

CHAPTER V

RESULTS AND DISCUSSIONS

This thesis dealt with studies on the selective reduction of NO by various hydrocarbons under excess oxygen conditions over ZSM-5 and Cu-silicate catalysts. The results and discussions of this study are as follows.

5.1 Effect of Hydrocarbons on the Selective Reduction of NO over Cu/Na-ZSM-5 zeolite in Oxidizing Atmosphere

The selective reduction of NO by various hydrocarbons in an excess oxygen at different temperatures was studied on Cu/Na-ZSM-5 having copper loading 1.05 wt.%, measured by atomic adsorption spectroscopy (AAS) method. The number of carbon atom was kept constant in all cases by adjusting the hydrocarbons concentration. Table 5.1 shows the concentration of various hydrocarbons used for the study.

Activity tests were carried out in a temperature range of 150-600 °C. The temperature dependence of NO conversion and hydrocarbons combustion are shown in Figures 5.1-5.4, respectively. Figure 5.1 presents the catalytic reduction of NO with the saturated hydrocarbons (C₁-C₄). The reduction of NO with the unsaturated hydrocarbons (C₂-C₃) are shown in Figures 5.2 and 5.3.

As shown in Figure 5.1, it was found that the NO reduction with methane was not appreciable until the reaction temperature was raised to 600 °C. On the contrary, the catalytic activity for ethane, propane, and butane as reductants

Table 5.1 Concentration of hydrocarbons used as the reductants for NO reduction

Hydrocarbon	Concentration (ppm)
Methane (CH ₄)	9000
Ethane (C ₂ H ₆)	4500
Ethylene (C ₂ H ₄)	4500
Propane (C ₃ H ₈)	3000
Propylene (C ₃ H ₆)	3000
Butane (C ₄ H ₁₀)	2250

reached the maximum conversions at the same temperature about 300 °C independent of the hydrocarbon. However, NO conversion of Cu/Na-ZSM-5 was the highest when butane was used as reductant. The order of the activity for NO reduction by the saturated hydrocarbons over Cu/Na-ZSM-5 at 300 °C was as follows, butane (100% conversion) > propane (95%) > ethane (91%) > methane (<5%). This result is consistent with the light-off temperatures data as shown in Table 5.2. The temperatures that showed 50% conversion for the reduction of NO with saturated compounds, ethane, propane, and butane were 260, 240, and 215 °C, respectively. For NO-CH₄ reaction, the light-off temperature for NO conversion was not found because the activity for NO reduction was less than 50% conversion during the reaction temperature range.

The decrement of the NO conversion with increasing temperature above the maximum NO conversion temperature was attributed to very severe catalytic oxidation of hydrocarbons by oxygen [31,32]. At higher temperature,

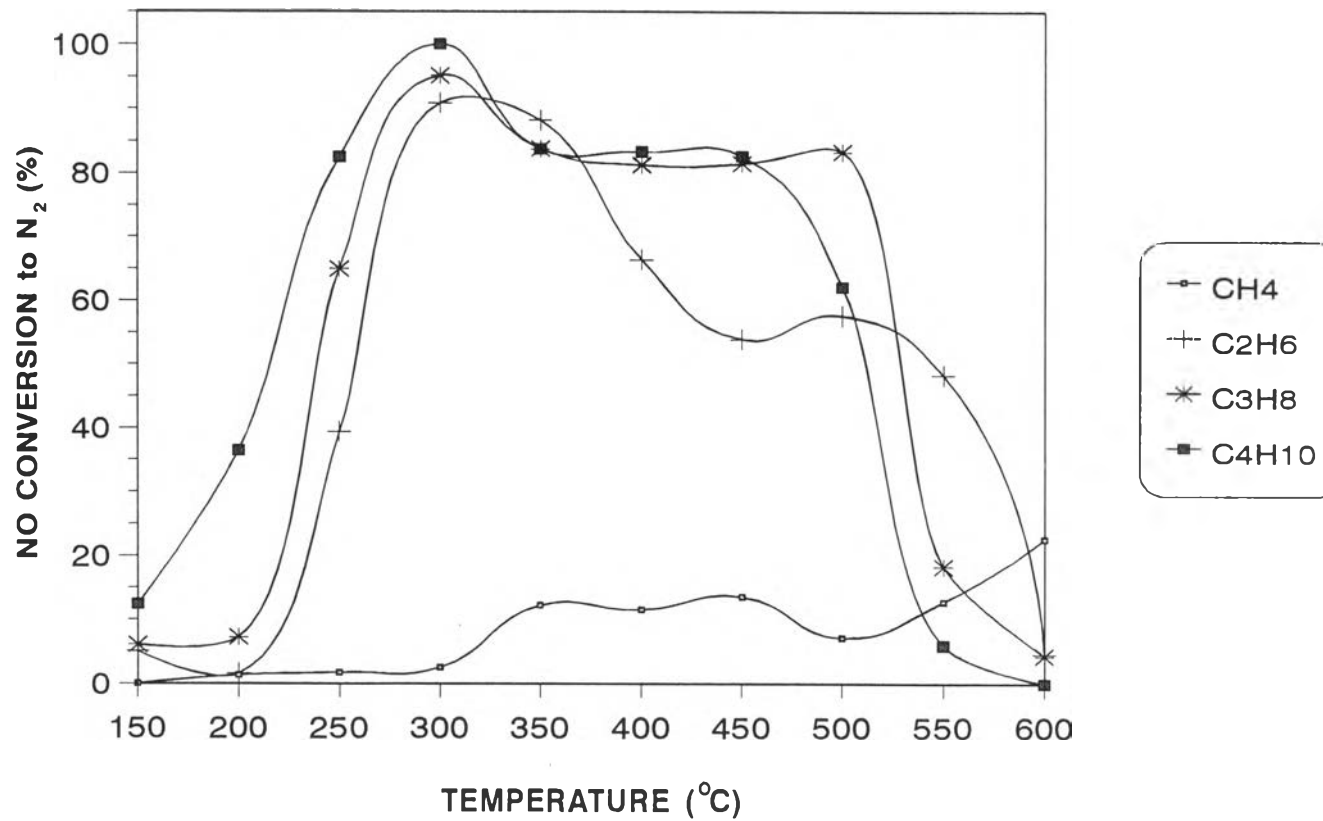


Figure 5.1 Effect of carbon number of saturated hydrocarbon in NO conversion on Cu/Na-ZSM-5 catalyst.

1000 ppm NO, 10% O₂, 9000 ppm CH₄ / 4500 ppm C₂H₆ / 3000 ppm C₃H₈ / 2250 ppm C₄H₁₀,

and balanced He, GHSV = 4000 h⁻¹.

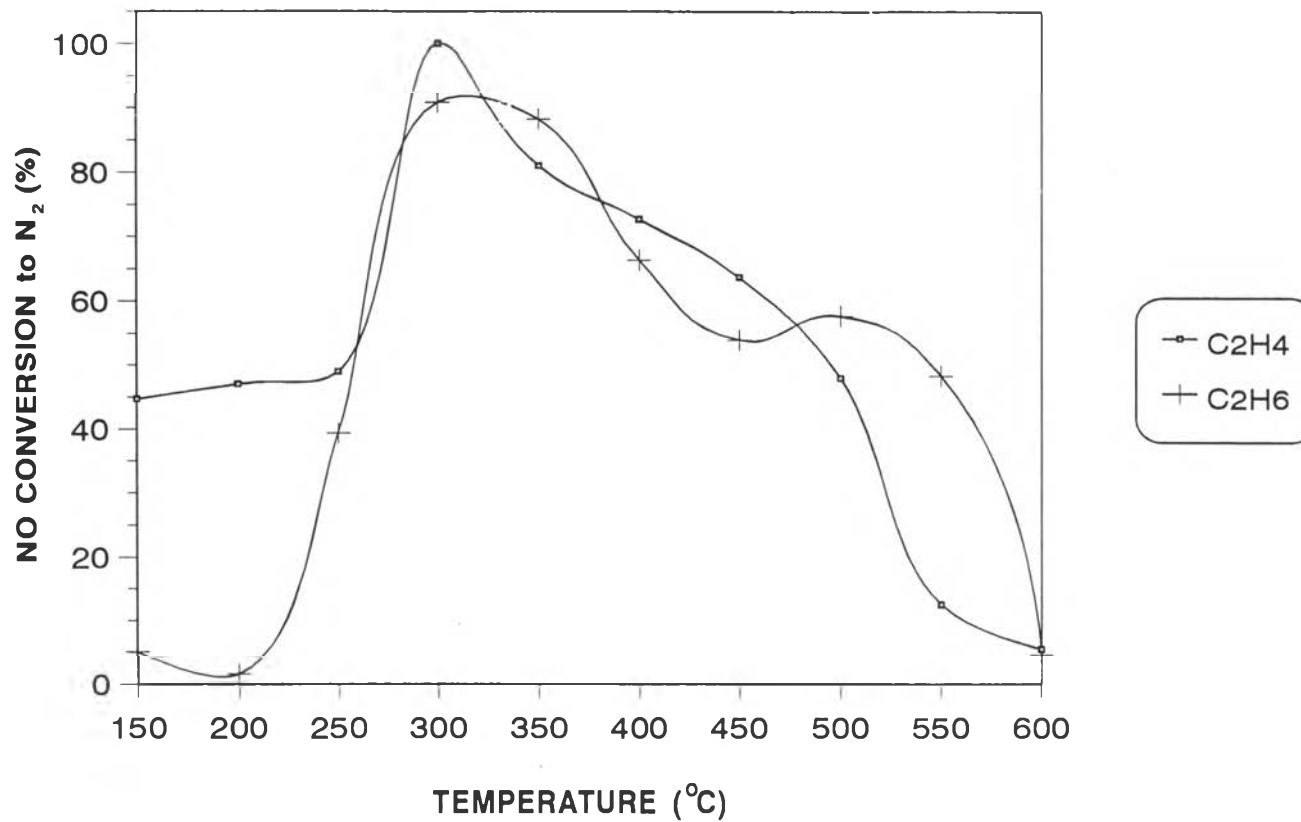


Figure 5.2 Effect of hydrocarbon saturation of C₂ compounds in NO conversion on Cu/Na-ZSM-5 catalyst.

1000 ppm NO, 10% O₂, 4500 ppm C₂H_x, and balanced He, GHSV = 4000 h⁻¹.

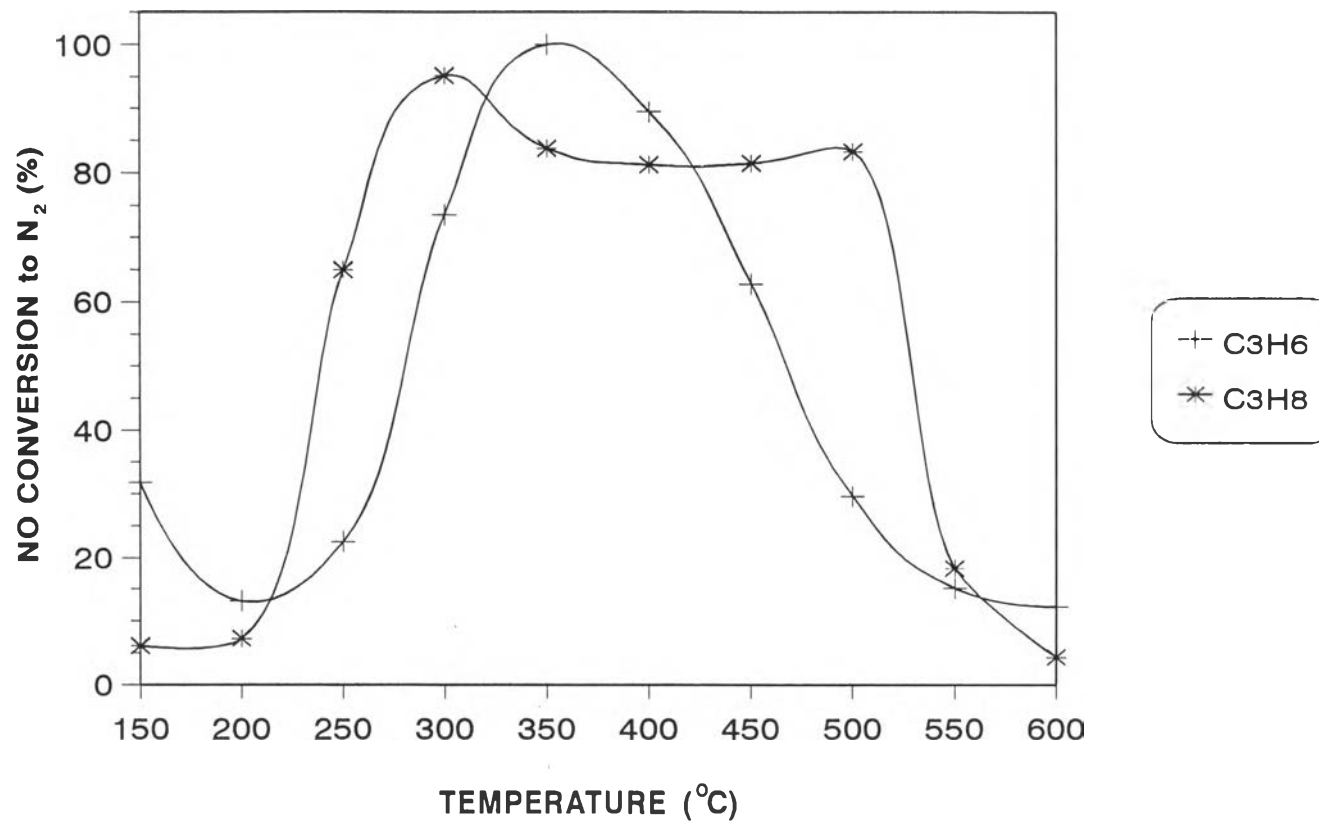


Figure 5.3 Effect of hydrocarbon saturation of C₃ compounds in NO conversion on Cu/Na-ZSM-5 catalyst.

1000 ppm NO, 10% O₂, 3000 ppm C₃H_x, and balanced He, GHSV = 4000 h⁻¹.

