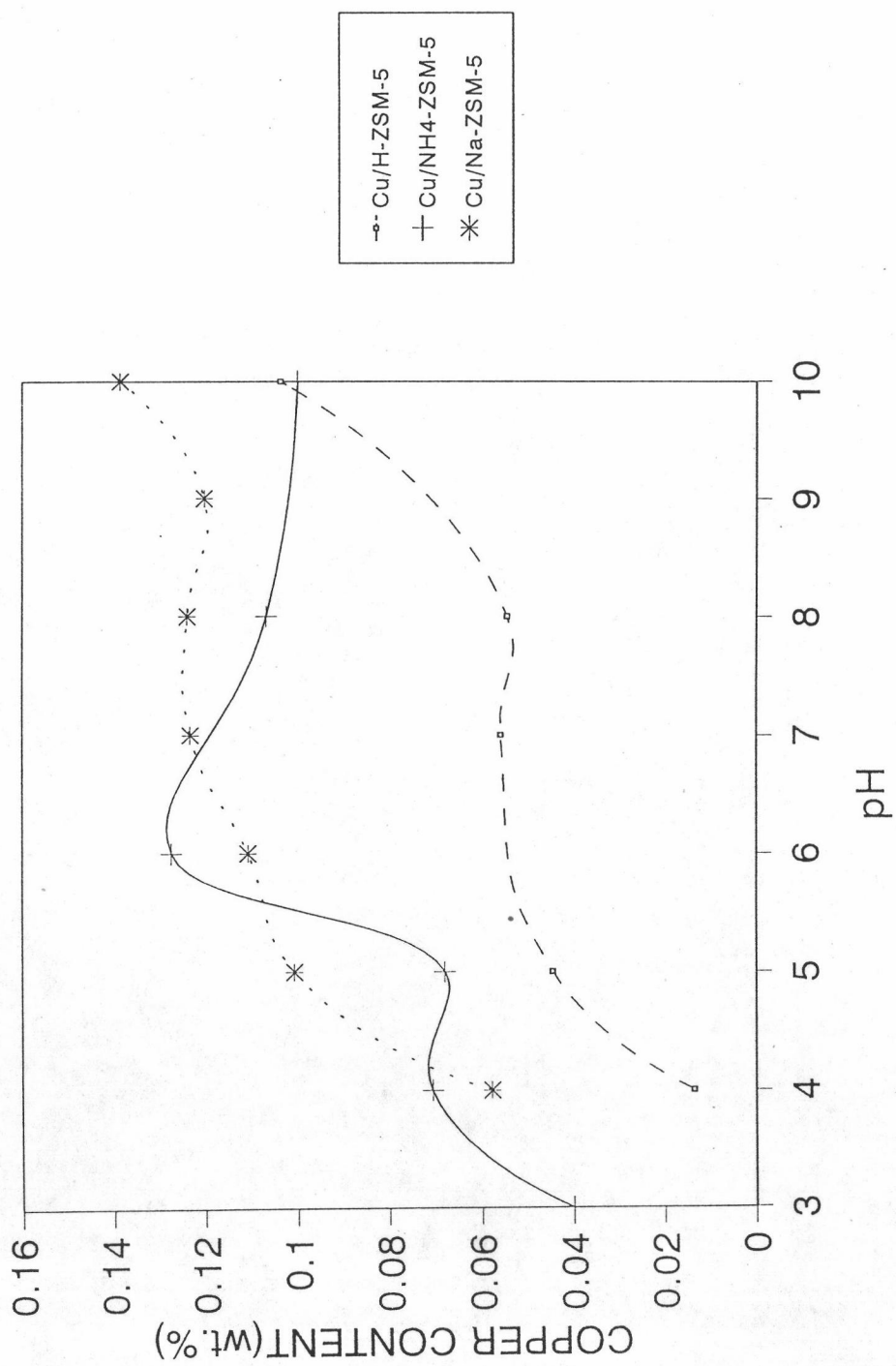
Figure 5.16 Copper content of Cu/ZSM-5 as a Function of pH (aqueous copper (II) nitrate

solution).

Table 5.10 Effect of addition of base to the ion-exchange copper of the resulting Cu/H-ZSM-5, Cu/NH$_4$-ZSM-5, and Cu/Na-ZSM-5 , ion exchange at room temperature, 1.5 g of mother zeolite and 40 ml of 0.03 M aqueous solution of copper nitrate.

Copper salt used (0.5wt.%)	ZSM-5 Form	Additive	Concentration of additive	pH after addition	Cu content (wt.%)
Cu(NO$_3$)$_2$·3H$_2$O	H-ZSM-5	NH$_4$OH	10%	4.0	0.0135
		NH$_4$OH	10%	5.0	0.0445
		NH$_4$OH	10%	7.0	0.0558
		NH$_4$OH	10%	8.0	0.0544
		NH$_4$OH	10%	10.0	0.1037
Cu(NO$_3$)$_2$·3H$_2$O	NH$_4$-ZSM-5	HNO$_3$	1 M	3.0	0.0400
		non	-	4.0	0.0706
		NH$_4$OH	10%	5.1	0.6790
		NH$_4$OH	10%	6.2	0.1274
		NH$_4$OH	10%	8.2	0.1068
		NH$_4$OH	10%	10.0	0.1000
Cu(NO$_3$)$_2$·3H$_2$O	Na-ZSM-5	HNO$_3$	1M	4.0	0.0577
		non	-	5.0	0.1007
		NH$_4$OH	10%	6.0	0.1107
		NH$_4$OH	10%	7.0	0.1233
		NH$_4$OH	10%	8.0	0.1240
		NH$_4$OH	10%	9.0	0.1202
		NH$_4$OH	10%	10.0	0.1386
Cu(NO$_3$)$_2$·3H$_2$O	NH$_4$-ZSM-5	NaOH	1 M	6.0	0.1274
	NH$_4$-ZSM-5	KOH	2 M	6.0	0.0916

5.7 Time Dependence of Copper Ion-exchange on Na-ZSM-5.

The ion-exchange conditions are described in table 5.11. The duration course of copper ion-exchange level is shown in figure 5.17 and table 5.11. The extents of the amount
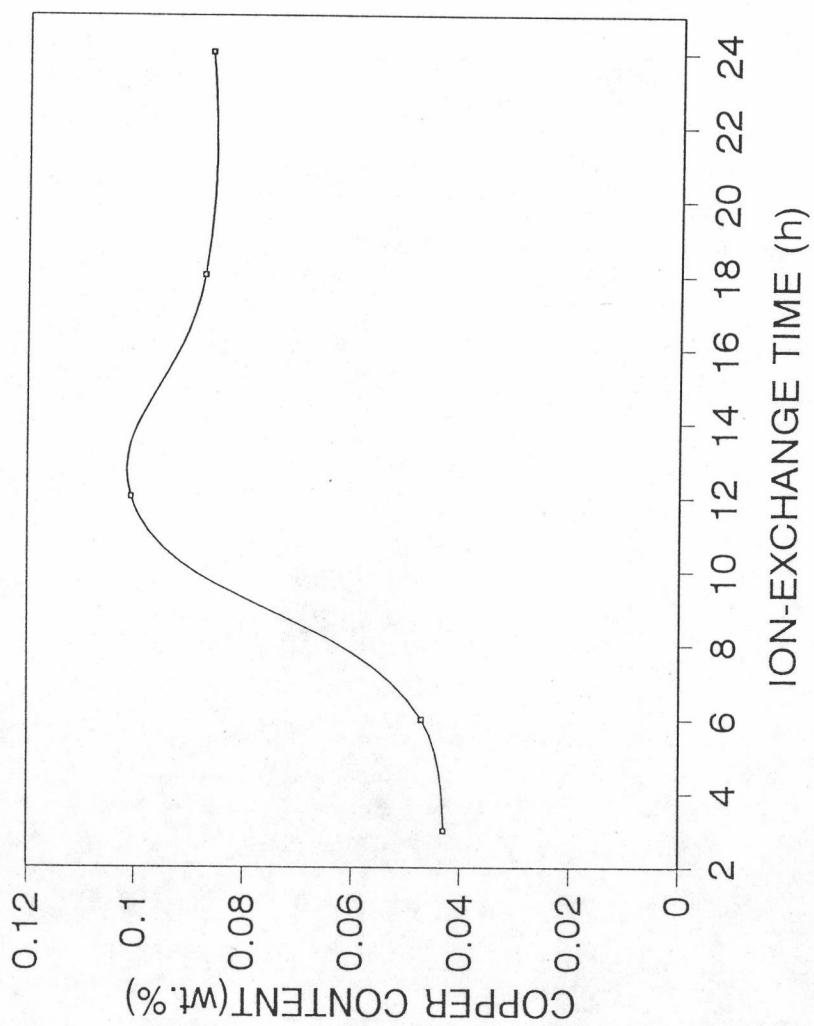
Figure 5.17 Ion-exchanged Time Dependence of Copper Content on Cu/Na-ZSM-5.

$(Cu(NO_3)_2 \cdot 3H_2O$ used for ion-exchange)

of copper content were gradually increased with ion-exchange time up to 12 hr of when it reached a steady state. Then ion-exchange time of 12 h was used to prepare copper ion-exchanged ZSM-5 catalysts.

Table 5.11   Cu/Na-ZSM-5 catalysts prepared on various time for ion-exchange at room temperature, 40 ml. of 0.003 M copper(II)nitrate and 1.5 g of mother zeolite.

Ion-exchange time (h)	Copper content (wt.%)
3	0.0431
6	0.0472
12	0.1007
18	0.0873
24	0.0862

The copper components of various catalysts were measured by AAS methods.

5.8 Temperature Dependence of Copper Ion-exchange on Na-ZSM-5.

Table 5.12 and figure 5.18 show the effect of ion-exchange temperature on amount of copper content and the condition of Cu/Na-ZSM-5 catalysts preparation. The catalysts had predominant amount of copper at around 80 ºC and copper ion-exchanged levelled off at 80 - 200 ºC. This suggests that the ion-exchange temperature affected amount of copper content of Cu/Na-ZSM-5 catalysts.
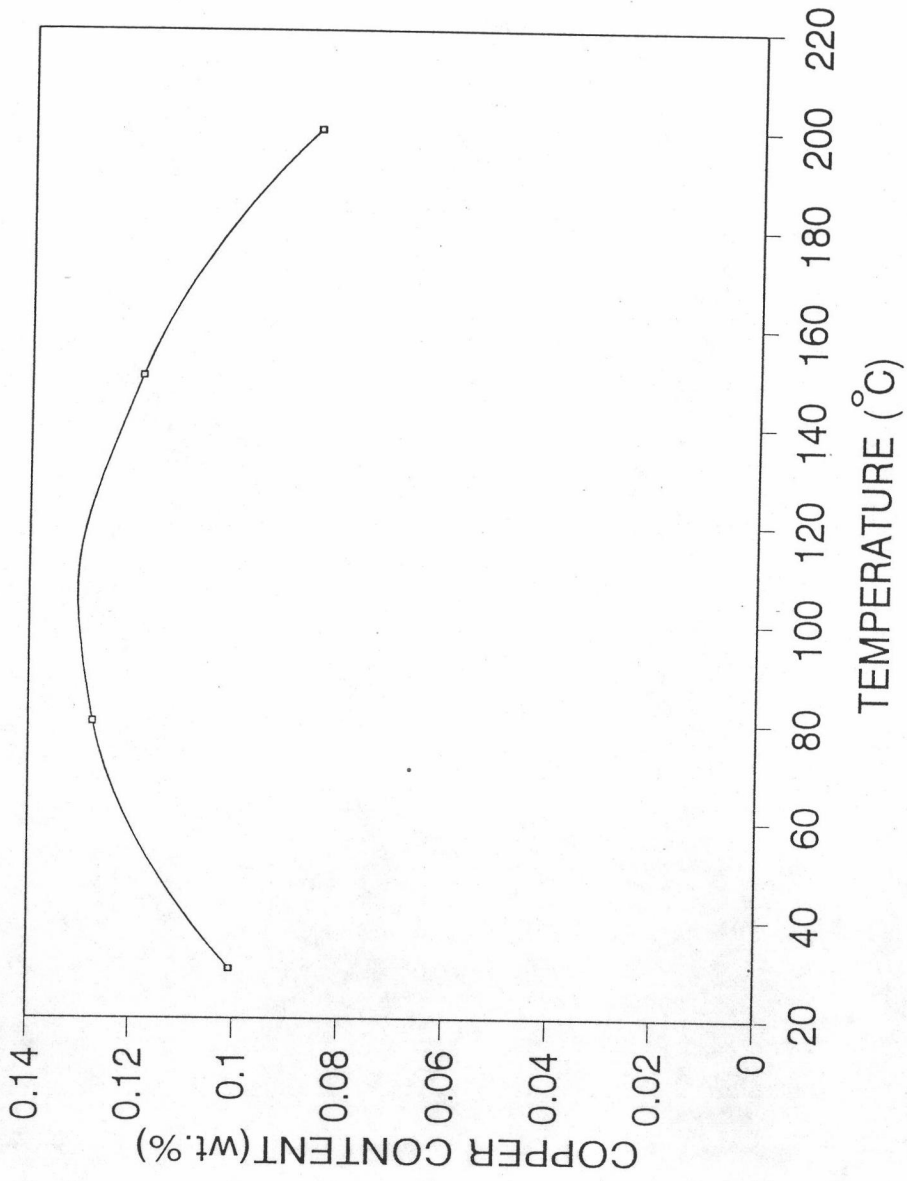
Figure 5.18 Temperature Dependence of Content on Cu/Na-ZSM-5.