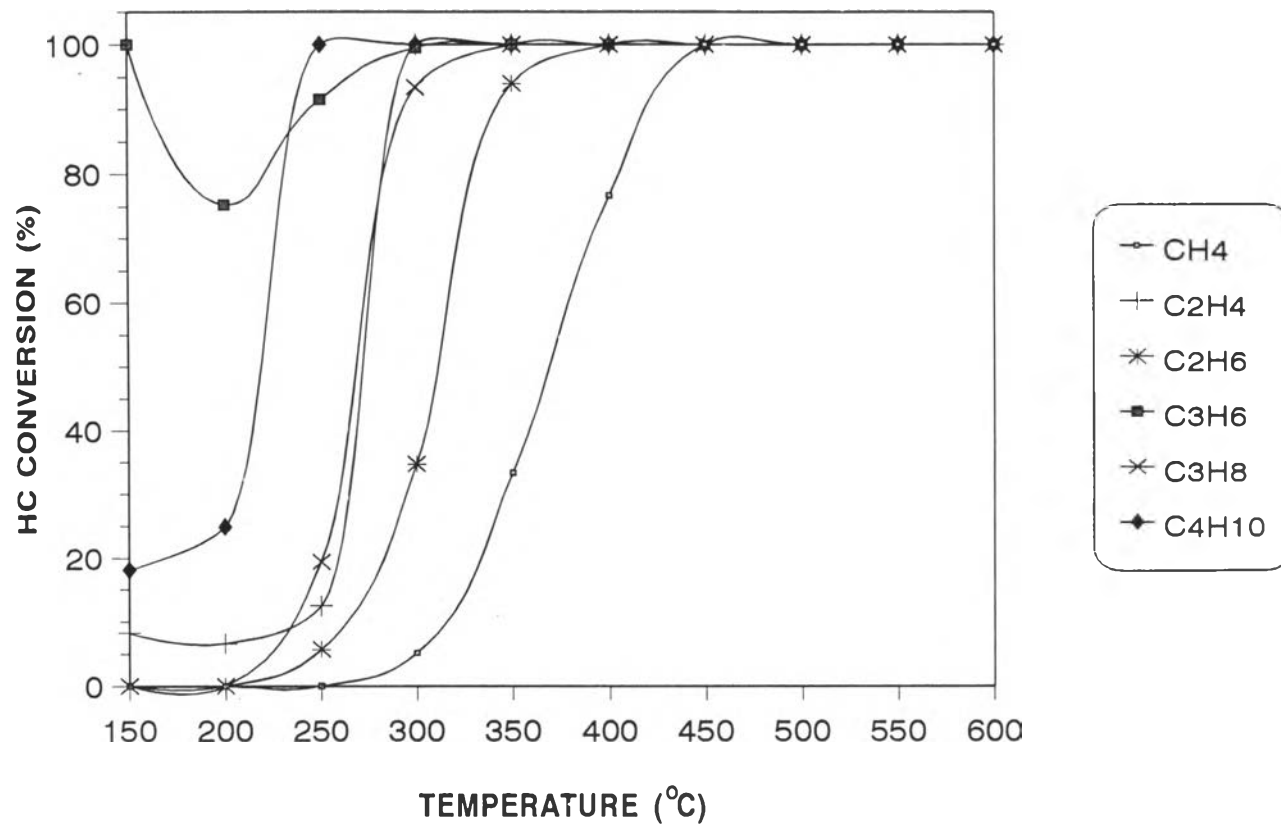


Figure 5.4 Temperature dependence of hydrocarbon conversion on Cu/Na-ZSM-5 catalyst.

1000 ppm NO, 10% O₂, 9000 ppm CH₄ / 4500 ppm C₂H_x / 3000 ppm C₃H_x / 2250 ppm C₄H₁₀,
and balanced He, GHSV = 4000 h⁻¹.

hydrocarbons combustion become a competitive reaction leading to a decrease in NO conversion due to the fact that a lower quantity of hydrocarbons are available for NO reduction.

Table 5.2 The light-off temperature for NO reduction by various hydrocarbons on Cu/Na-ZSM-5 catalyst

Hydrocarbon	Light-off Temperature (°C)	
	NO Conv.	HC Conv.
CH ₄	-	365
C ₂ H ₄	260	270
C ₂ H ₆	260	310
C ₃ H ₆	280	-
C ₃ H ₈	240	270
C ₄ H ₁₀	215	215

Figure 5.2 shows the effectiveness of ethane and ethylene to reduce NO to N₂ at various temperatures. It was seen that ethylene was a superior reductant than ethane. The same results were observed by Ault and Ayen [25]. The maximum NO conversions at 300 °C were 91% and 100% when ethane and ethylene were used as reductants, respectively.

The results of NO reduction by propane and propylene were summarized in Figure 5.3. The temperature of maximum NO conversion in NO-C₃H₈ reaction was lower than that in NO-C₃H₆ reaction. The shift of this temperature is possibly due to the deactivation of the catalyst by accumulated coke deposited

in the pore of catalyst. The conclusion was confirmed by the temperature-programmed oxidation (TPO) studies as shown in Figures 5.5 and 5.6. It was found that the amount of coke with propylene was greater than with propane. The carbon content observed on spent catalysts with propylene and propane were 0.057 and 0.052 wt.%, respectively. This can conclude that coke build up from propylene blocks the active sites on the catalyst. Superior effectiveness of propane in comparison to propylene has also been reported by d'Itri and Sachtler [30]. For pore size distribution studies, the results in Figure 5.7 clearly show that pore size distribution of Cu/Na-ZSM-5 after reaction with propane was slightly higher than with propylene at pore diameter about 4 Å. This reason can be attributed to the above conclusion that the formed coke from propylene blocks the pore structure and decreases the pore volume of the catalyst. However, the different pore sizes distribution of fresh 35%Cu/Na-ZSM-5 compared with spent catalyst will be explained in the characterization part.

From Table 5.2, the light-off temperatures for NO reduction with propane and propylene were 240 and 280 °C, respectively. This is consistent with above result that propane was an effective reductant for NO than propylene.

Effect of temperature on the conversion of various hydrocarbons to CO and CO₂ are shown in Figure 5.4. Methane was found to be the most difficult hydrocarbon to oxidize and propylene was the easiest. In general, an increase in carbon number decreased the temperature for a given conversion. For example, the light-off temperatures, temperatures necessary for 50% conversion of the saturated compounds, methane, ethane, propane, and butane were 365, 310, 270, and 215 °C, respectively. For a given carbon number, the required temperature decreased with degree of saturation such as the light-off temperatures of ethane and ethylene were 310 and 270 °C, respectively.

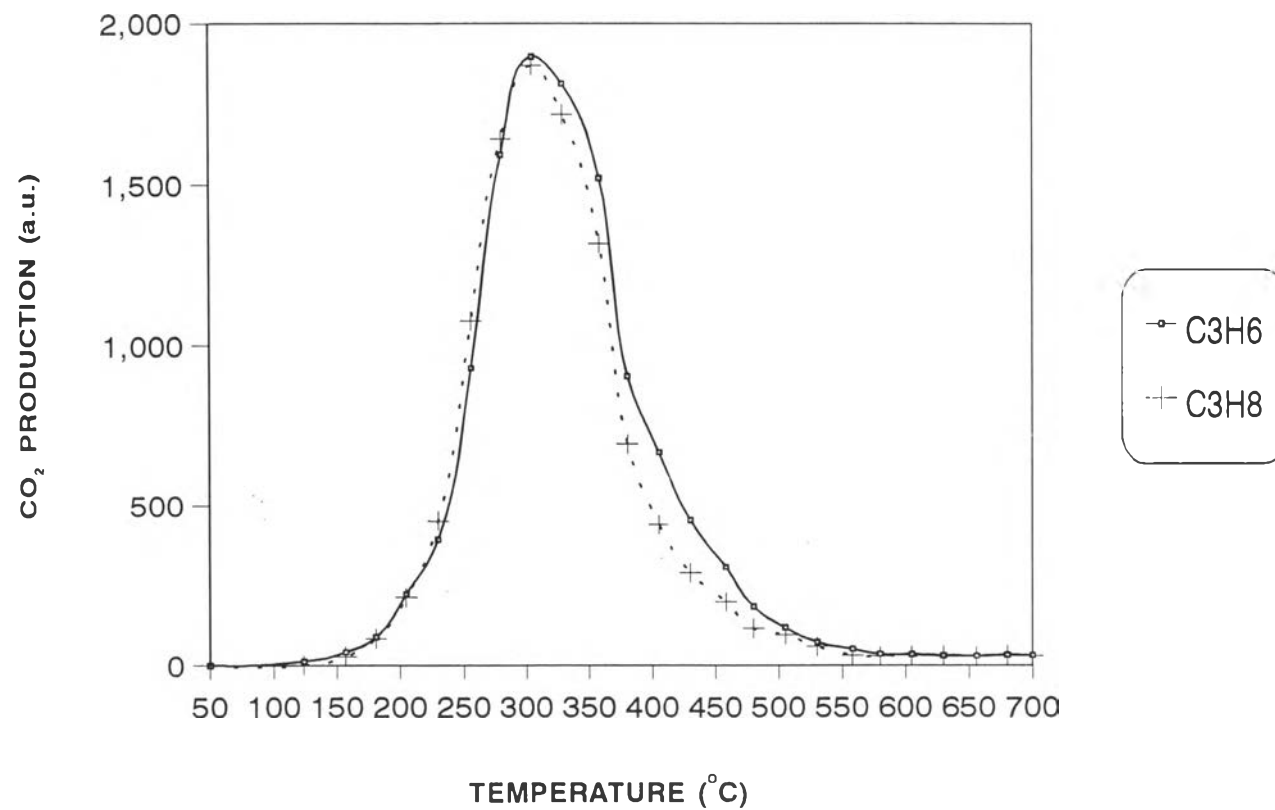


Figure 5.5 TPO curves of Cu/Na-ZSM-5 catalyst after the reaction with propane and propylene.

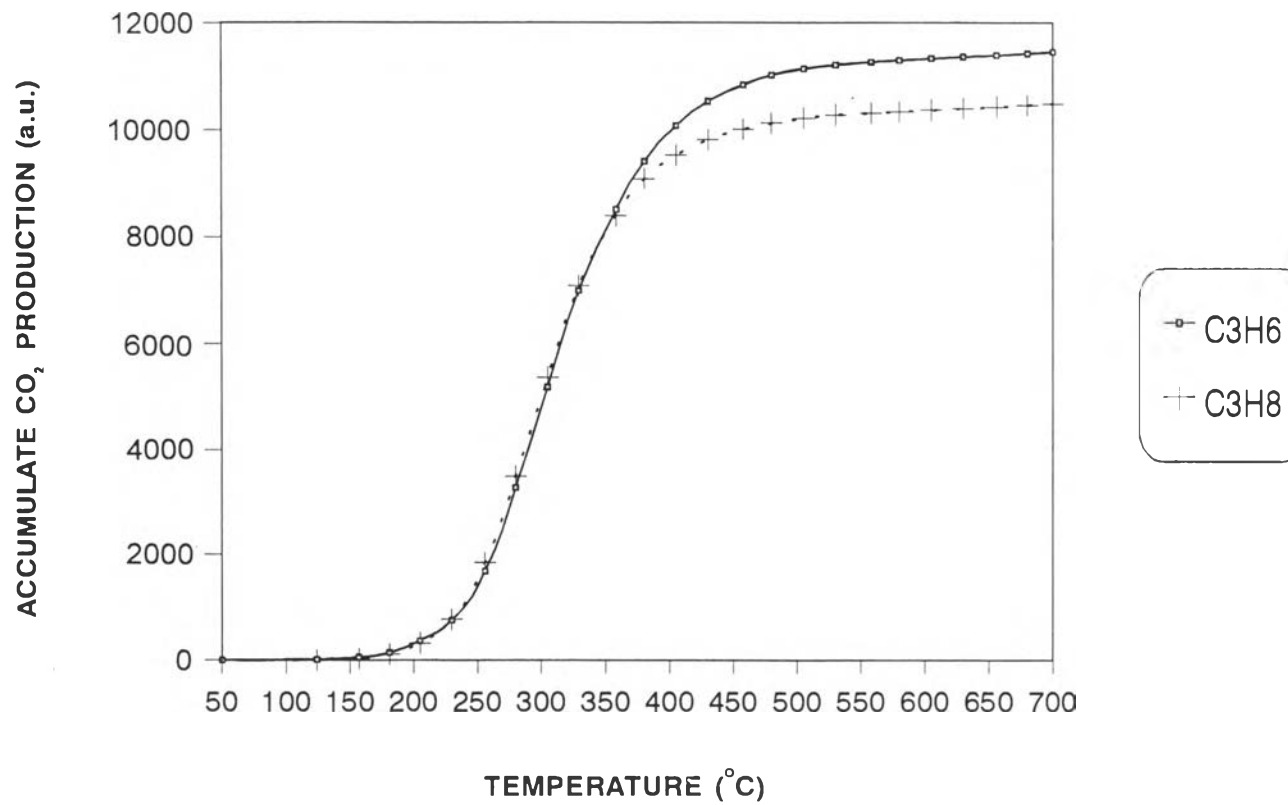


Figure 5.6 Comparison of cumulative CO₂ production between Cu/Na-ZSM-5 after the reaction with propane and propylene.

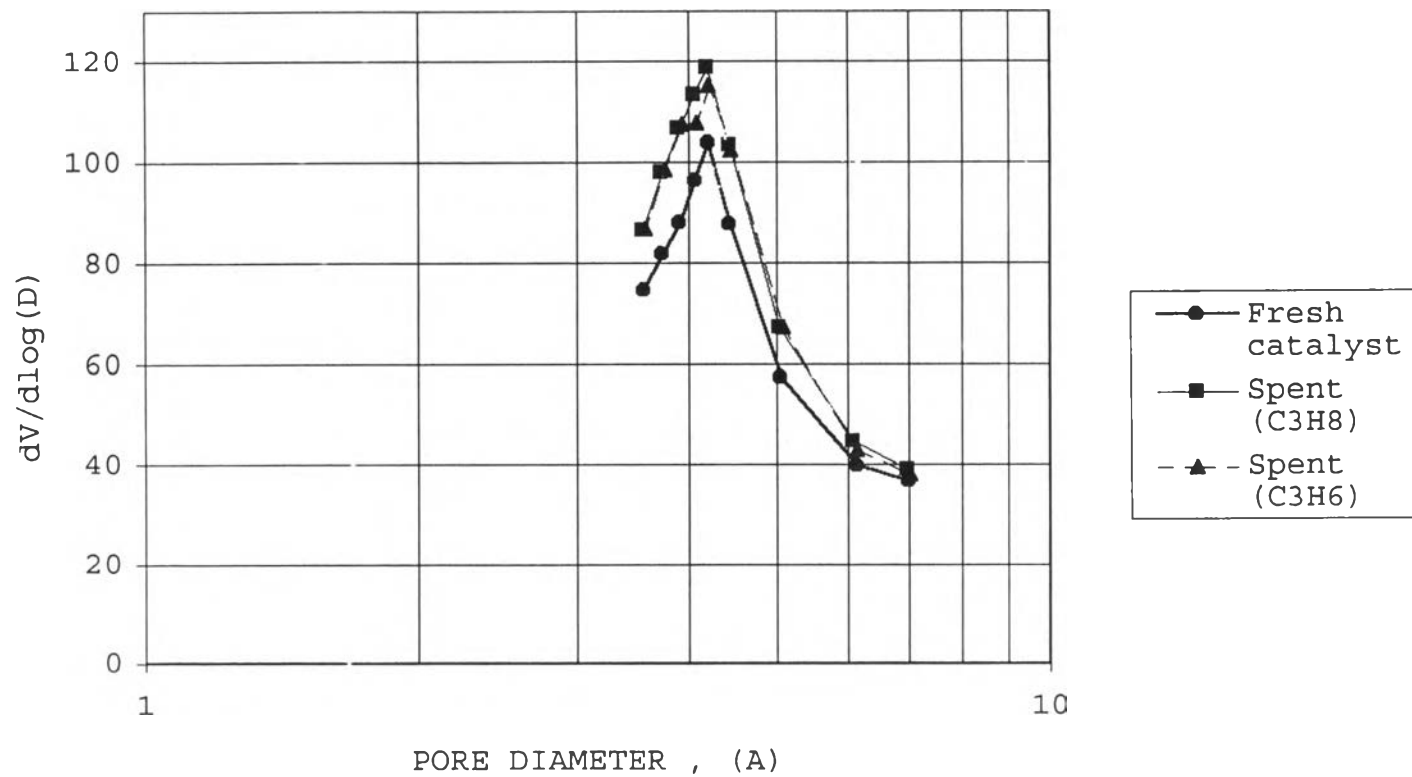


Figure 5.7 Comparison of pore size distribution between fresh and spent Cu/Na-ZSM-5 after the reaction with propane and propylene.

In addition, propylene showed the conversion higher than 50% throughout the reaction temperature range. These results are consistent with the previous work of Accomazzo and Nobe [53].

5.2 Effect of Catalyst Form on the Selective Reduction of NO by Propane in the Presence of Excess Oxygen

In this study, the catalytic activities for NO reduction on Na-Cu-silicate, Cu/Na-silicalite, and Cu/Na-ZSM-5 having Cu wt.% of 0.2 were investigated at temperature in the range of 150 to 600 °C. The amount of copper contents on Cu-exchanged and Cu-silicate catalysts measured by AAS method are shown in Table 5.3. It was found that Na-silicalite (Al-free catalyst) required the amount of Cu for ion-exchanging more than Na-ZSM-5 [39]. The results of NO to N₂ conversion and C₃H₈ conversion as a function of the reaction temperature are shown in Figures 5.8 and 5.9, respectively. Cu/Na-ZSM-5 zeolite was substantially more active compared to Na-Cu-silicate and Cu/Na-silicalite. Furthermore, the catalytic activity of Na-Cu-silicate was almost as low as that of Cu/Na-silicalite. This indicates that Cu-incorporated and Cu-exchanged zeolites (Al-free) do not show the different results whereas the catalyst having amount of Al shows the higher activity. Consequently, the catalytic activity for NO reduction may be affected by the Al content .

Table 5.4 summarizes the light-off temperatures for NO conversion and C₃H₈ conversion of various catalysts. Since NO conversions of 0.25% Cu/Na-silicalite and Na-Cu-silicate were always lower than 50%, therefore, the both catalysts had no light-off temperatures for NO. In addition, 0.2% Cu/Na-ZSM-5 showed the lowest light-off temperature for C₃H₈ conversion compared with the

others. From these results, one can conclude that 0.2% Cu/Na-ZSM-5 was the best catalyst for NO reduction with C_3H_8 .

Table 5.3 The copper contents of various catalysts which were measured by AAS method

Catalysts	Metal containing method	Copper contents (wt.%)
0.2% Cu/Na-ZSM-5	ion-exchange	0.205
0.25% Cu/Na-silicalite	ion-exchange	0.215
Na-Cu-silicate	incorporate	0.204

Table 5.4 The light-off temperature of the prepared catalysts

Catalysts	Light-off Temperature (°C)	
	NO Conv.	C_3H_8 Conv.
0.2% Cu/Na-ZSM-5	340	395
0.25% Cu/Na-silicalite	-	500
Na-Cu-silicate	-	505

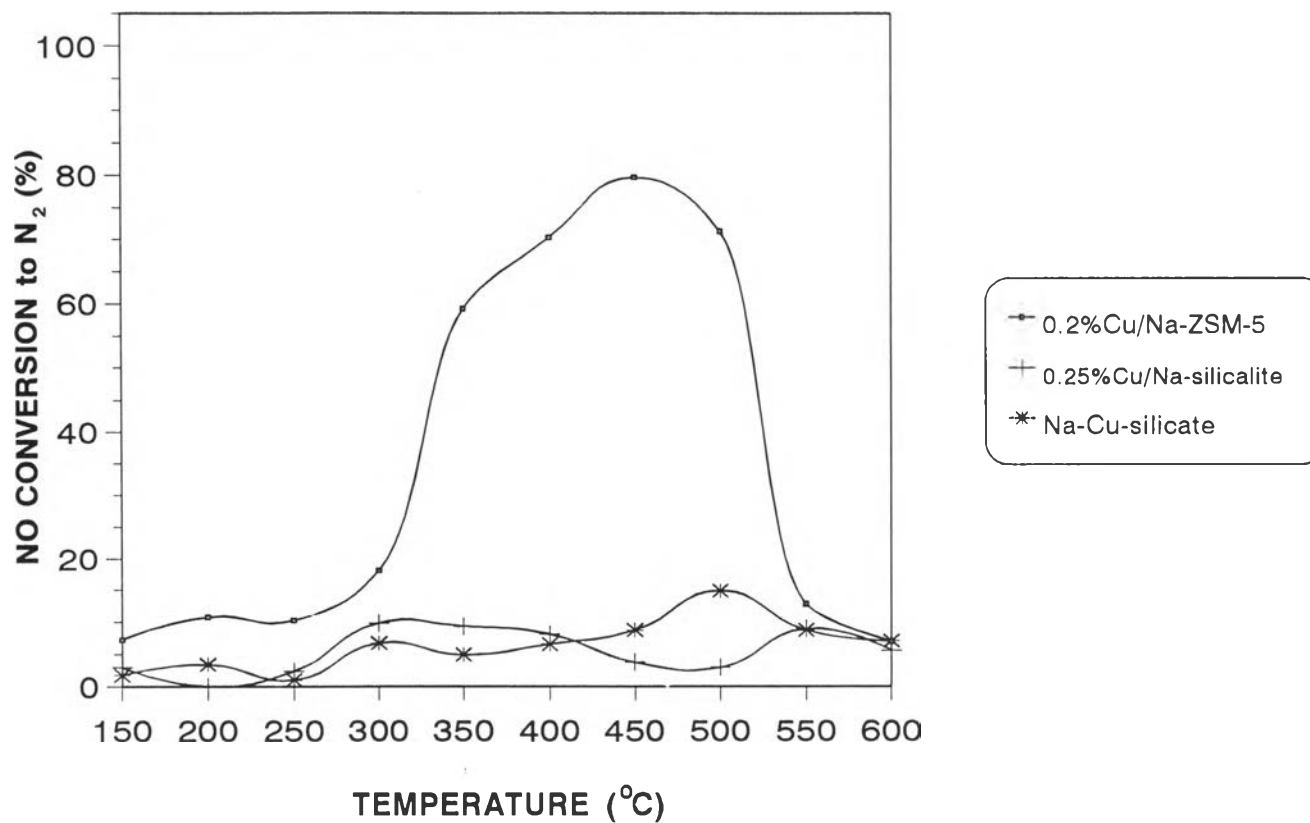


Figure 5.8 Temperature dependence of NO conversion on various Cu containing catalysts (Cu=0.2 wt.%).

1000 ppm NO, 10% O₂, 3000 ppm C₃H₈, and balanced He, GHSV = 4000 h⁻¹.

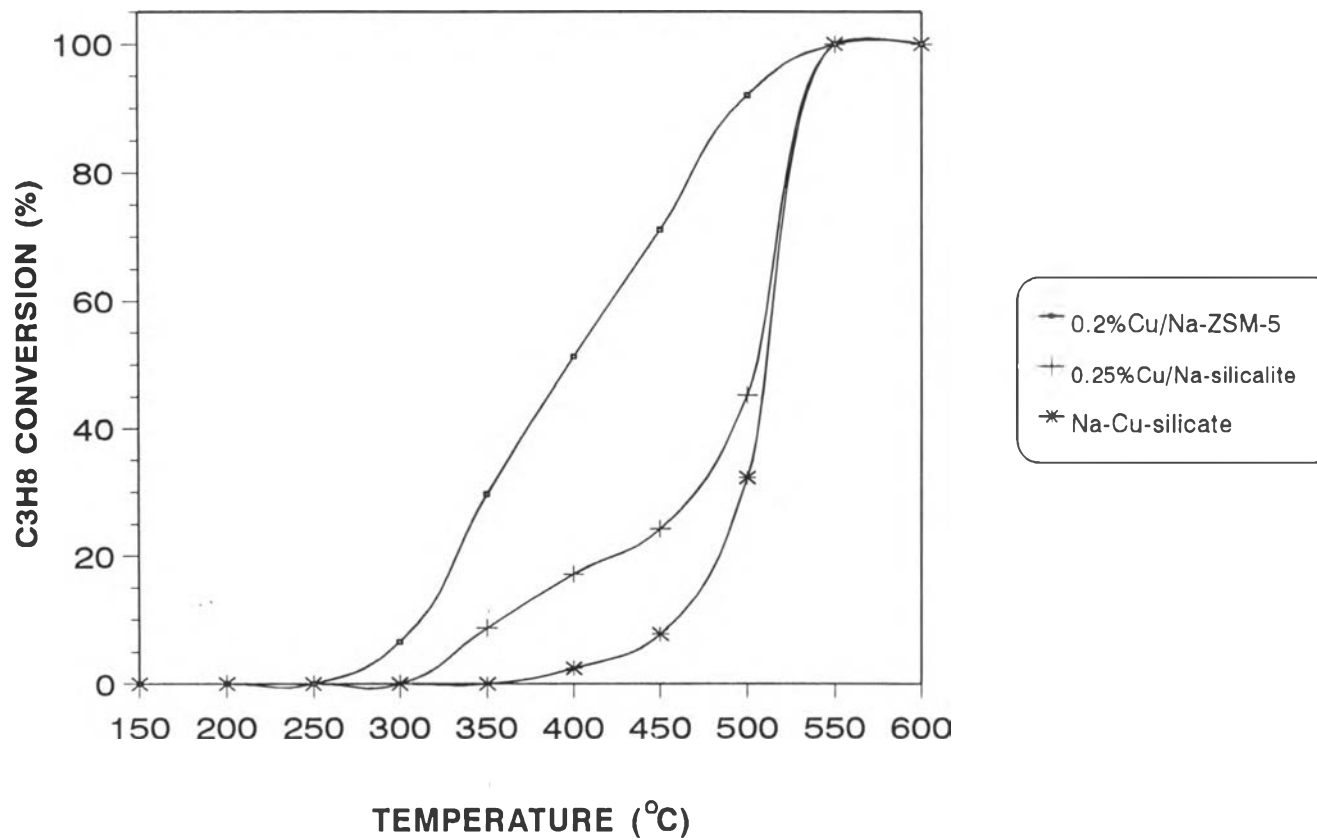


Figure 5.9 Temperature dependence of C₃H₈ conversion on various Cu containing catalysts

(Cu=0.2 wt.%). 1000 ppm NO, 10% O₂, 3000 ppm C₃H₈, and balanced He, GHSV = 4000 h⁻¹.

5.3 Effect of Silicon to Aluminum Ratio in H-ZSM-5 on Selective Reduction of NO by Propane in Oxidizing Atmosphere

The selective reduction of nitric oxide by propane in the presence of a large excess of oxygen was investigated on proton-exchanged ZSM-5 with Si/Al = 20, 50, 3200, and ∞ over a wide range of temperature. The observed Si/Al ratio in H-ZSM-5 catalysts measured by AAS method are presented in Table 5.5. Figures 5.10 and 5.11 show the catalytic activity for NO reduction and C₃H₈ combustion of H-ZSM-5 with various Si/Al ratio. It is found that the slight difference in Si/Al ratio does not show the different conversion of NO and C₃H₈. The large increment of Si/Al ratio decreased the NO conversion into N₂ and C₃H₈ conversion into CO and CO₂.

Table 5.5 The observed Si/Al ratio in H-ZSM-5 by AAS method

Charged Si/Al ratio	Observed Si/Al ratio
20	17
50	37
3200	beyond upper limit
∞	beyond upper limit

The light-off temperatures for NO reduction and C₃H₈ combustion of H-ZSM-5 with various Si/Al ratio catalysts are summarized in Table 5.6. The much lower Si/Al ratio in H-ZSM-5 showed the lower light-off temperatures for NO and C₃H₈. This can be concluded that the lower Si/Al ratio in H-ZSM-5 is the better

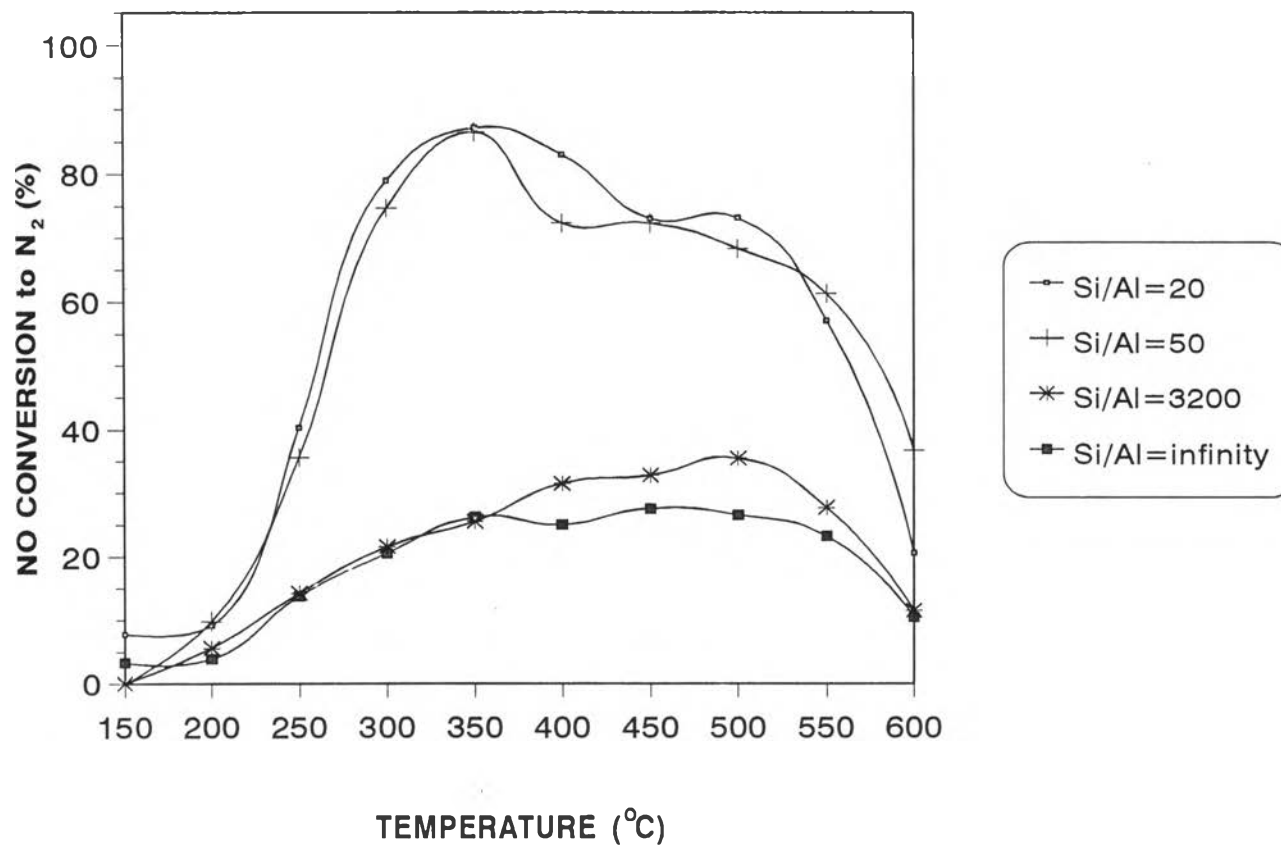


Figure 5.10 Effect of Si/Al ratio in NO conversion on various H-ZSM-5 catalysts.