$(Cu(NO_3)_2 \cdot 3H_2O$ used for ion-exchange)

Table 5.12 Effect of ion-exchange temperature on copper content of Cu/Na-ZSM-5 catalyst.

Ion-exchange Temperature ($^\circ$C)	Copper content (wt.%)	Control pressure
30	0.1007	atmospheric pressure
80	0.1275	atmospheric pressure
150	0.1185	90 psig
200	0.0849	135 psig

Preparation of catalyst: Ion-exchange time = 12 h, 40 ml. of 0.003M copper(II)nitrate, 1.5 g of mother zeolite. The copper contents of catalysts were measured by AAS methods.

5.9 Effect of Copper Content for Catalytic activities on various Copper Ion-exchanged ZSM-5 Zeolites.

In this study, effects of copper content of catalyst which prepared by using copper ion-exchange with various form of ZSM-5 on catalytic activities for NO reduction were investigated. The dependency of the activities of Cu/H-ZSM-5 catalysts at the temperature range 150 - 600 $^\circ$C on the amount of copper content is shown in figure 5.19. Cu/H-ZSM-5 catalysts having amount of copper contents of 0.0440 and 0.1000 wt.% were examined. When the amount of copper content was increased from 0.0440 wt.% to 0.1000 wt.% on Cu/H-ZSM-5 catalysts, the temperature of maximum NO conversion decreased from 450 $^\circ$C to 350 $^\circ$C. As a result, the temperature of maximum NO conversion deceased with increasing Cu ion-exchanged level of Cu/H-ZSM-5 catalysts.

Figure 5.20 shows the dependence of the activities of Cu/NH$_4$-ZSM-5 catalysts at the temperature range of 150 - 600 $^\circ$C on the amount of copper content. The order of the
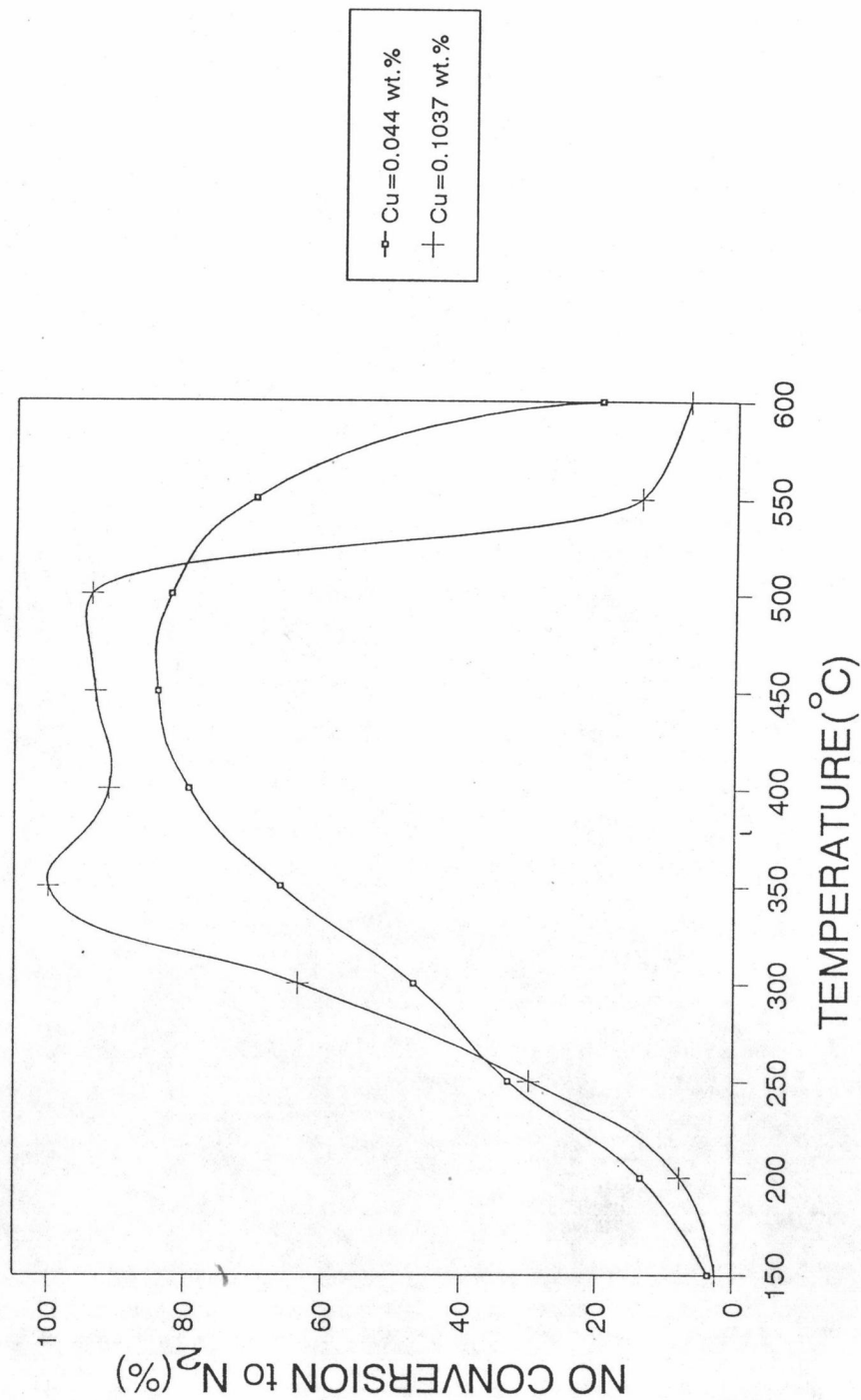
Figure 5.19 Effect of Copper Content for NO conversion on various Cu/H-ZSM-5 Catalysts.

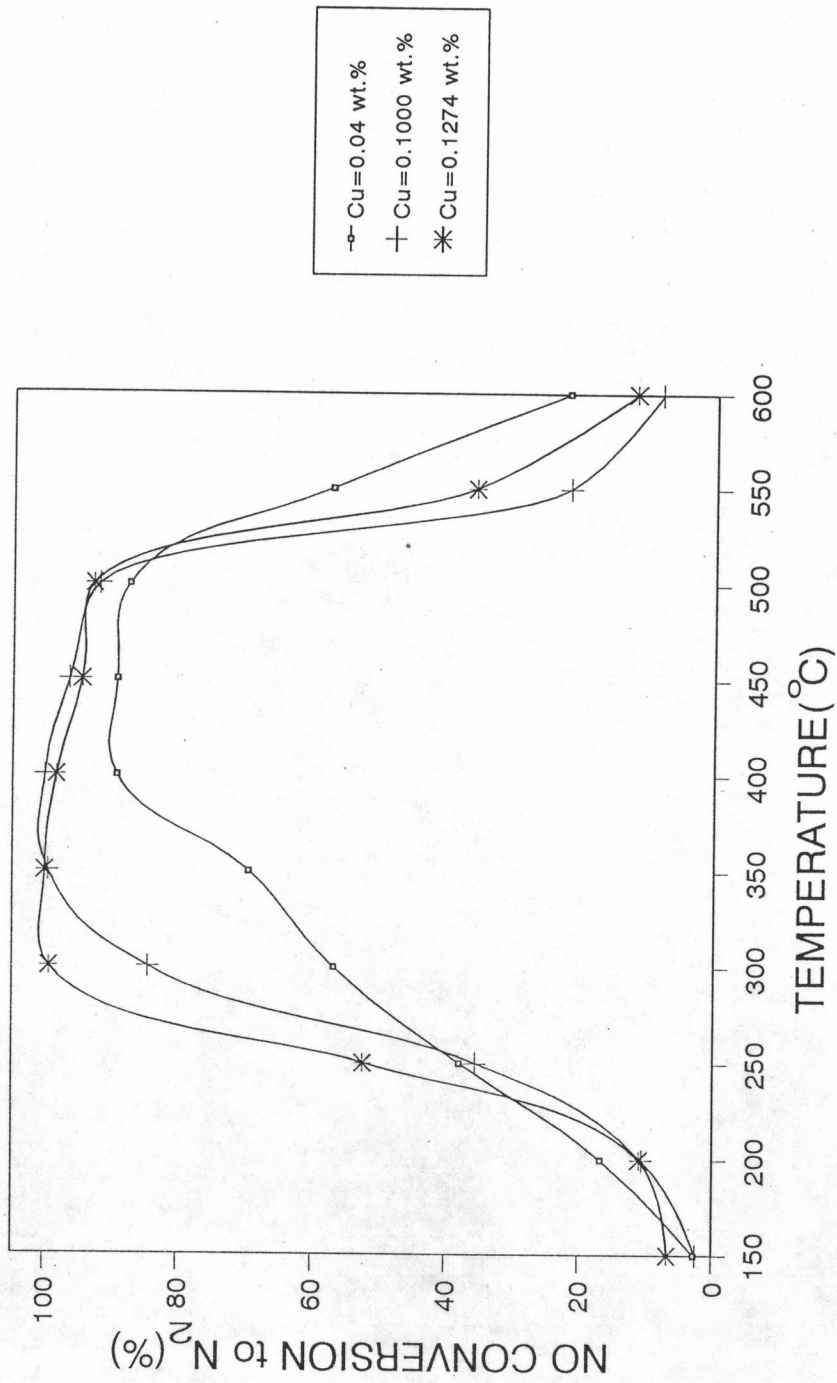1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced He, GHSV = 4000 h^{-1}.