1000 ppm NO, 10% O₂, 3000 ppm C₃H₈, and balanced He, GHSV = 4000 h⁻¹.

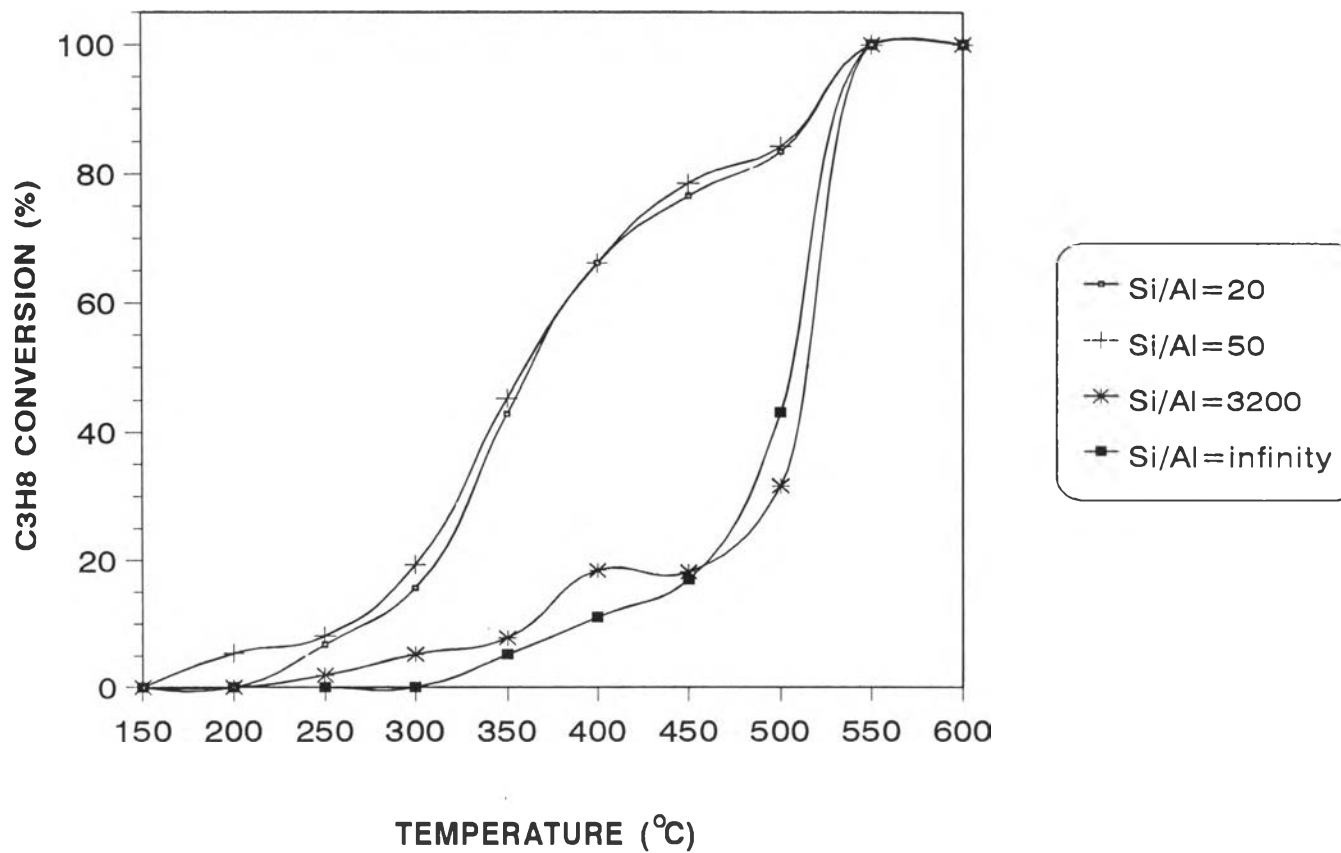


Figure 5.11 Temperature dependence of C₃H₈ conversion on various H-ZSM-5 catalysts.

1000 ppm NO, 10% O₂, 3000 ppm C₃H₈, and balanced He, GHSV = 4000 h⁻¹.

catalyst for NO reduction by C_3H_8 . As a result, When the amount of Al content was increased, NO and C_3H_8 conversions were also increased. This is possibly owing to the increment in acidity of the catalyst [42].

Table 5.6 The light-off temperature of H-ZSM-5 with various Si/Al ratio

Catalysts	Light-off Temperature ($^{\circ}C$)	
	NO Conv.	C_3H_8 Conv.
Si/Al = 20	260	360
Si/Al = 50	265	365
Si/Al = 3200	-	510
Si/Al = ∞	-	500

5.4 Effect of Copper Content on the Selective Reduction of NO under the Reaction Condition of Excess Oxygen with a Small Amount of Propane

Selective catalytic reduction of NO with propane and oxygen was investigated on Na-form and H-form of both Cu-exchanged ZSM-5 and Cu-Al-silicate. The results in this study will be categorized into two parts.

1. Na-form catalyst

Figures 5.12 and 5.13 show the catalytic activity for NO reduction on Cu/Na-ZSM-5 and Cu-MFI-105 catalysts which prepared by Iwamoto laboratory [32] at the temperature range of 150-600 $^{\circ}C$. The description of catalysts are

summarized in Table 5.7. As shown in Figure 5.12, when the amount of copper content was increased from 0 wt.% to 0.205 wt.%, 1.05 wt.%, and 4.05 wt.% on Cu/Na-ZSM-5 catalysts, the temperature of maximum NO conversion decreased from 500 °C (54% NO conversion) to 450 °C (80%), 300 °C (95%), and 300 °C (100%). Moreover, the light-off temperatures for both NO and propane conversion in Table 5.8 are shown to decrease with an increase in copper content of Cu/Na-ZSM-5 catalysts. It was thus concluded that the catalyst with higher copper content exhibited the higher catalytic activity.

Table 5.7 The description of various catalysts

Catalysts	Abridged notation	Copper content (wt.%)	Description
0.2%Cu/Na-ZSM-5	Cu/Na-ZSM-5	0.205	The preparation procedure was described in Chapter IV
35% Cu/Na-ZSM-5	Cu/Na-ZSM-5	1.05	
Cu-MFI-105	Cu/Na-ZSM-5	4.05	The preparation procedure was described on [32]

The dependency of the activities of Na-Cu-Al-silicate catalysts at the temperature range of 150-600 °C on the amount of copper content was reported by W. Pattaraprakorn [54] as shown in Figure 5.14. It was found that Na-Al-silicate (Cu=0 wt.%) exhibited the maximum NO conversion at 500 °C and the temperature of maximum NO conversion was decreased with a little increasing copper content in Na-Cu-Al-silicate. On the contrary, Na-Cu-Al-silicate with

higher copper content (2.228 wt.%) showed no activity for NO reduction. This indicates that the catalyst with low copper content showed higher activity compared with Na-Al-silicate but the catalytic activity for NO reduction severe decreased when the catalyst with higher copper content was used.

2. H-form catalyst

W. Engopasanan [55] studied the effect of copper content in Cu/H-ZSM-5 for the reaction of gas containing NO, C₃H₈, and O₂. As shown in Figure 5.15, when the amount of copper content in Cu/H-ZSM-5 was increased from 0 wt.% to 0.040 wt.% and 0.104 wt.%, the temperature of maximum NO conversion changed from 300 °C to 450 °C and 400 °C. For light-off temperature determination, as shown in Table 5.8, it was seen that H-ZSM-5 showed the lowest light-off temperature (250 °C) followed by Cu/H-ZSM-5 with copper content of 0.134 wt.% (265 °C) and Cu/H-ZSM-5 with copper content of 0.040 wt.% showed the highest light-off temperature (310 °C). This indicates that Cu-exchanged H-ZSM-5 exhibited the activity for NO reduction lower than H-ZSM-5 although the catalytic activity increased with an increase in Cu-exchange level. Consequently, the increment of copper content in the catalyst did not increase the catalytic activity for NO reduction compared with H-ZSM-5 but broadened the temperature window of maximum NO conversion.

Effect of copper content on catalytic activity for NO reduction was also investigated on H-Cu-Al-silicate catalysts at the temperature range of 150-600 °C [54]. The NO conversion in Figure 5.16 indicates that the temperature of maximum conversion of H-Al-silicate (Cu-free) was lower compared with that of H-Cu-Al-silicate. However, the temperature of maximum NO conversion of H-Cu-Al-silicate decreased with an increase in copper content of the catalyst.

In addition, H-Al-silicate showed the lowest light-off temperature as summarized in Table 5.8. When the amount of copper content in H-Cu-Al-silicate was increased from 0 wt.% to 0.040 wt.% and 0.134 wt.%, the light-off temperature changed from 250 °C to 310 °C and 290 °C. As a result, the activity for NO reduction decreased when H-Cu-Al-silicate catalyst was used compared with H-Al-silicate (Cu-free) and H-Cu-Al-silicate with low copper content showed the catalytic activity and thermal stability lower than H-Cu-Al-silicate with high copper content. This results are consistent with the above results of Cu/H-ZSM-5.

Figure 5.17 [54] shows the comparison of the catalytic activity of Cu-MFI-105 (Cu=4.05 wt.%), Na form and H form of Cu-Al-silicate (Cu=2.228 wt.%), and Cu/Na-Cu-Al-silicate. It was observed that for high copper content catalysts, Cu-exchanged Na-ZSM-5, Cu-MFI-105, showed high activity for NO reduction whereas Cu-incorporated zeolite, H-Cu-Al-silicate, performed the broad temperature window of maximum NO conversion. The light-off temperatures of the catalysts in Table 5.8 show that and Cu/Na-Cu-Al-silicate exhibited the light-off temperature close to Cu-MFI-105. This suggests that Cu/Na-Cu-Al-silicate was the most active catalyst compared with Cu-MFI-105 and H-Cu-Al-silicate. Furthermore, Cu/Na-Cu-Al-silicate showed high thermal stability. Thus Cu/Na-Cu-Al-silicate, the catalyst with both copper ion-exchange and incorporate, also showed the both advantages of Cu-exchanged and Cu-incorporated catalysts. The reason of this results should be available in the further study.

Table 5.8 The light-off temperature of various catalysts

Catalyst	Copper content (wt.%)	Light-off temperature (°C)		Temperature window (°C)*	Ref.
		NO conv.	C ₃ H ₈ conv.		
1. Na-form catalyst Cu/Na-ZSM-5	0	485	-	-	[55]
	0.205	335	395	-	this work
	1.050	240	270	275	this work
	4.050	225	255	245	this work
Na-Cu-Al-silicate	0	455**	-	65***	[54]
	0.490	315**	-	95***	[54]
	0.502	320**	-	60***	[54]
	2.228	-	-	-	[54]
2. H-form catalyst Cu/H-ZSM-5	0	250	-	190	[55]
	0.040	310	-	235	[55]
	0.104	265	-	240	[55]
H-Cu-Al-silicate	0	250	-	190	[55]
	0.502	310	-	200	[54]
	2.228	290	-	285	[54]
Cu/Na-Cu-Al-silicate	2.350, 2.228	230	-	295	[54]

* Temperature window defined as the range of temperature at 70% NO conversion

** The temperature which showed 35% NO conversion

*** The range of temperature at 35% NO conversion

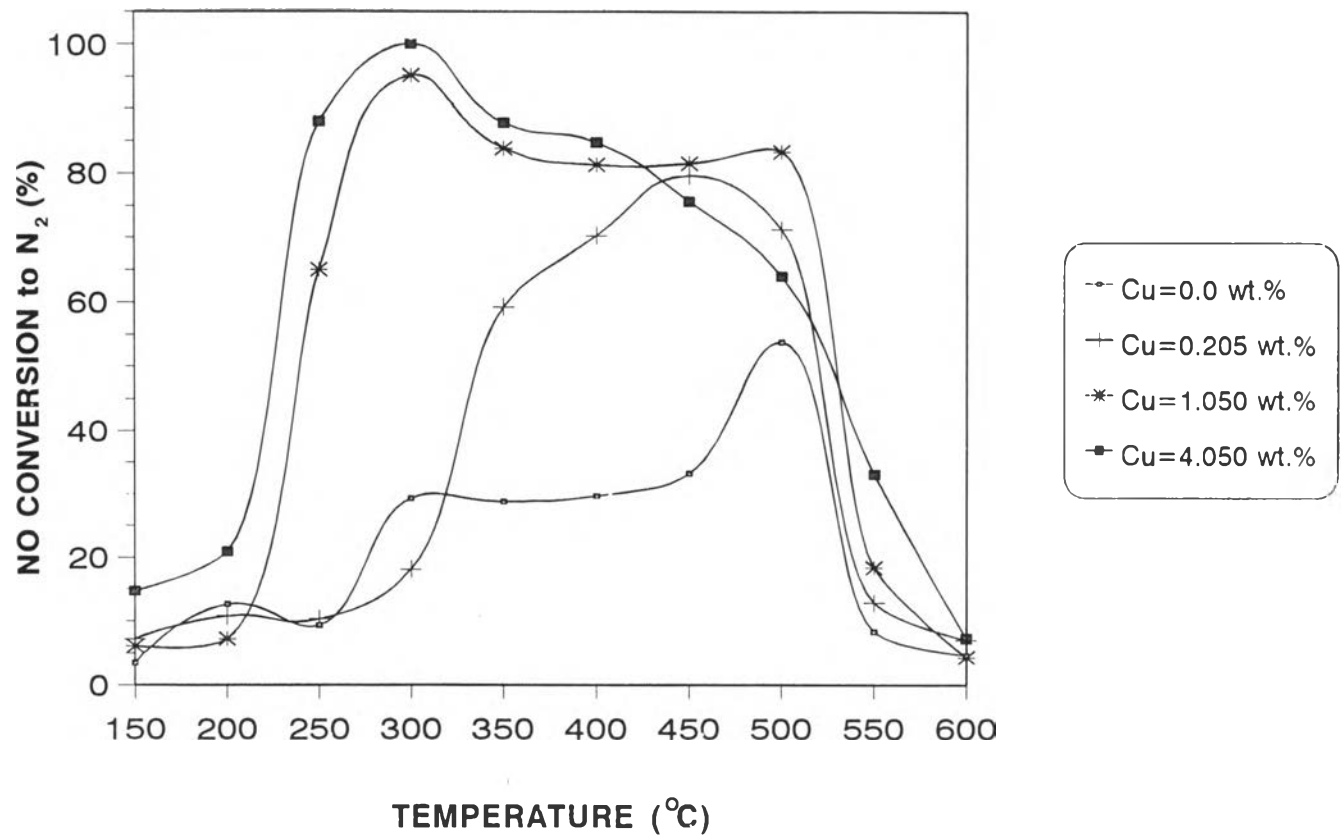


Figure 5.12 Effect of copper content in NO conversion on various Cu/Na-ZSM-5 catalysts.