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Figure 5.20 Effect of Copper Content for NO conversion on various Cu/NH$_4$-ZSM-5

Catalysts.1000 ppm NO, 3000 ppm C$_3$H$_8$, 10 %O$_2$, and balanced He,
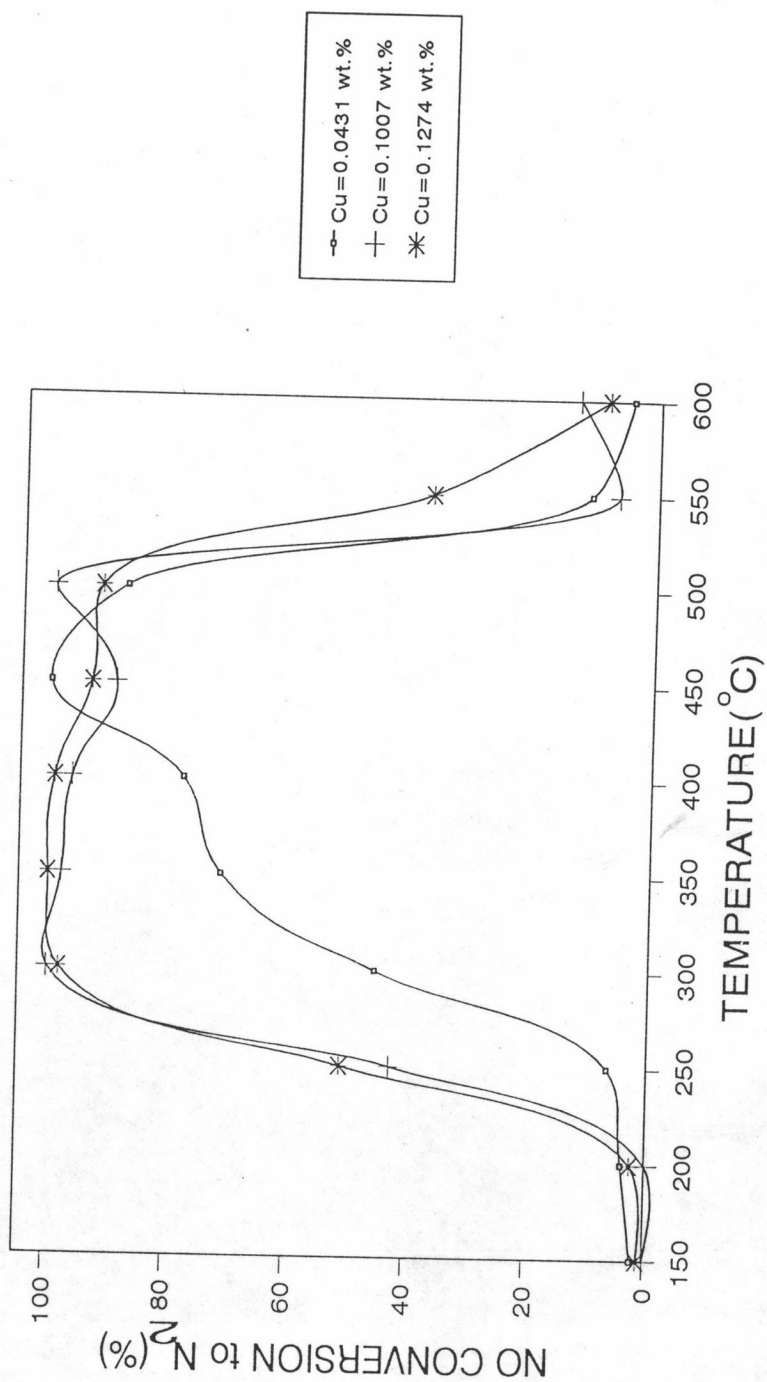
GHSV = 4000 h^{-1}.

Figure 5.21 Effect of Copper Content for NO conversion on various Cu/Na-ZSM-5 Catalysts.

1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced He, GHSV = 4000 h^{-1}.

temperature of the maximum activity for the reduction of NO on the amount of copper content of Cu/NH$_4$-ZSM-5 was Cu = 0.0400 wt.%(400 ^{o}C) ~ Cu = 0.1000 wt.%(400 ^{o}C) > Cu = 0.1274 wt.%(300 ^{o}C). This suggests that the lower 0.1 wt.% of copper content of Cu/NH$_4$-ZSM-5 catalyst had little influence on its activity for NO reduction, it was due to the effect of the presence of NH$_4^+$ ion on Cu/NH$_4$-ZSM-5 catalysts. Influence of amount of copper content on the decrease of temperature of maximum conversion was observed on Cu/NH$_4$-ZSM-5 having copper content above ca. 0.12 wt.%.

As shown in figure 5.21, when the amount of copper content in Cu/Na-ZSM-5 catalyst was increased from 0.0431 wt.% to 0.1007 and 0.1275 wt.% the temperature of maximum NO conversion was decreased from 450 ^{o}C to 300 and 300 ^{o}C, respectively.

Clearly, the catalytic activity is depended on both the copper ion and former ion such as Na$^+$, NH$_4^+$, and H$^+$ content.

5.10 Comparison of the Catalytic Activities for NO Reduction on Cu-MFI-105 and Cu/Na-ZSM-5 catalysts.

The description of catalysts are summarized in table 5.13. Figure 5.22 compares NO conversion on Cu/Na-ZSM-5 and Cu-MFI-105 as a function of reaction temperature. Figure 5.23 shows catalytic activity of propane oxidation on Cu/Na-ZSM-5 catalysts. It was found that Cu-MFI-105 showed higher catalytic activity in NO conversion than Cu/Na-ZSM-5 at the temperature range of 150 - 300 ^{o}C and showed lower catalytic activity than Cu/Na-ZSM-5 above 300 ^{o}C under these reaction conditions. C$_3$H$_8$ was completely consumed on Cu/Na-ZSM-5 and Cu-MFI-105 above 350 and 300 ^{o}C, respectively. The high oxidation ability of Cu-MFI-105 would rather limit the reaction of NO to N$_2$ at the temperature range of 300 - 600 ^{o}C with the presence of excess oxygen [86].
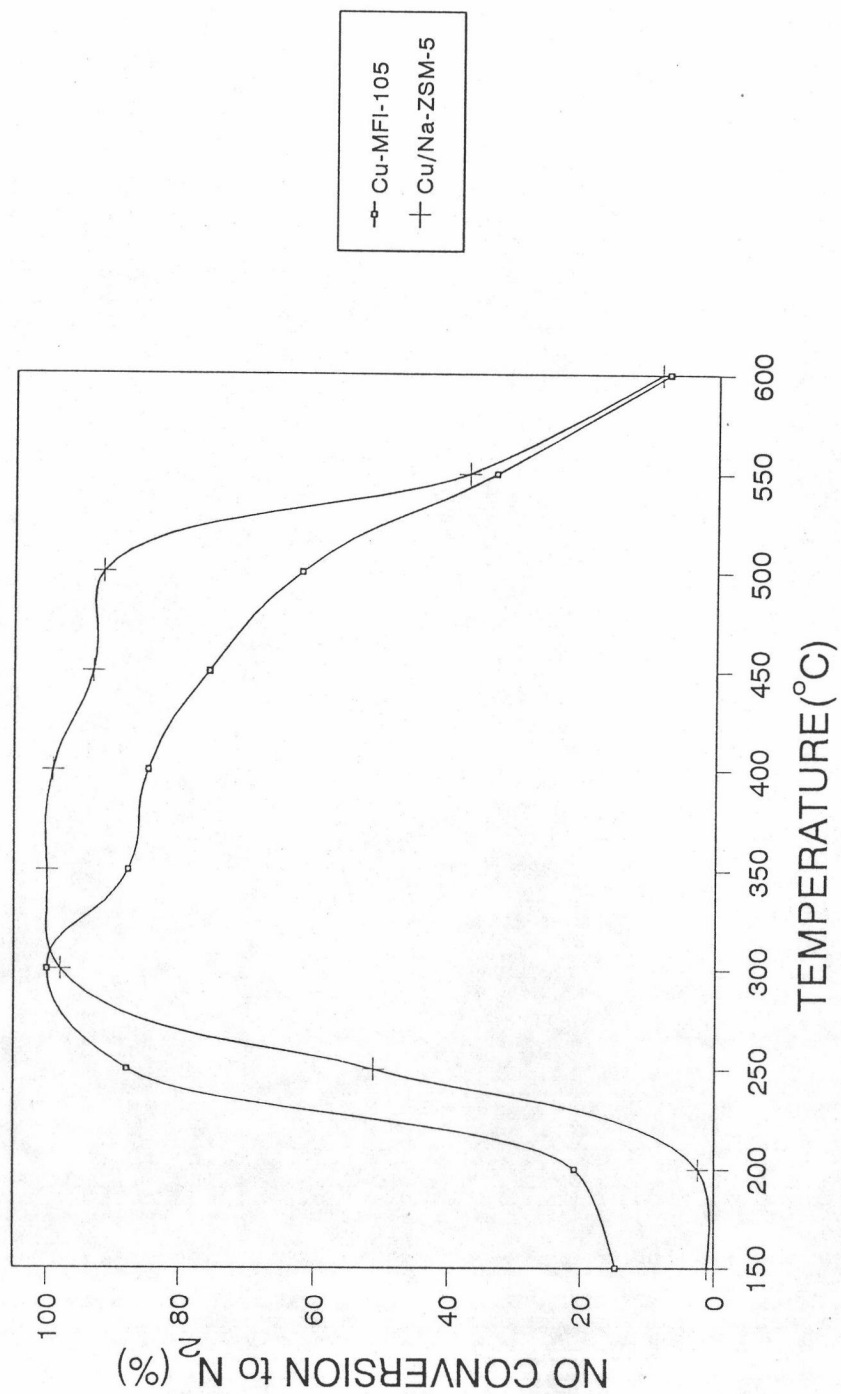
Figure 5.22 Temperature Dependence of NO Conversion on Cu-MFI-105 and Cu/Na-ZSM-5

Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced He, GHSV = 4000 h^{-1}.

Figure 5.23 Temperature Dependence of Propane Conversion on Cu-MFI-105 and Cu/Na-

ZSM-5 Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced He,

GHSV = 4000 h^{-1}.
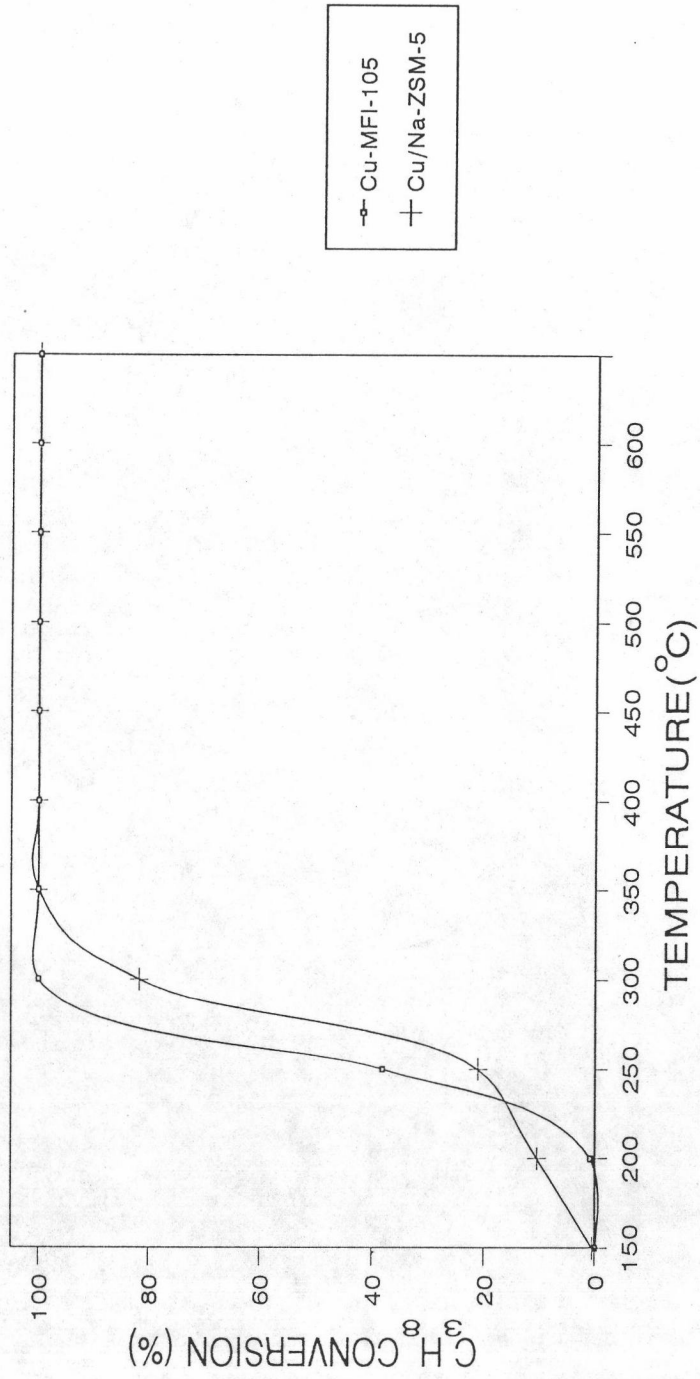
These results suggest that the catalytic activity of copper ion-exchanged Na-ZSM-5 catalyst for this reaction was affected by the amount of copper content of catalyst. The catalytic activity of catalysts for propane oxidation increased with the increase of the amount of copper content in the reaction temperature range. The catalytic activity of propane oxidation in the high reaction temperature range limited the catalytic activity of NO reduction. The advantages of Cu/Na-ZSM-5 on comparison with Cu-MFI-105 are lower amount of copper content and higher catalytic activity for NO reduction at the wide range of reaction temperature.

Table 5.13 The copper ion-exchanged Na-ZSM-5 catalysts used.

Catalysts	Abridged notation	Amount of Copper Content(wt.%)	Description
Cu/Na-ZSM-5	Cu/Na-ZSM-5	0.1275	Na-ZSM-5 having Si/Al = 50 prepared by rapid crystallization method was ion-exchanged by using 0.003 M aqueous solution of copper nitrate at 80 $^{\circ}$C.
Cu-MFI-105	Cu/Na-ZSM-5	4.05	The preparation procedure was described on reference [55].

5.11 Effect of Oxygen Concentration of Catalytic Activity for NO Reduction.

NO conversion on catalysts in the reaction gas containing NO, O_2, and C_3H_8 was examined. Figure 5.24 shows effect of the oxygen concentration for NO conversion on H-ZSM-5 and Cu/H-ZSM-5 catalysts. In the experiment of H-ZSM-5, NO and C_3H_8 concentrations were constant, and O_2 concentrations were varied 0% and 10%. The temperature dependence of NO conversion with different O_2 concentrations using H-ZSM-5

is shown in figure 5.24. With 0% O_2 concentration, NO conversion was gradually increased from 150 °C and reached the maximum conversion at around 550 °C and then decreased at temperatures higher than 550 °C. In case of 10% O_2 concentration, NO conversion was drastically increased from 150 °C, and showed the highest conversion at 350 °C, and decreased temperatures higher than 350 °C. Similar experiments using Cu/H-ZSM-5 were examined and the results are shown in figure 5.24. The NO conversion on Cu/H-ZSM-5 was lower compared with that of H-ZSM-5. The NO conversion of Cu/H-ZSM-5 for 5% O_2 concentration was higher in the wide range of temperature compared with 10% O_2 concentration. The temperature that showed the highest NO conversion shifted lower with the increase in O_2 concentration for these catalysts.

Results for NH_4-ZSM-5 and Cu/NH_4-ZSM-5 catalysts are shown in figure 5.25. With 10, 5, and 0 % O_2, NO conversion on Cu/NH_4-ZSM-5 catalyst is shown to be a mountain - shaped curvature. The range of temperature 150-600 °C, NO conversion with respect to O_2 concentration were in the order of 5% > 10% > 0%. This study reveals that the high oxidation ability would rather limit the NO reduction in the presence of excess oxygen. The maximum activity of each O_2 concentration was observed at 350 - 450 °C. Activities of NH_4-ZSM-5 were similar to those of H-ZSM-5 and Cu/H-ZSM-5. The maximum NO conversions were observed at 400 and 550 °C with 10% and 0% O_2, respectively. The temperatures that showed the highest NO conversion were shifted lower with the increase in O_2 concentration for NH_4-ZSM-5 catalyst.

The results of Na-ZSM-5 and Cu/Na-ZSM-5 are shown in figure 5.26. With 0% O_2,NO conversion on Na-ZSM-5 was lower than 10% at all of the reaction temperature range. When O_2 concentration was 10%, NO conversion increased from 150 to 600 °C and reached maximum conversion at 500 °C. The experiments using Cu/Na-ZSM-5 catalysts were conducted. The NO conversion on Cu/Na-ZSM-5 was higher than that of Na-ZSM-5.
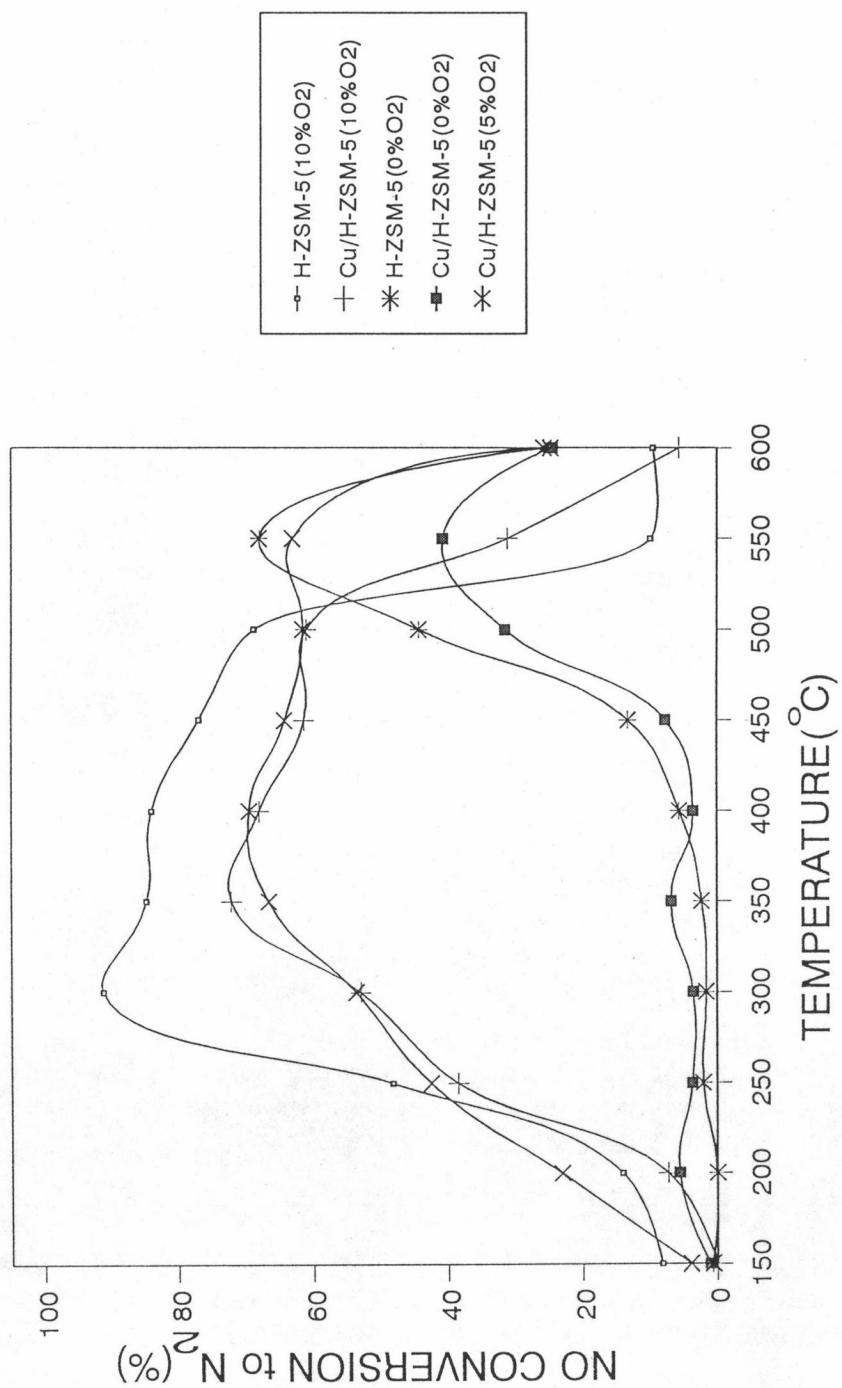
Figure 5.24 Effect of Oxygen Concentration in NO Conversion on H-ZSM-5 and Cu/H-ZSM-5

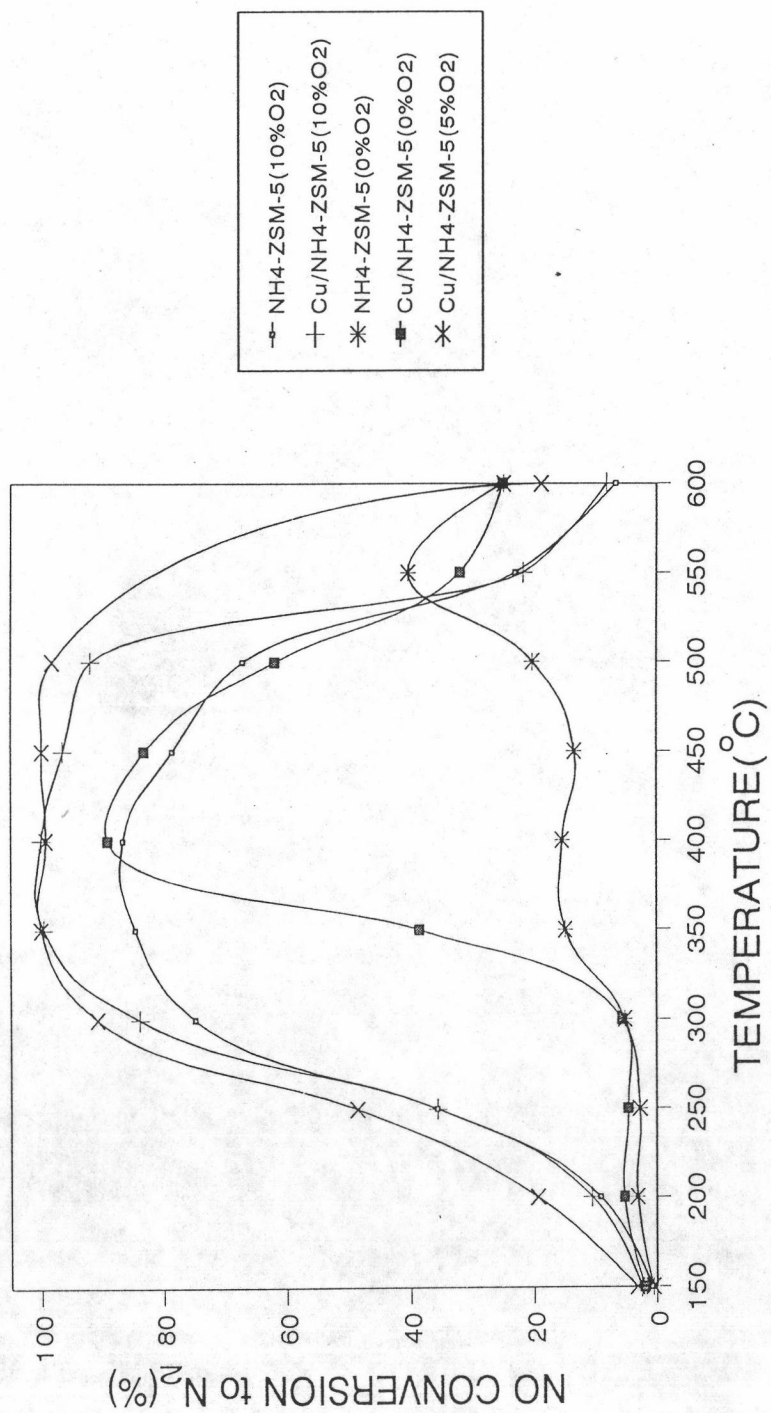Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced He,

GHSV = 4000 h^{-1}.