1000 ppm NO, 10% O₂, 3000 ppm C₃H₈, and balanced He, GHSV = 4000 h⁻¹.

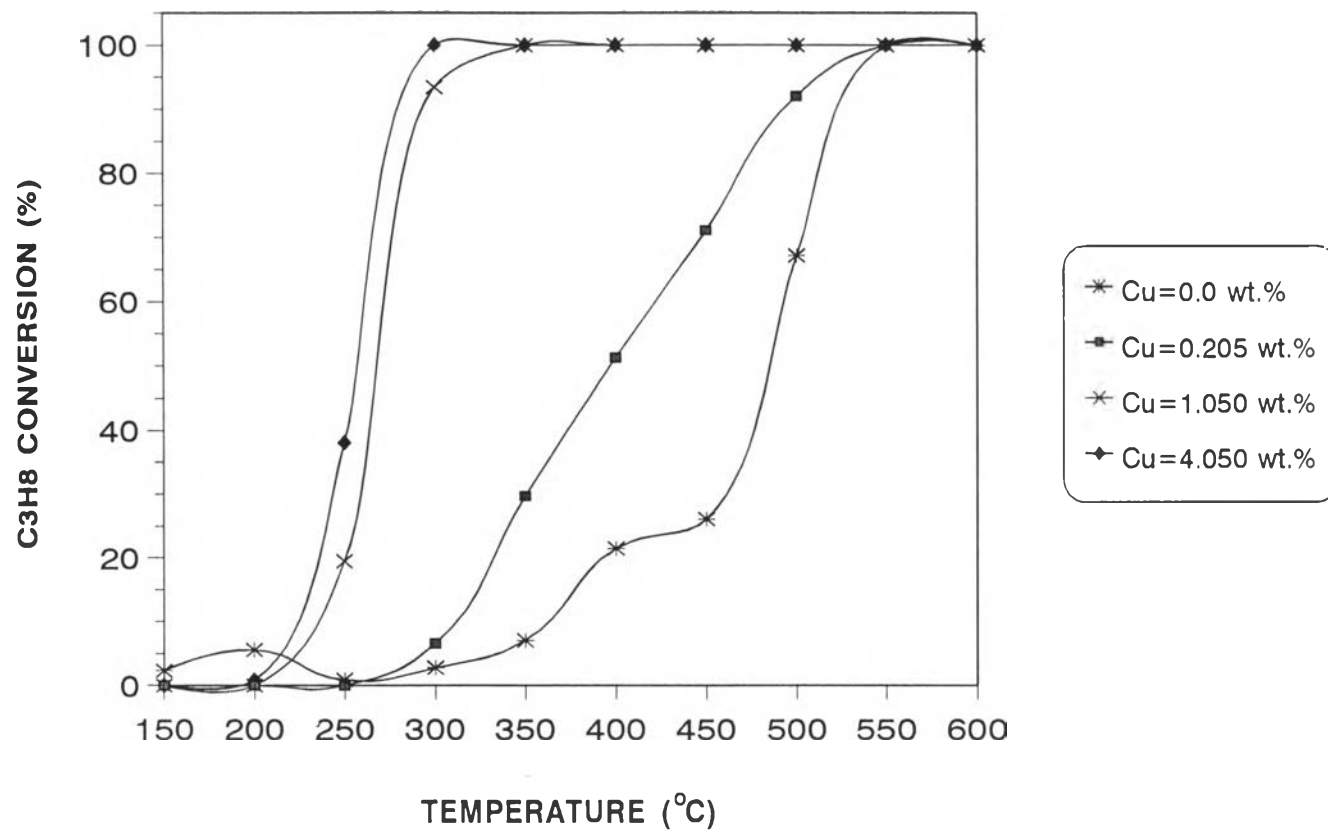


Figure 5.13 Temperature dependence of C₃H₈ conversion on various Cu/Na-ZSM-5 catalysts.

1000 ppm NO, 10% O₂, 3000 ppm C₃H₈, and balanced He, GHSV = 4000 h⁻¹.

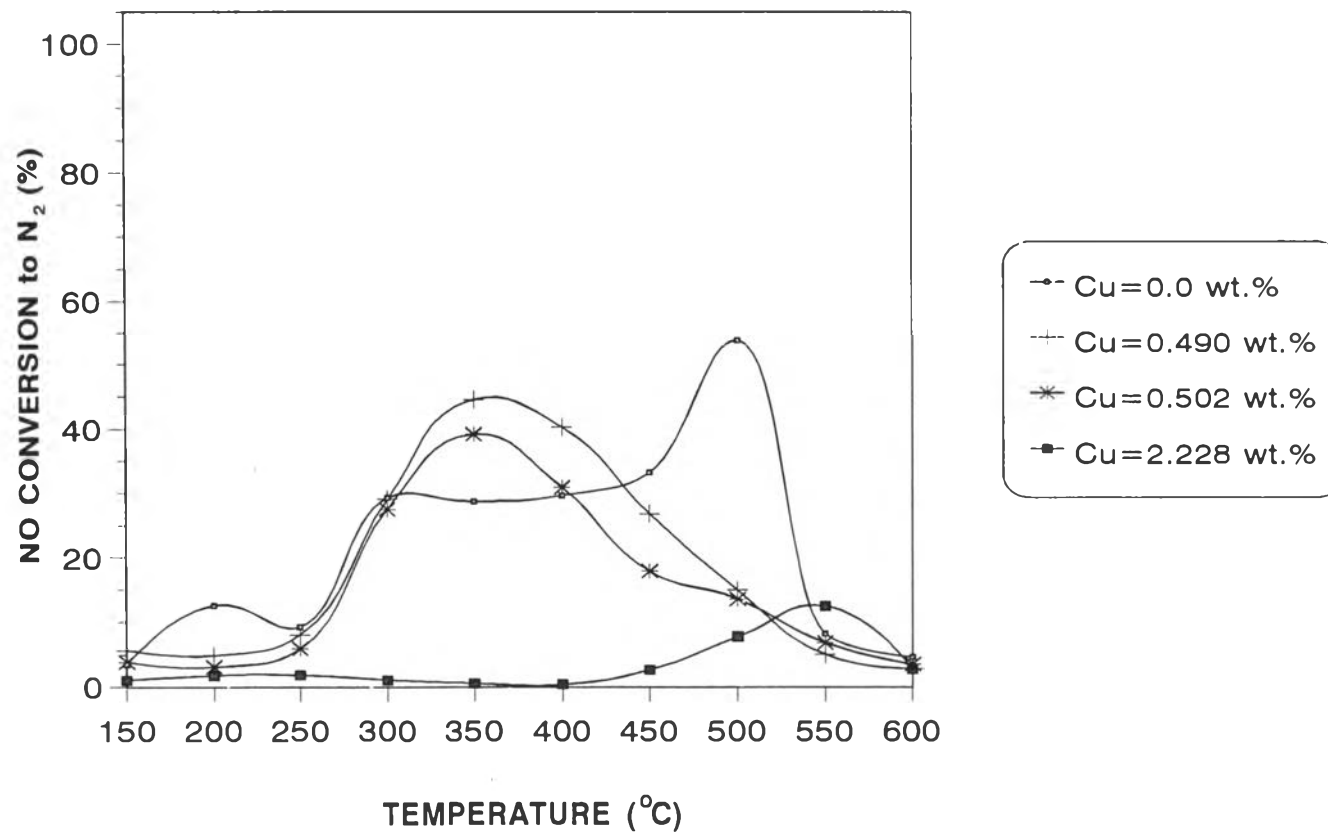


Figure 5.14 Effect of copper content in NO conversion on various Na-Cu-Al-silicate catalysts [55].

1000 ppm NO, 10% O₂, 3000 ppm C₃H₈, and balanced He, GHSV = 4000 h⁻¹.

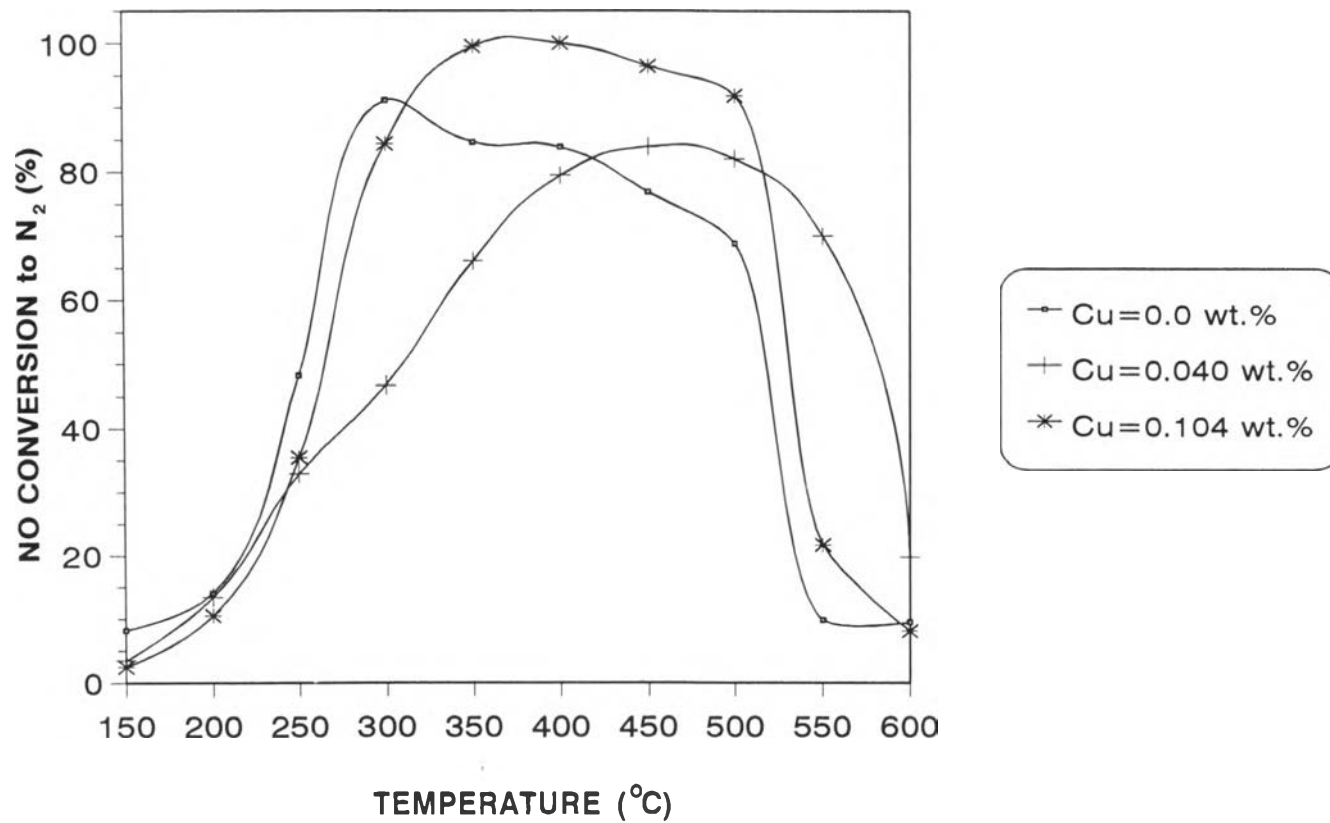


Figure 5.15 Effect of copper content in NO conversion on various Cu/H-ZSM-5 catalysts [56].

1000 ppm NO, 10% O₂, 3000 ppm C₃H₈, and balanced He, GHSV = 4000 h⁻¹.

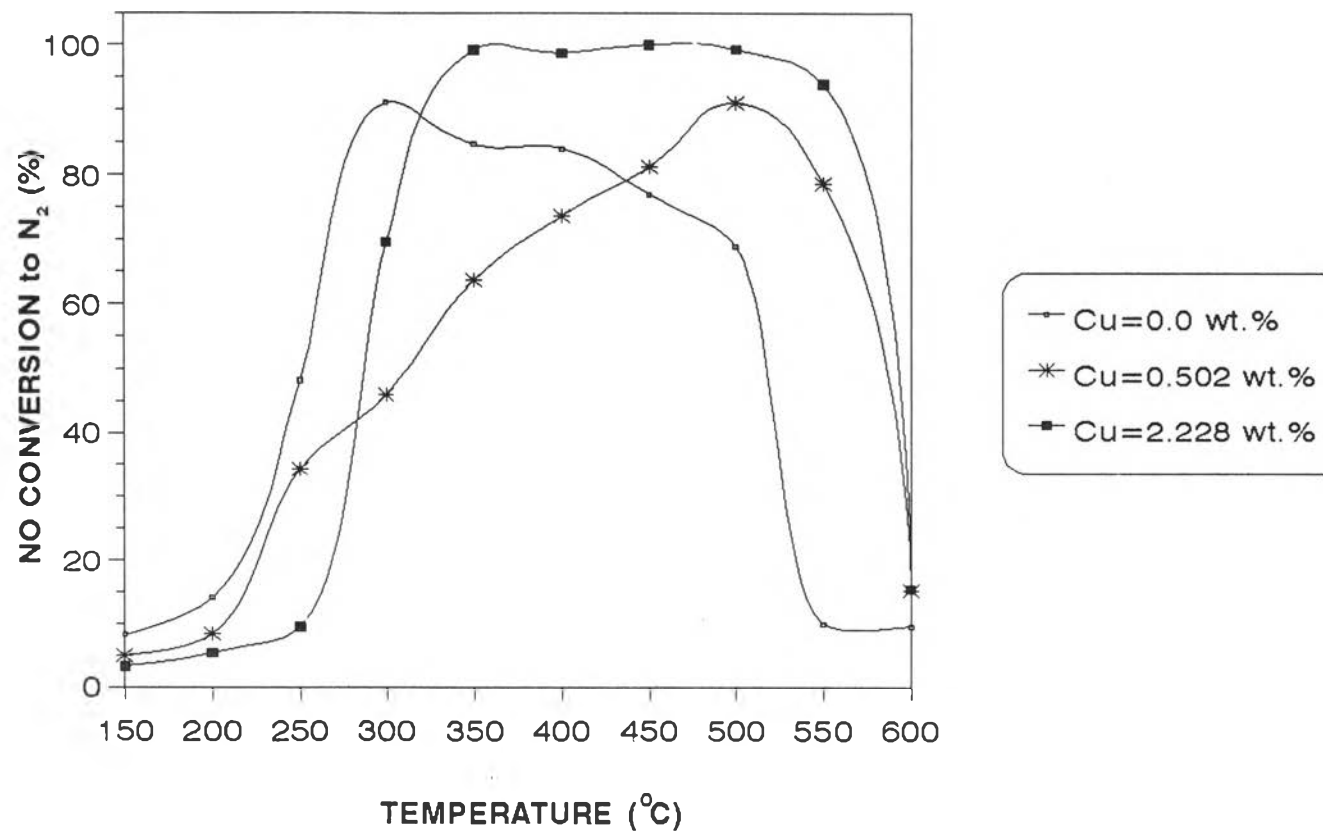


Figure 5.16 Effect of copper content in NO conversion on various H-Cu-Al-silicate catalysts [55].