Figure 5.25 Effect of Oxygen Concentration in NO Conversion on NH4-ZSM-5 and Cu/NH4-ZSM-5 Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 0--10 %O_2, and balanced He, GHSV = 4000 h^{-1}.
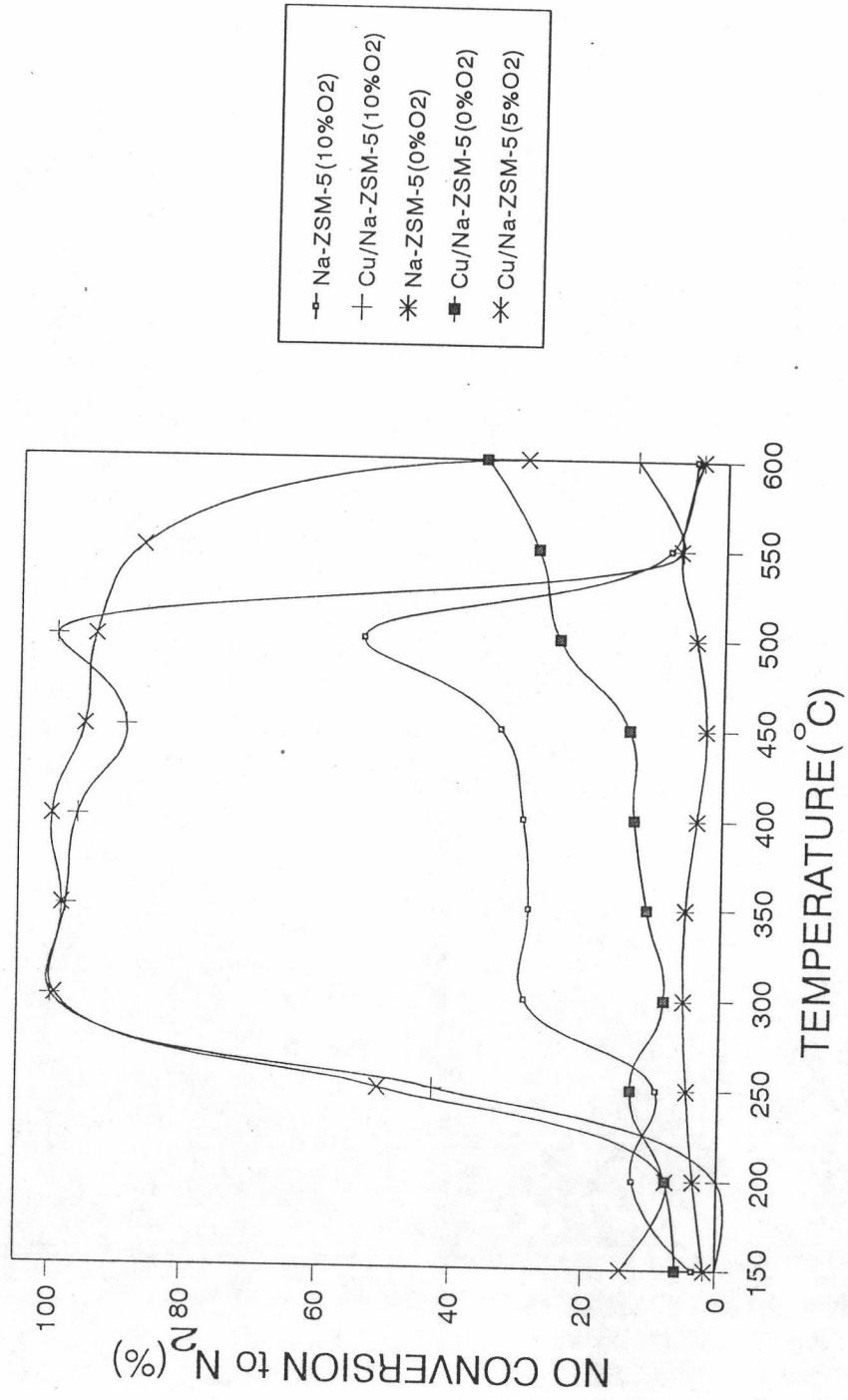
Figure 5.26 Effect of Oxygen Concentration in NO Conversion on Na-ZSM-5 and Cu/Na-

ZSM-5 Catalysts. 1000 ppm NO, 3000 ppm C_3H_8, 0--10 %O_2, and balanced He,

GHSV = 4000 h^{-1}.

With 0% O_2, NO conversion on Cu/Na-ZSM-5 gradually increased from 150 to 600 ^oC. When O_2 concentrations are 5 and 10%, the NO conversion on Cu/Na-ZSM-5 was shown to be a mountain - shaped curvature. 5% O_2 concentration showed higher activity than 10% O_2 concentration at around 300 - 600 ^oC.

In this study, the effect of oxygen concentration to catalytic activity for NO conversion on catalyst can be compared with the oxygen sensitivity of catalysts. Table 5.14 and 5.15 show oxygen sensitivity for NO reduction on various cation-exchanged ZSM-5 and metallosilicates, respectively. The oxygen sensitivities of metallosilicates were calculated from data of Inui et. al [86]. The oxygen sensitivity is defined as ratio of difference of the highest NO conversion temperature with the highest NO conversion temperature with 10% O_2 in feed gas as:

$$\text{Oxygen Sensitivity} = \frac{T_{\text{max. conv.}} - T_{\text{max. conv.(10\% O2)}}}{T_{\text{max. conv.(10\% O2)}}}$$

where $T_{\text{max. conv.}}$ is the temperature of maximum NO conversion with any oxygen concentration and $T_{\text{max. conv.(10\% O2)}}$ is the temperature of maximum NO conversion with 10% of oxygen (temperature, in units of ^oC).

When the concentration of oxygen was increased from 0% to 10%, the order of oxygen sensitivity of catalysts was Cu-MFI-105 ~ Cu/Na-ZSM-5 > H-ZSM-5 ~ Cu/H-ZSM-5 > NH_4-ZSM-5 > Na-ZSM-5 > Cu/NH_4-ZSM-5, as shown in figure 5.27. When the oxygen concentration was increased from 0% to 5%, the order of oxygen sensitivity of catalysts was as follows: Cu/H-ZSM-5 > Cu/Na-ZSM-5 ~ Cu/NH_4-ZSM-5 ~ Cu-MFI-105.

The order of oxygen sensitivity of metallosilicates was H-Fe-silicate > H-Ni-silicate > H-Al-silicate ~ H-Ga-silicate, as shown in figure 5.28.

From these results, it is found that oxygen sensitivity of Cu/Na-ZSM-5 and Cu-MFI-105 catalysts was the same for NO reduction by propane and higher that of the catalysts listed in table 5.14 and 5.15. On the other hand, Cu/NH$_4$-ZSM-5 catalyst was the lowest oxygen sensitivity for NO reduction by propane among the listed catalysts as shown in table 5.14 and 5.15.

The temperature of maximum NO conversion of Cu/NH$_4$-ZSM-5 catalysts hardly depended on variation of oxygen concentrations. It is thus concluded that Cu/NH$_4$-ZSM-5 catalysts are the strong candidates for practical removal of NO in the wide range of oxygen concentrations.

Table 5.14 Oxygen sensitivity of various ion-exchanged ZSM-5 catalysts with oxygen concentration for NO conversion.

Catalyst	Oxygen concentration (wt%)	Temperture of maximun conversion (^{o}C)	Sensitivity
H-ZSM-5	0	550	0.57
	10	350	0
Cu/H-ZSM-5	0	550	0.57
	5	400	0.14
	10	350	0
Na-ZSM-5	0	600	0.2
	10	500	0

Table 5.14 continued

Catalyst	Oxygen concentration (wt%)	Temperture of maximun conversion (^{o}C)	Sensitivity
Cu/Na-ZSM-5	0	600	1.0
	5	300	0
	10	300	0
NH$_4$-ZSM-5	0	550	0.375
	10	400	0
Cu/NH$_4$-ZSM-5	0	400	0
	5	350	0.22
	10	400	0
Cu-MFI-105	0	600	1.0
	5	300	0
	10	300	0

Feed gas 1000 ppm NO, 3000 ppm C_3H_8, 0 -- 10 % O_2, balance He, GHSV = 4000 h^{-1}.

Table 5.15 Oxygen sensitivity of various types of metallosilicates with oxygen concentration

for NO conversion[86].

Metallosilicate	Oxygen concentration (wt.%)	Temperature of maximum conversion (^{o} C)	Oxygen sensivity
H-Fe-silicate	0.5	600	1.4
	1.0	300	0.2
	2.0	300	0.2
	10.0	250	0

Table 5.15 continued

Metallosilicate	Oxygen concentration (wt.%)	Temperature of maximum conversion (^{o}C)	Oxygen sensivity
H-Ga-silicate	0	600	0.09
	0.5	600	0.09
	2.0	600	0.09
	10.0	550	0
H-Ni-silicate	0.0	600	0.71
	0.5	600	0.71
	2.0	450	0.29
	10.0	350	0
H-Al-silicate	0	600	0.09
	2.0	600	0.09
	10.0	550	0

Feed gas: 1000 ppm NO, 3000 ppm C_3H_8 , 0 -- 10 % O_2, balance He, GHSV = 30000 h^{-1}.

Table 5.16 The copper contents of various catalysts which were measured by AAS method.

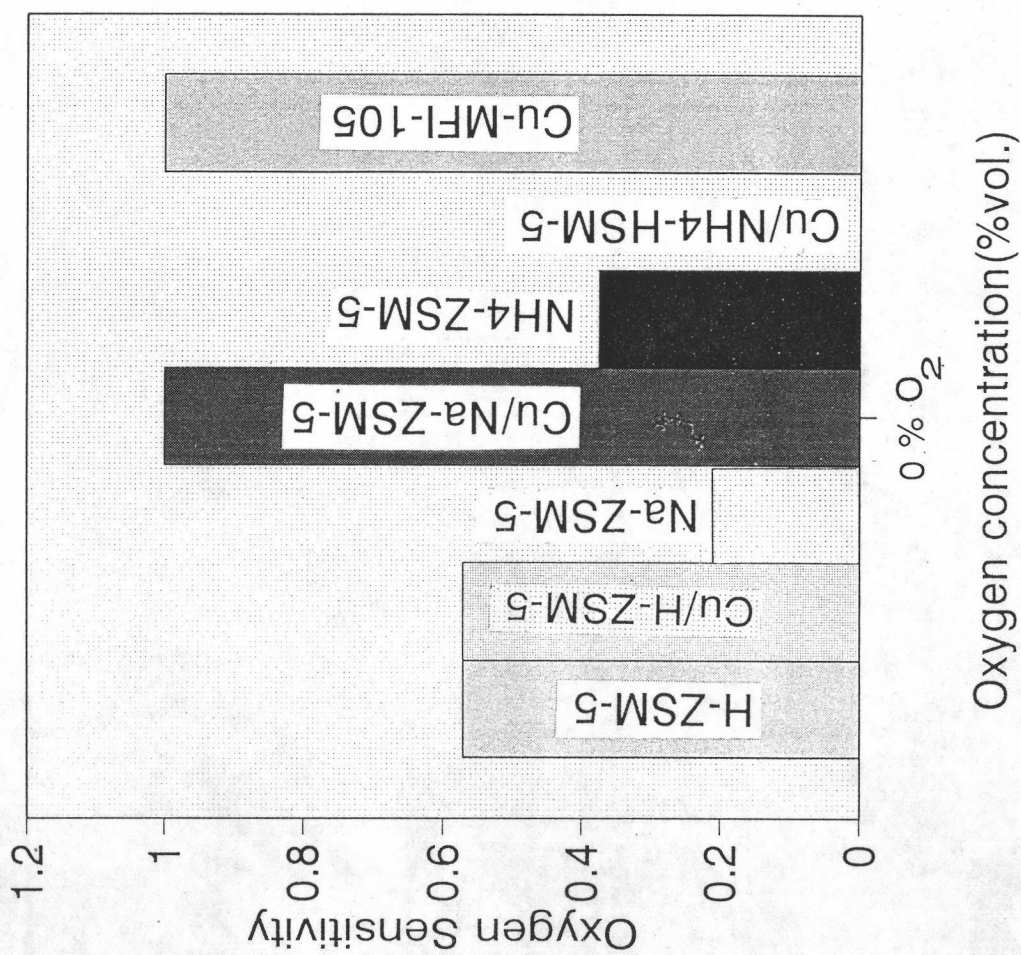| Catalyst sample	Copper contents (Ion-exchange Cu (wt.%))
Cu/H-ZSM-5	0.0135
Cu/NH$_4$-ZSM-5	0.1000
Cu/Na-ZSM-5	0.1007
Cu-MFI-105	4.050

Figure 5.27 Oxygen sensitivity of various ZSM-5 Catalysts with Oxygen Concentration on NO

Conversion. 1000 ppm NO, 3000 ppm C_3H_8,   0 %O_2, and balanced He,
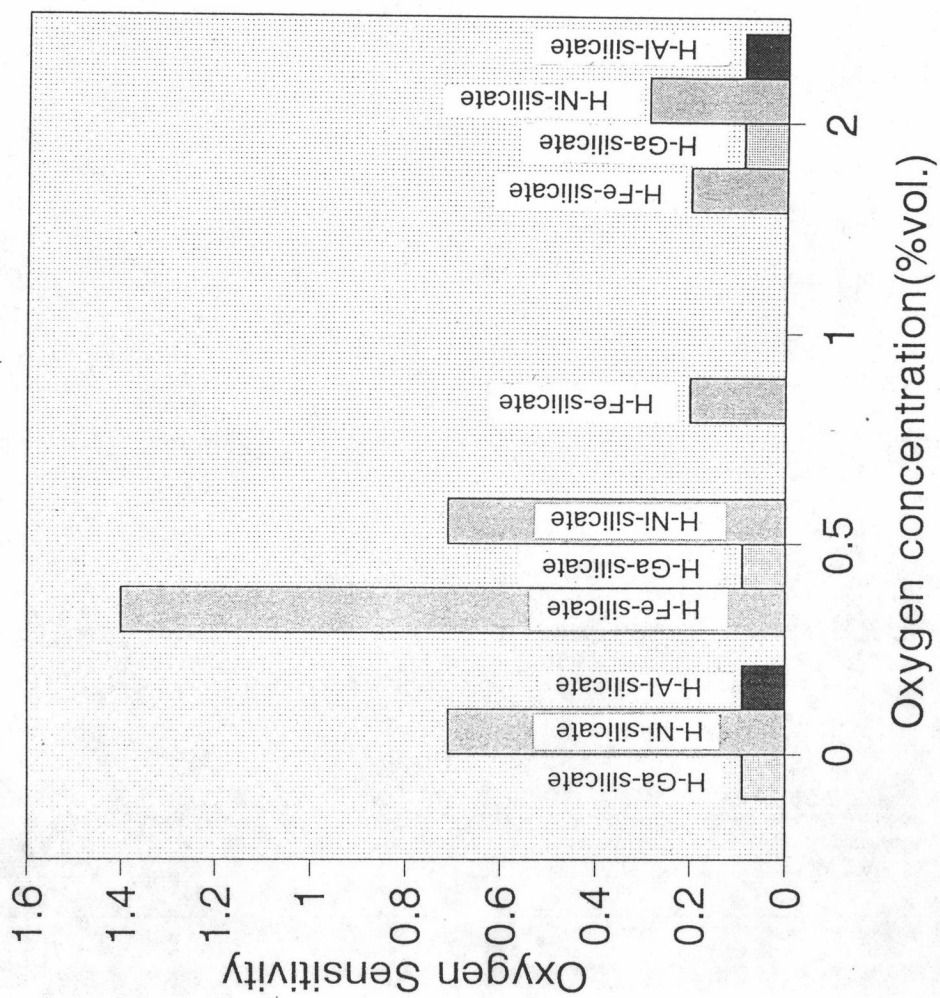
GHSV = 4000 h^{-1}.

Figure 5.28 Oxygen sensitivity of various Metallosilicates with Oxygen Concentration on NO

Conversion. 1000 ppm NO, 3000 ppm C_3H_8, 10 %O_2, and balanced He,

GHSV = 30000 h^{-1}.

5.12 Effect of Remaining Cation in NO Conversion over Various Forms of ZSM-5 and Cu/ZSM-5 Catalysts.

In this study, effect of remaining cation of catalysts which were prepared by using copper ion-exchange with various forms of ZSM-5 and parent zeolites(H-ZSM-5, NH_4-ZSM-5, and Na-ZSM-5) on catalytic activity for reduction of NO was investigated.

The results of reduction of NO on various catalysts by propane are summarized in figure 5.29, 5.30, 5.31, 5.32, and 5.33.

Figure 5.29 and 5.30 compares the catalytic activities of various forms of ZSM-5 at 0 % O_2 and 10 % O_2 in feed gas, respectively. When O_2 concentration is 0 %, the order of the maximum activity was H-ZSM-5(550 ^{o}C) > NH_4-ZSM-5(550 ^{o}C) > Na-ZSM-5(550 ^{o}C). With increasing oxygen concentration , NO conversion increased at the range of low temperature and decreased at the range of high temperature. With 10.0 % O_2 , the order of temperature of the maximum activity was H-ZSM-5(300 ^{o}C) < NH_4-ZSM-5(400 ^{o}C) < Na-ZSM-5(500 ^{o}C).

Figure 5.31 and 5.32 show temperature dependence of Cu/NH_4-ZSM-5(Cu = 0.1000 wt.%) and Cu/Na-ZSM-5(Cu = 0.1007 wt.%) at 0 % and 5.0 % of oxygen concentration, respectively.

With oxygen free feed gas, Cu/NH_4-ZSM-5 showed predominant activity for NO conversion at around 350-400 ^{o}C, and conversion decreased during 400 - 600 ^{o}C. For Cu/Na-ZSM-5, the obtained results were quite different from Cu/NH_4-ZSM-5, NO conversion on

Cu/Na-ZSM-5 gradually increased from 150 $^{\circ}$C to 600 $^{\circ}$C. The difference of the catalytic properties between remained NH_4^+ ion and Na^+ ion on catalytic activities of ZSM-5 are characteristic during 300 - 500 $^{\circ}$C. Cu/NH_4-ZSM-5 was more active for the reduction of NO than Cu/Na-ZSM-5 during 300 - 500 $^{\circ}$C. When oxygen concentration is 5.0 %, NO conversion on the both of catalysts greatly increased at wide range of reaction temperature. The NO conversion with 5.0 % in feed gas was higher compared with 0 % O_2 in feed gas. Higher oxygen concentration resulted in higher NO conversions for these of catalysts. In case of high oxygen concentration, effect of copper content(ca. 0.10 wt.%) was greater than that of remaining cations(NH_4^+ and Na^+ ion).

As shown in figure 5.33, Cu/H-ZSM-5(Cu = 0.1037 wt.%), Cu/NH_4-ZSM-5(Cu = 0.1000 wt.%), and Cu/Na-ZSM-5(Cu = 0.1007 wt.%) exhibited activities for NO conversion with 10.0 % O_2 concentration attained their maximunm NO conversion(100 %), at 350, 350, and 300 $^{\circ}$C, respectively. The same results were observed in the activities of reduction of NO on these catalysts for wide range of temperature.

Figure 5.34 shows activities for NO conversion on Cu/NH_4-ZSM-5(Cu = 0.1274 wt.%) and Cu/Na-ZSM-5(Cu = 0.1275 wt.%) and under a large excess oxygen condition with coexistence of a low concentration of propane. These catalysts exhibited the same results for NO conversion at wide range of temperature.

From these results, the following reaction scheme was assumed by Iwamoto [55] for eqn.1 and Hamada [39] for eqn.2, 3, and 4.

$$2NO \longrightarrow N_2 + O_2 \tag{1}$$

$$NO + O_2 \longrightarrow NO_2 \tag{2}$$

$$NO_2 + C_3H_8 \longrightarrow N_2 + CO_2 + CO + H_2O \tag{3}$$

$$C_3H_8 + O_2 \longrightarrow CO_2 + CO + H_2O \tag{4}$$

For the purpose of elucidating the effect of remaining cation for the removal of nitric oxide, the reaction mechanism was mentioned. When Cu/NH_4-ZSM-5 and Cu/Na-ZSM-5 having Cu wt.% of 0.10 were examined for activities of NO conversion with oxygen-free feed gas condition. The reaction, $2NO \rightarrow N_2 + O_2$ (eqn.1) proceeds at first on the catalyst and then a part of O_2 produced reacts further with unreacted NO, $NO + O_2 \rightarrow NO_2$ (eqn.2), and C_3H_8, $C_3H_8 + O_2 \rightarrow N_2 + CO_2 + CO + H_2O$ (eqn.3). Theoretically, the direct decomposition of NO (eqn.1) is difficult and that was observed at high temperature. Therefore, the direct decomposition of NO (eqn.1) is rate controlling step of reaction mechanism under the absence of oxygen in feed gas condition.

From these results described above, it can be suggested that the difference of activities for the direct decomposition of NO (eqn.1) depend on remaining cation, i.e., NH_4^+, and Na^+ ion with the same amount of proper copper content. The activity of NO conversion on Cu/NH_4-ZSM-5(Cu ~ 0.1 wt.%) was higher than that of Cu/Na-ZSM-5 catalyst(Cu ~ 0.1 wt.%).

On the other hand, the presence of excess oxygen condition, Cu/NH_4-ZSM-5 and Cu/Na-ZSM-5 having amount of copper content c.a. 0.10 wt.% gave nearly the same results of activities for NO conversion. The effect of remaining cation on the direct decomposition of NO was not clearly observed. This means the NO conversion proceeds via the difference mechanism and NO decomposition is the rate controlling step under the condition of excess oxygen.

When NH_4-ZSM-5 and Na-ZSM-5 (Cu-free) were tested for activities of NO conversion with oxygen-free feed condition. The activity for NO conversion was also affected by the difference types of remaining cation as the previous suggestion.