1000 ppm NO, 10% O₂, 3000 ppm C₃H₈, and balanced He, GHSV = 4000 h⁻¹.

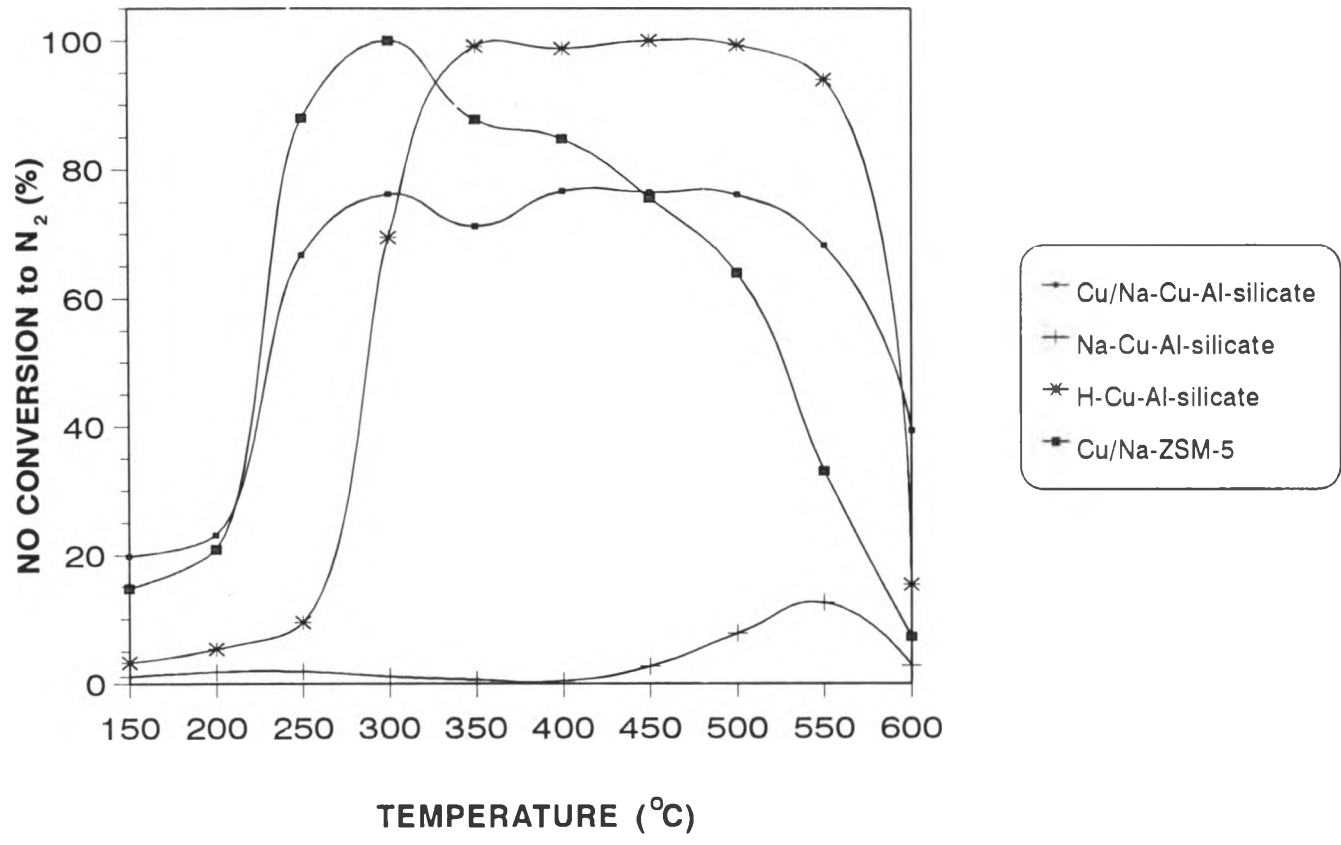


Figure 5.17 Comparison of NO conversion between Cu-MFI-105, Na form and H form of Cu-Al-silicate, and Cu/Cu-Al-silicate

5.5 Characterization of the Catalyst

From the results of this study, the prepared zeolite catalysts exhibited the different activity for the selective reduction of NO by a small amount of hydrocarbon in oxidizing atmosphere. This is owing to the characteristic of the catalyst.

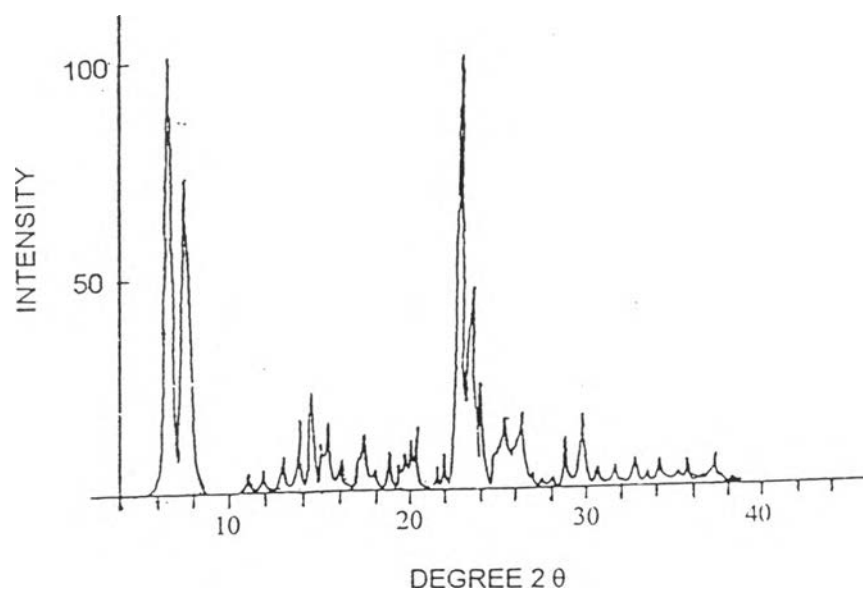
5.5.1 X-ray Diffraction Pattern

XRD patterns for the crystals are shown in Figure 5.18. All of the patterns of various catalysts prepared in this laboratory were almost similar to that of ZSM-5 of Mobil Oil Corporation [56]. This indicates that the copper-silicate and copper-exchanged ZSM-5 also have the pentasil pore-opening structure - the same crystalline structure as ZSM-5. The absence of XRD peaks of copper oxides suggests that copper is highly dispersed in the crystal. Consequently, the metal loading do not change the structure of ZSM-5.

5.5.2 Specific Surface Area and Pore Size Distribution

BET surface areas for the catalysts are shown in Figure 5.19. The surface areas of Cu-exchanged ZSM-5 and H-ZSM-5 having various Si/Al ratio were almost as high as Na-ZSM-5. On the other hand, BET surface areas of Cu-exchanged silicalite and Cu-silicate crystals were still higher than 300 m²/g. This indicates that the specific area of the catalyst was little affected by the metal loading.

Figure 5.20 shows the pore size distribution of the crystals. It was found that the pore size distribution of the catalysts were almost the same. The most pore size of the metal loaded catalysts were approximately equal to that of



a) H-ZSM-5 of Mobil Oil Corporation [53]

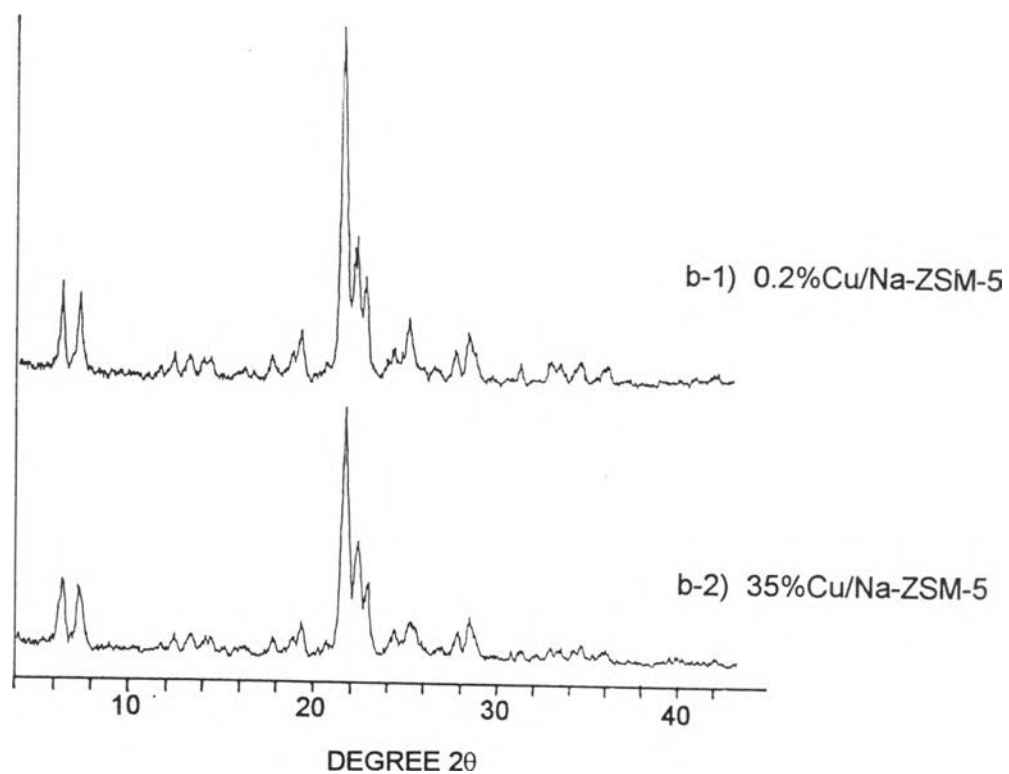


Figure 5.18 X-ray Diffraction Patterns for

a) H-ZSM-5 of Mobil Oil Corporation [53].

b) metal loaded and non-loaded ZSM-5 and Cu-silicate.

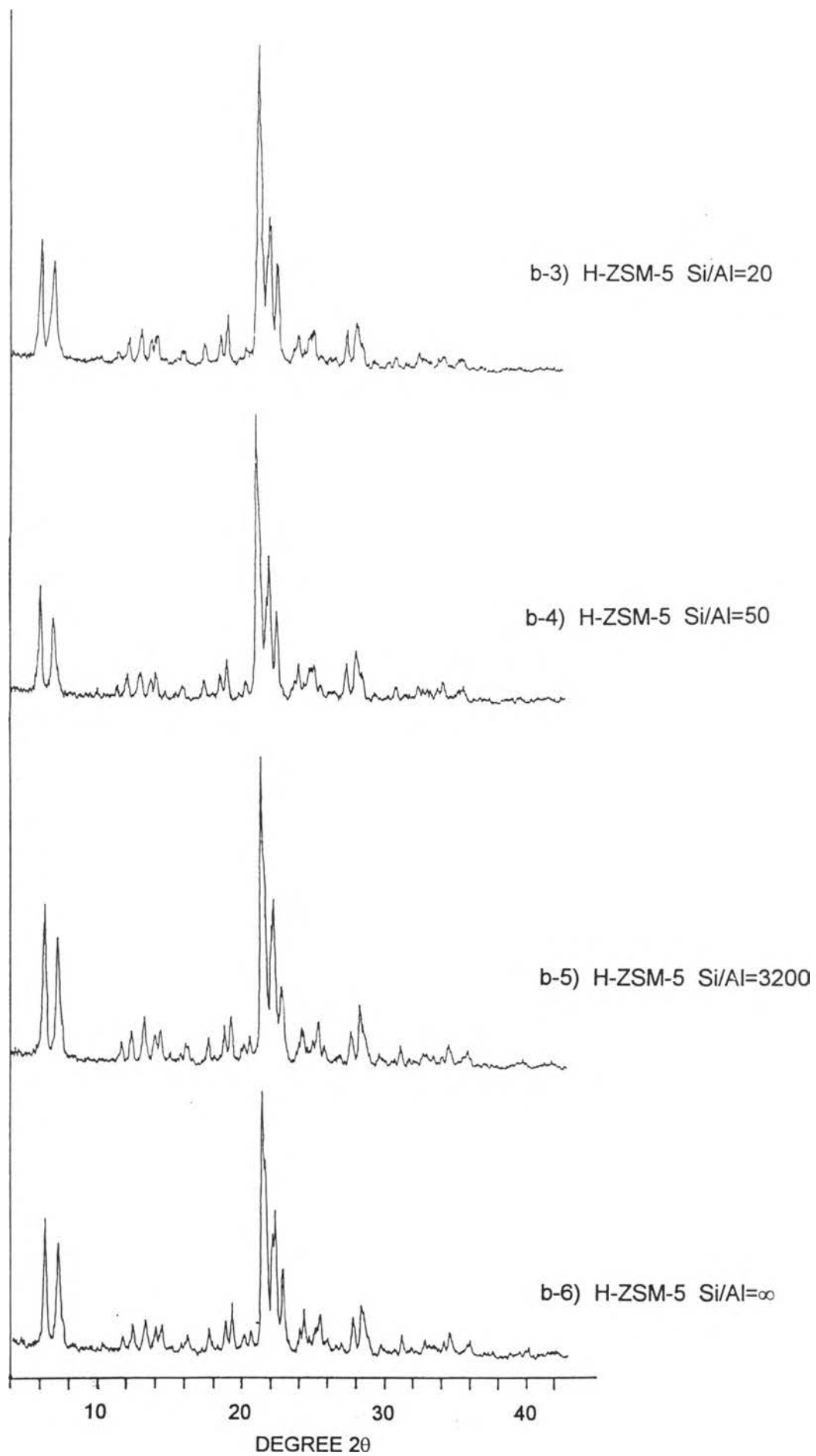
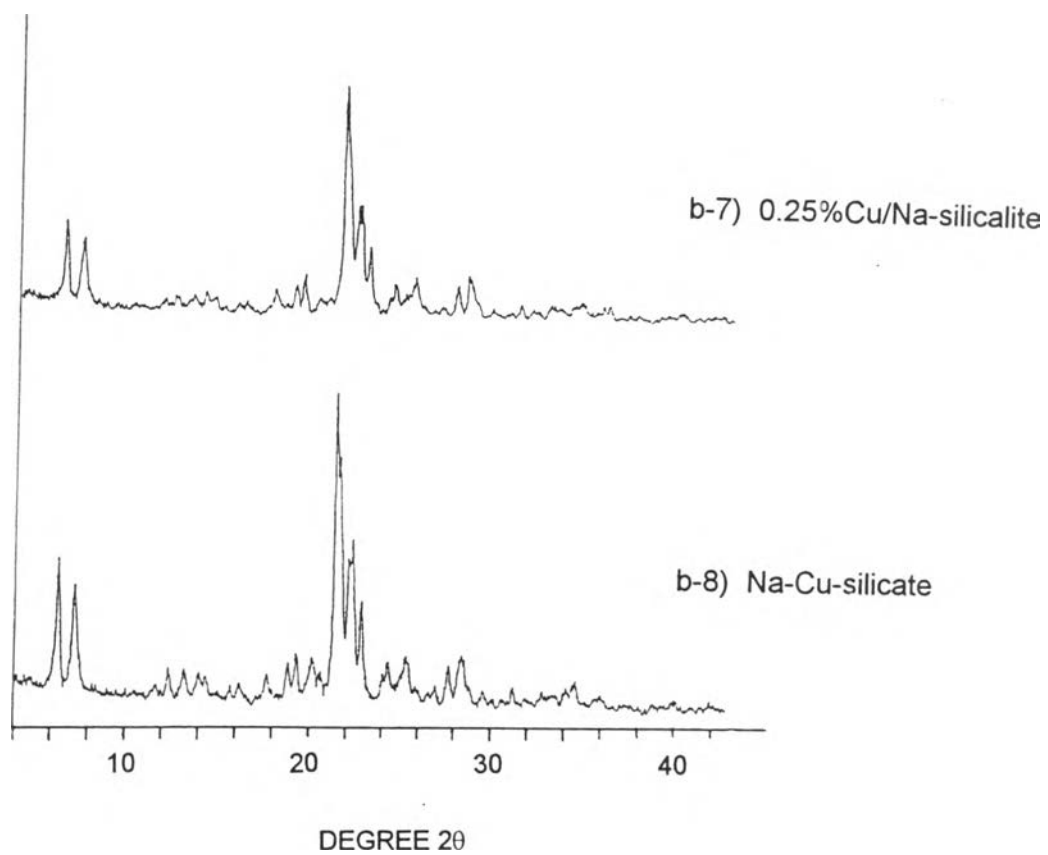