Cu/NH$_4$-ZSM-5 catalyst with the proper copper content is the highest active catalyst for the reduction of NO in NO + C$_3$H$_8$ system. NH$_4^+$ ion is effective remaining cation for reduction of NO. In this reaction condition, it is found that the activities of NO conversion on H-ZSM-5 is higher than that of NH$_4$-ZSM-5. As a result, it is postulated that NH$_3$ gas is not released by Cu/NH$_4$-ZSM-5.
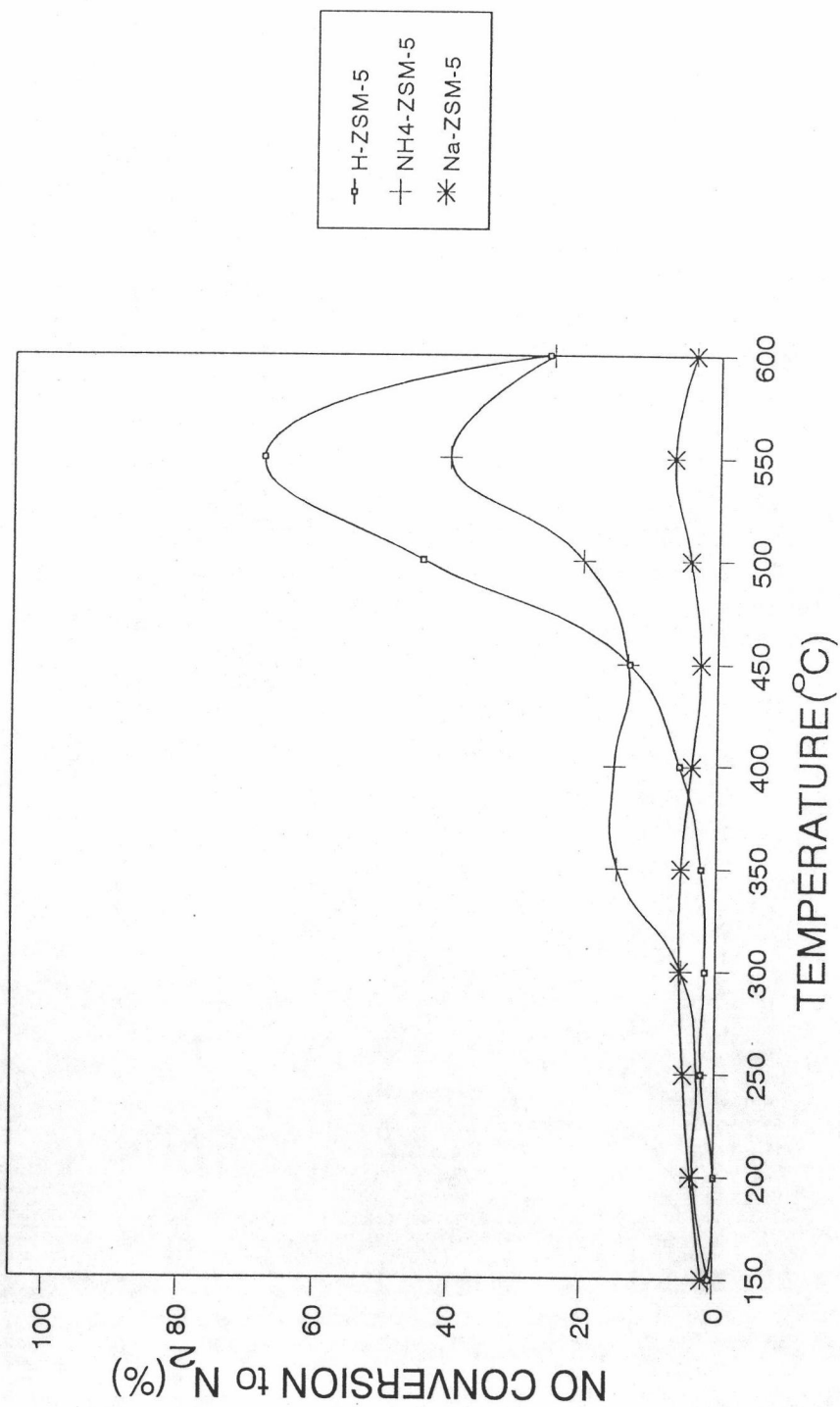
Figure 5.29 Effect of Remaining Cation in NO Conversion over various Forms of ZSM-5 Catalysts.

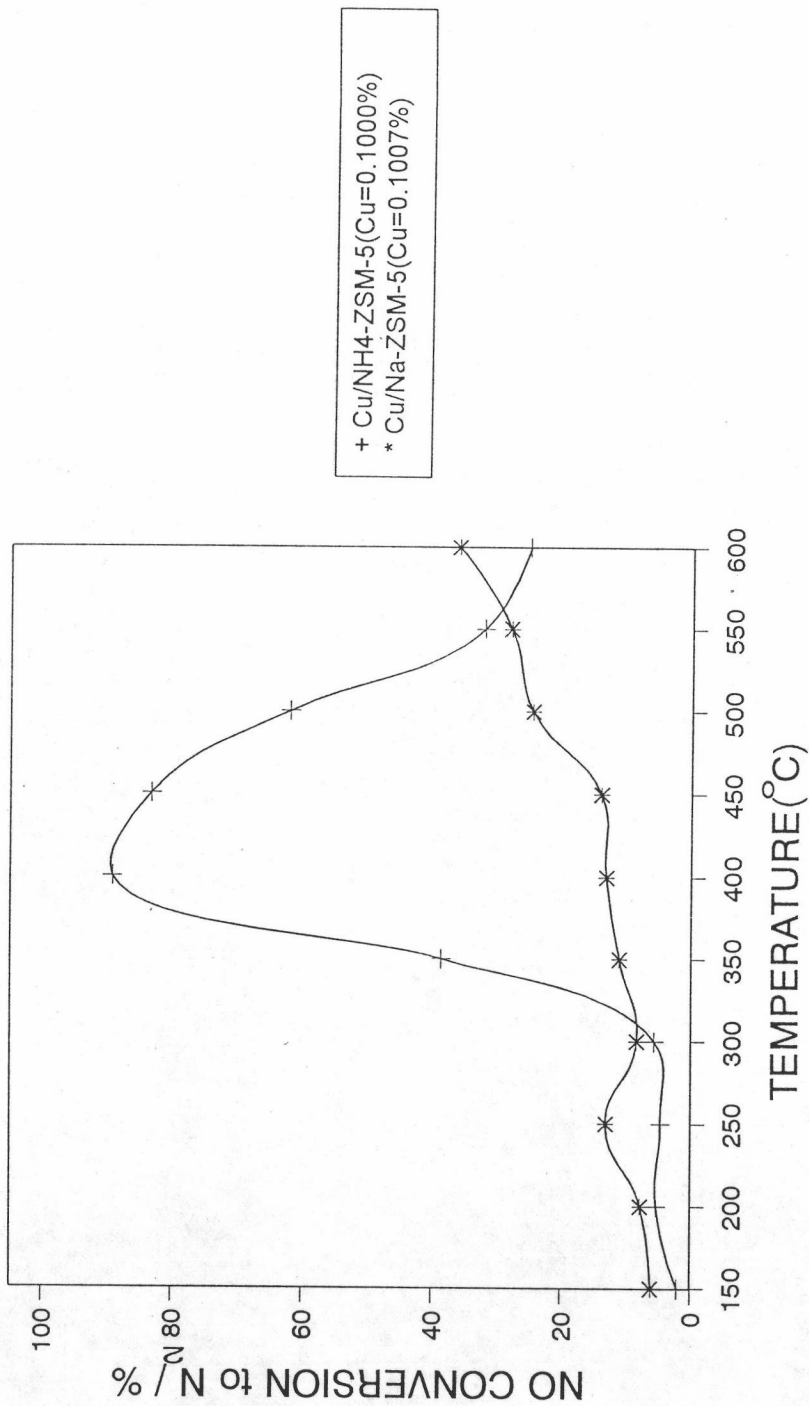1000 ppm NO, 3000 ppm C_3H_8, 0 % O_2, and balance He, GHSV = 4000 h^{-1}.
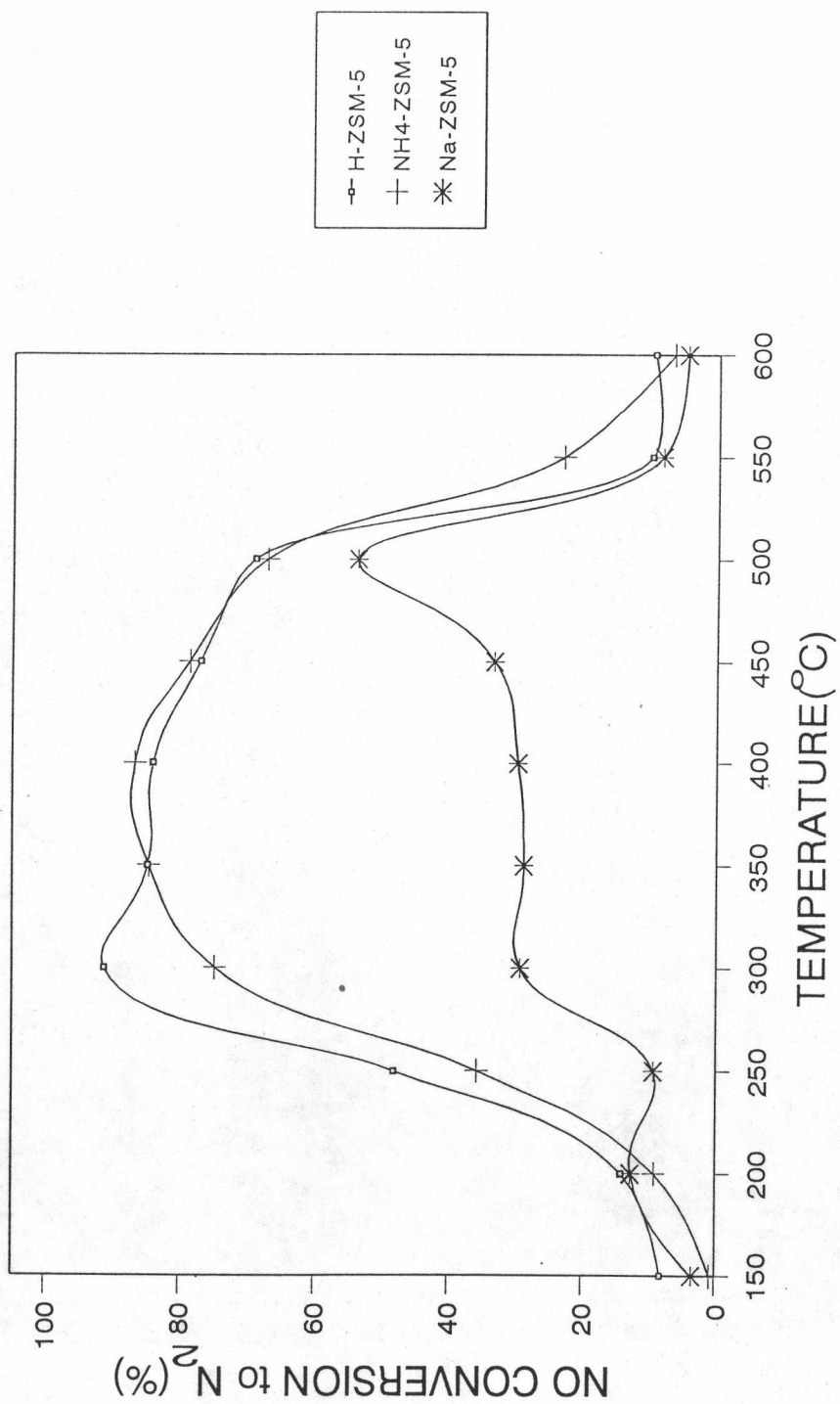
Figure 5.30 Effect of Remaining Cation in NO Conversion over various Forms of ZSM-5 Catalysts.