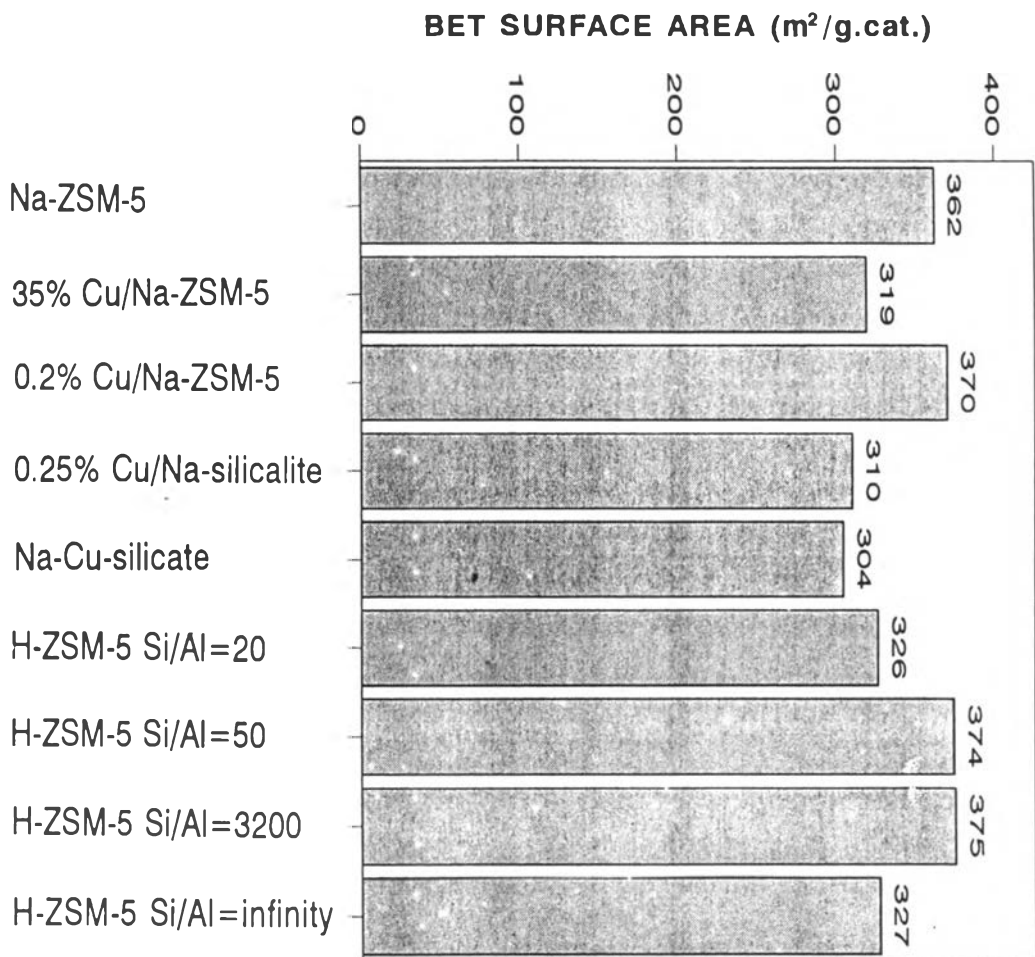
Figure 5.18 continued.



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

Figure 5.18 continued.

Figure 5.19 BET surface areas of the catalysts.



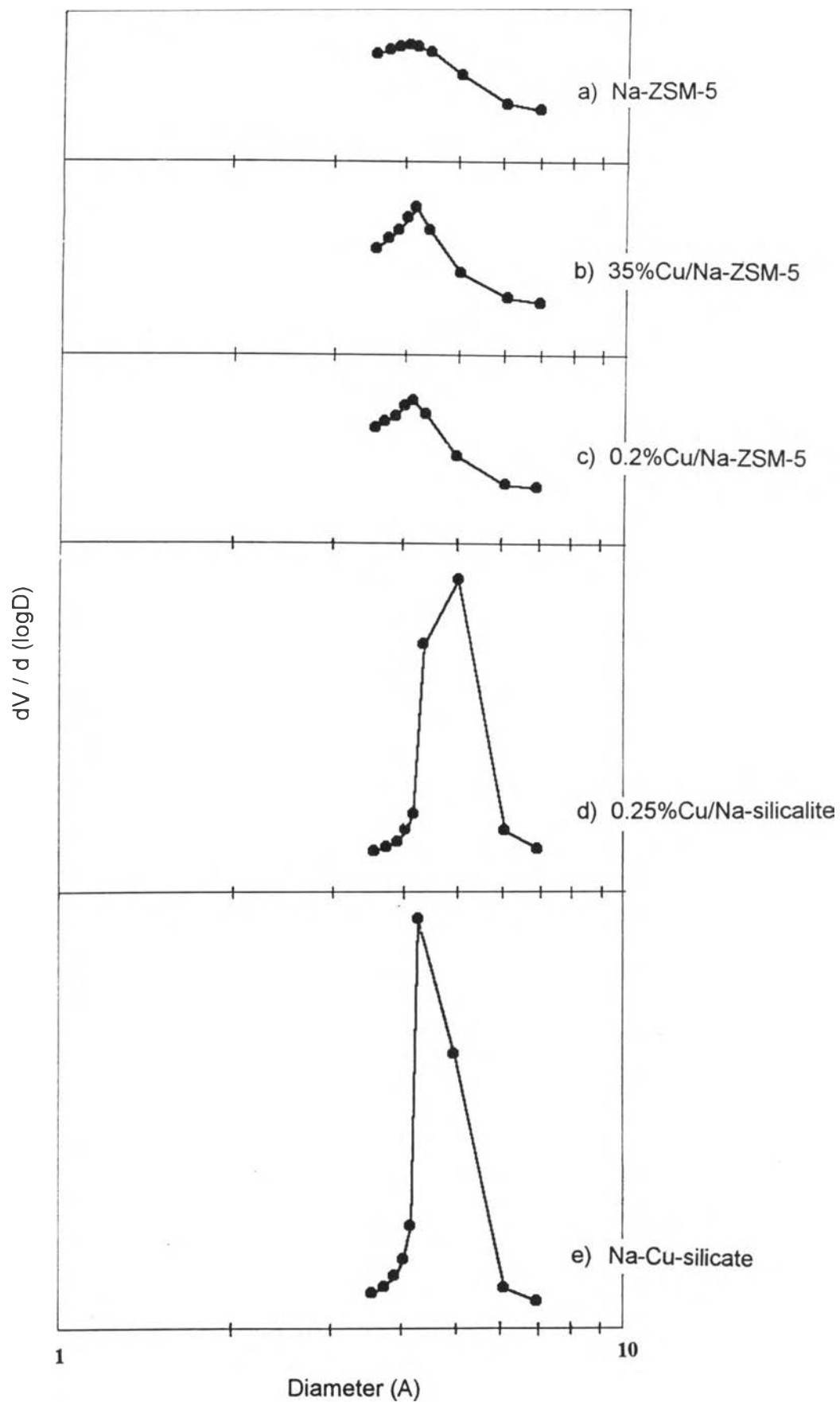


Figure 5.20 Pore size distribution of metal loaded and non-loaded ZSM-5 and Cu-silicate.

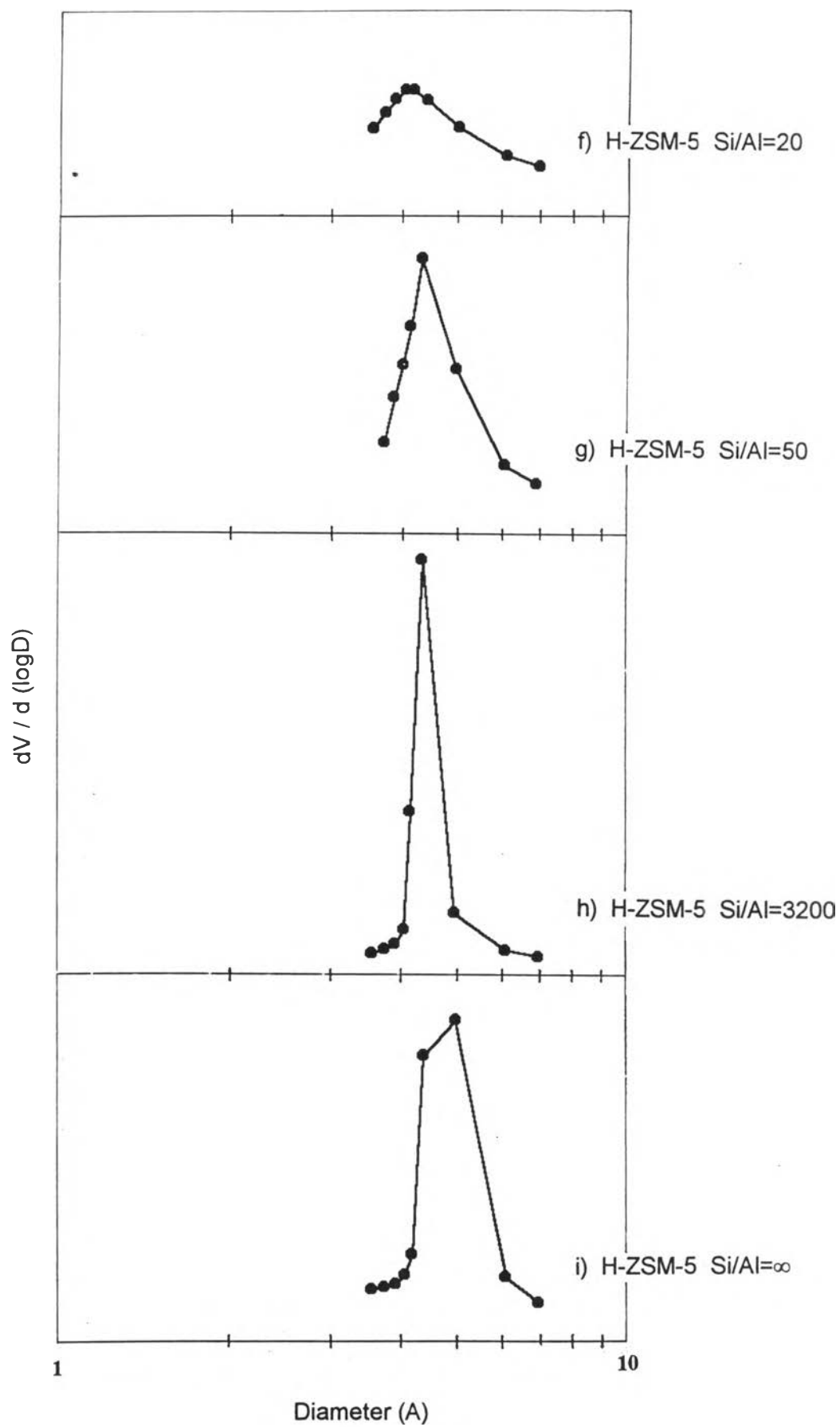


Figure 5.20 continued.

unloaded ZSM-5. All of the catalysts had the most pore size at pore diameter of from about 4 to 5 Å. However, the plot in Figure 5.20 also shows the different pore volume of the crystals. This is consistent with the previous research observed that the size of the cations in the pores will affect the void volume of a given structure [39].

Figures 5.21-5.23 show the comparison of pore size distribution curves between fresh and spent catalysts after reaction with propane. Pore size distribution of fresh 35%Cu/Na-ZSM-5 compared with spent catalyst in Figure 5.21 clearly shows that pore size distribution curve of spent catalyst was higher than that of fresh catalyst. Moreover, BET surface area and total pore volume of 35%Cu/Na-ZSM-5 after the reaction were larger than those before the reaction as presented in Table 5.9. The result of coke formation on the catalyst surface suggests that the pore structure of the catalyst has been developed by the coke deposition on its surface. The obtained results are consistent with the previous paper of Kirszensztejn et al. [57]. They reported that coke had its own porous structure which was developed on the basis of the catalyst porous system.

Table 5.9 BET surface area and total pore volume of fresh and spent 35%Cu/Na-ZSM-5

35%Cu/Na-ZSM-5	BET surface area (m ² /g)	Total pore volume (cc/g)
Fresh catalyst	319	0.2217
Spent catalyst	368	0.2426

In the case of 0.2%Cu/Na-ZSM-5, Figure 5.22 indicates that pore size distribution is nearly unchanged comparison of experiments before and after the reaction. This corresponds to the results of BET surface area and total pore volume determination in Table 5.10 that shows little variable values for spent catalyst compared with fresh catalyst.

Table 5.10 BET surface area and total pore volume of fresh and spent

0.2%Cu/Na-ZSM-5

0.2%Cu/Na-ZSM-5	BET surface area (m ² /g)	Total pore volume (cc/g)
Fresh catalyst	370	0.2523
Spent catalyst	358	0.2154

The plot in Figure 5.23 illustrates pore size distribution between fresh and spent Na-Cu-silicate. It indicates that pore size distribution curve of Na-Cu-silicate decreased after the reaction. In addition, BET surface area and total pore volume of spent catalyst were less than those of fresh catalyst as shown in Table 5.11. The lower NO and C₃H₈ conversions compared with Cu/Na-ZSM-5 catalyst suggests that the decreased pore size distribution, BET surface area, and total pore volume are possibly owing to thermal decomposition of the catalyst which caused the collapsed pore structure. This can be confirmed by thermal decomposition study on 35%Cu/Na-ZSM-5 which is the better catalyst. It was seen that the decrement of pore size distribution, BET surface area, and total pore volume for the thermal decomposed catalyst in

Figure 5.24 and Table 5.12 are corresponding to the above results of Na-Cu-silicate.