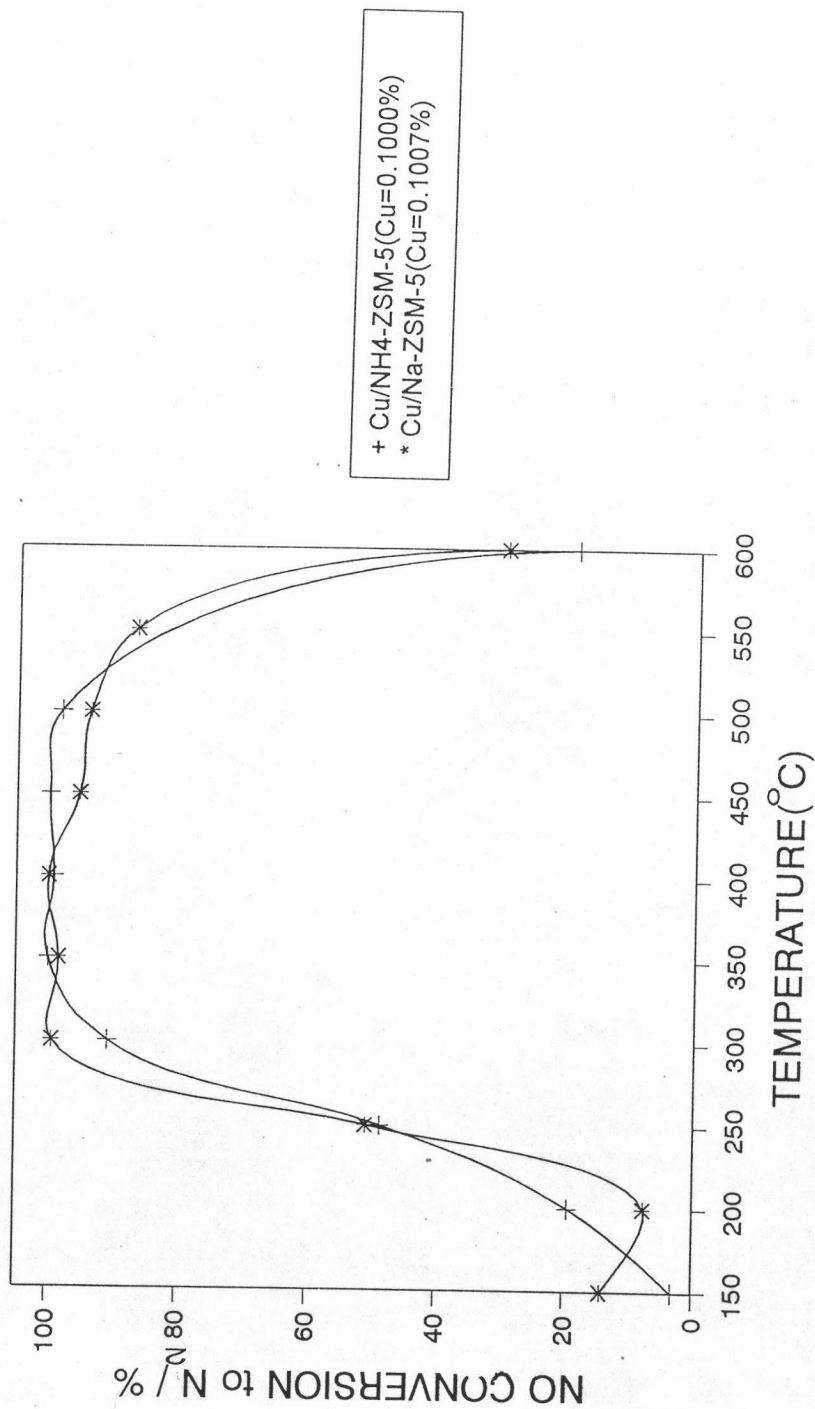1000 ppm NO, 3000 ppm C_3H_8, 10 % O_2, and balance He, GHSV = 4000 h^{-1}.

Figure 5.31 Effect of Remaining Cation in NO Conversion over various Cu/ZSM-5 Catalysts.(Cu = 0.10 wt.%)

1000 ppm NO, 3000 ppm C_3H_8, 0 % O_2, and balance He, GHSV = 4000 h^{-1}.

Figure 5.32 Effect of Remaining Cation in NO Conversion over various Cu/ZSM-5 Catalysts.(Cu = 0.10 wt.%)

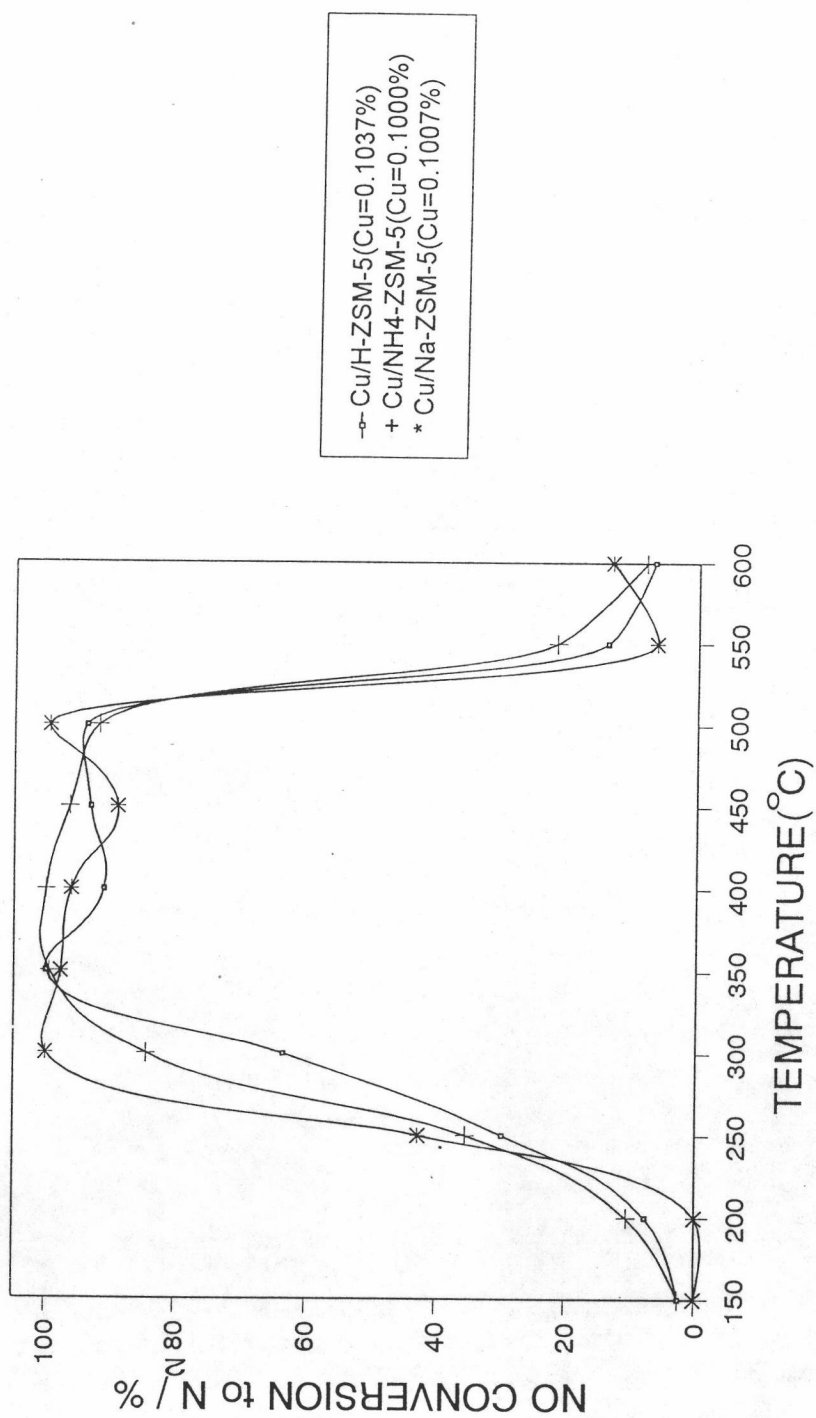1000 ppm NO, 3000 ppm C_3H_8, 5.0 % O_2, and balance He, GHSV = 4000 h^{-1}.

Figure 5.33 Effect of Remaining Cation in NO Conversion over various Cu/ZSM-5 Catalysts.(Cu = 0.10 wt.%)

1000 ppm NO, 3000 ppm C_3H_8, 10.0 % O_2, and balance He, GHSV = 4000 h^{-1} .

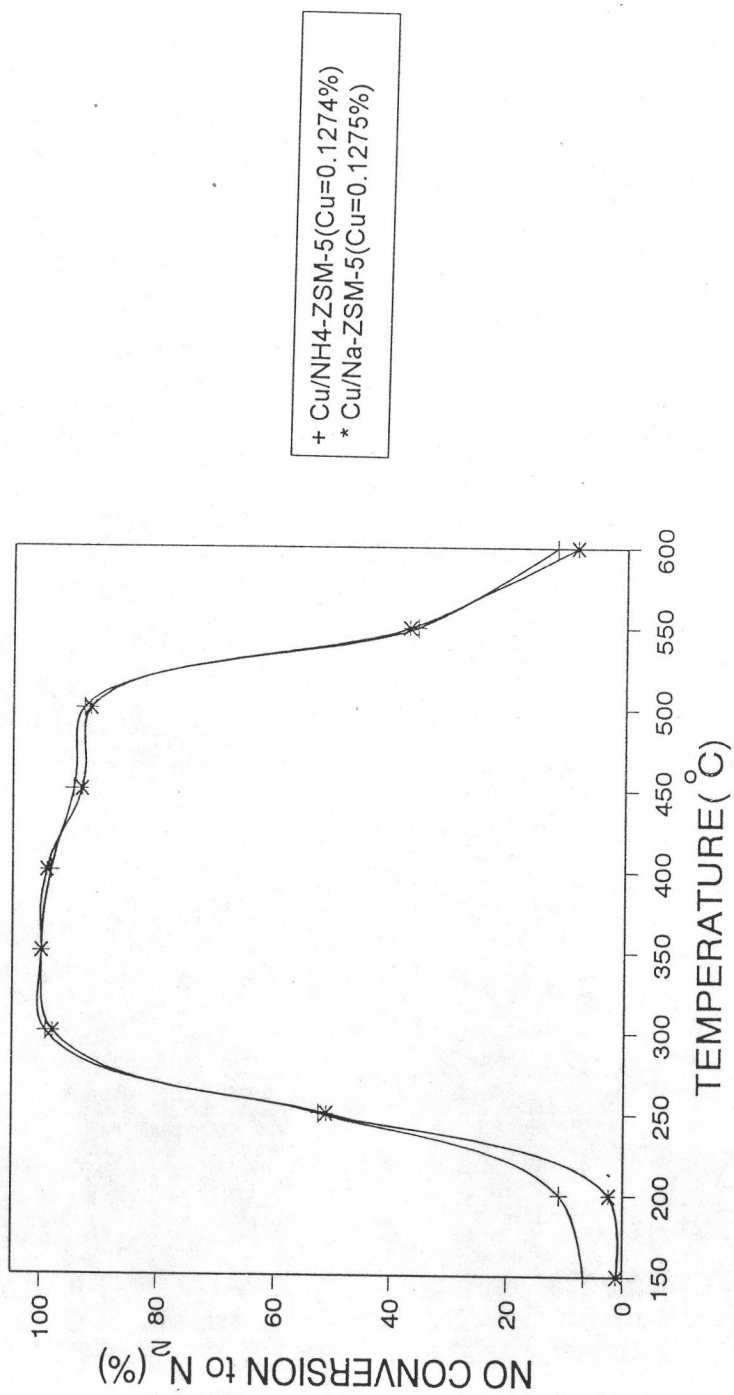+ Cu/NH4-ZSM-5(Cu=0.1274%)
* Cu/Na-ZSM-5(Cu=0.1275%)

Figure 5.34 Effect of Remaining Cation in NO Conversion over various Cu/ZSM-5 Catalysts.(Cu = 0.12 wt.%)

1000 ppm NO, 3000 ppm C_3H_8, 10.0 % O_2, and balance He, GHSV = 4000 h^{-1}.