Table 5.11 BET surface area and total pore volume of fresh and spent Na-Cu-silicate

Na-Cu-silicate	BET surface area (m ² /g)	Total pore volume (cc/g)
Fresh catalyst	304	0.2295
Spent catalyst	241	0.1771

Table 5.12 BET surface area and total pore volume of fresh and thermal decomposed 35%Cu/Na-ZSM-5

35%Cu/Na-ZSM-5	BET surface area (m ² /g)	Total pore volume (cc/g)
Fresh catalyst	319	0.2217
Thermal decomposed catalyst	297	0.2092

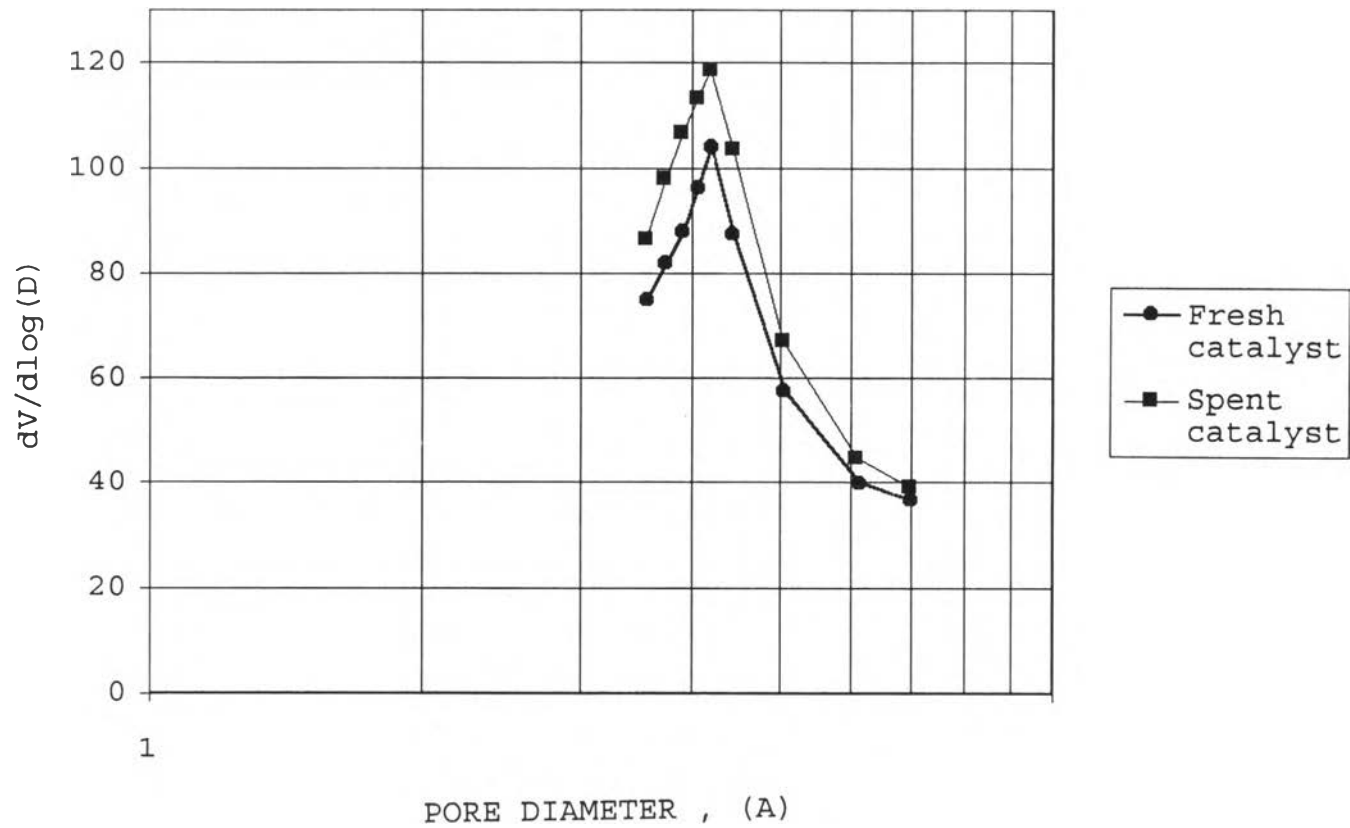


Figure 5.21 Comparison of pore size distribution between fresh and spent 35%Cu/Na-ZSM-5.

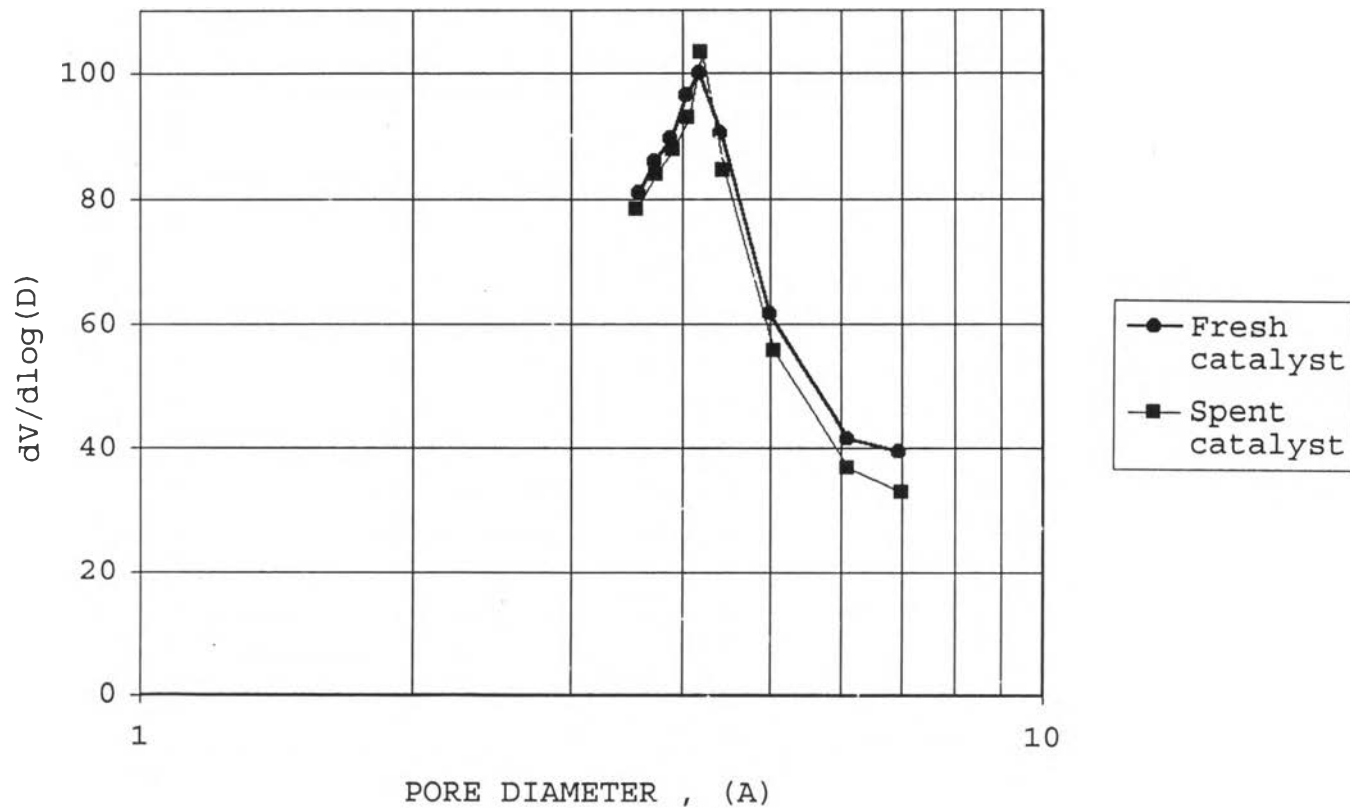


Figure 5.22 Comparison of pore size distribution between fresh and spent 0.2%Cu/Na-ZSM-5.

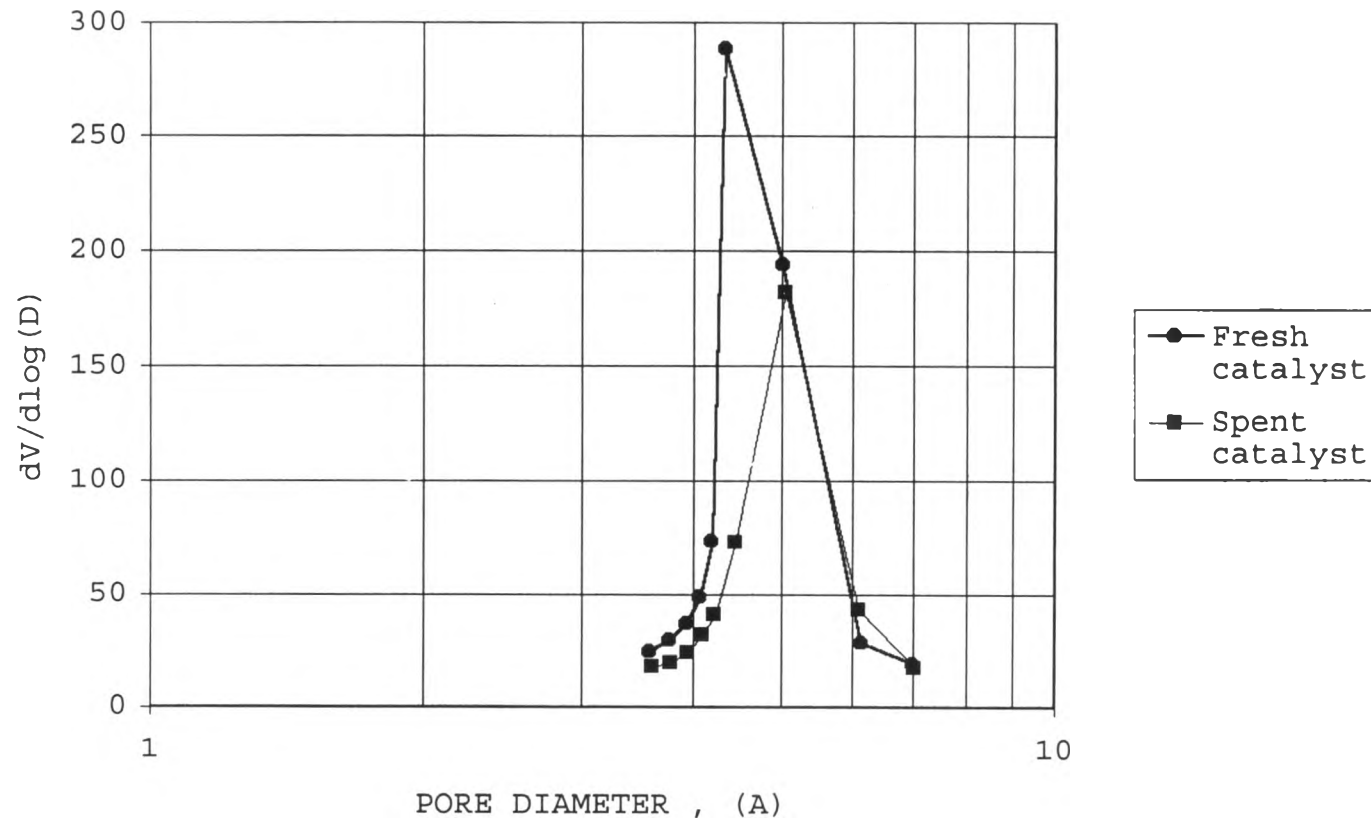


Figure 5.23 Comparison of pore size distribution between fresh and spent Na-Cu-silicate.

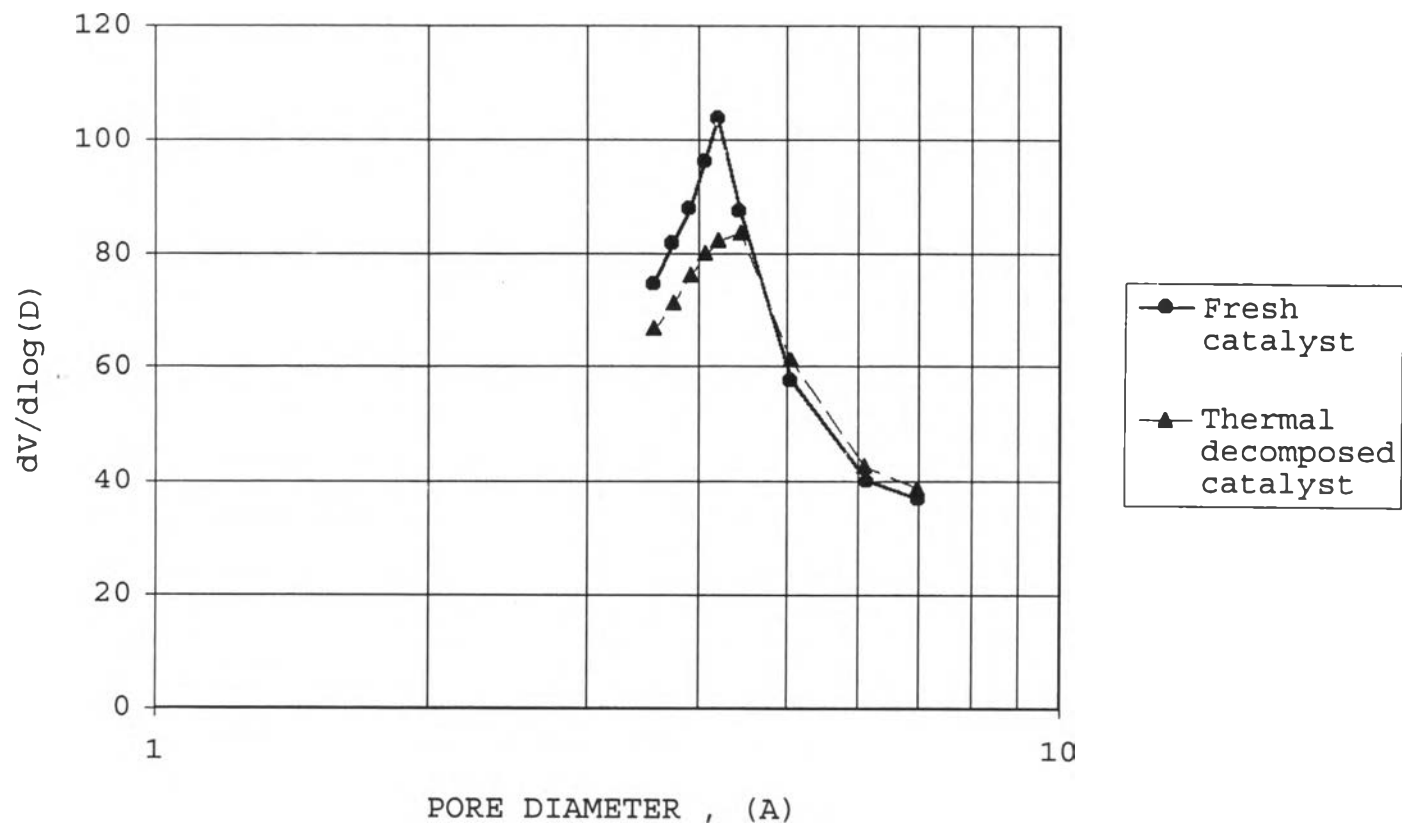
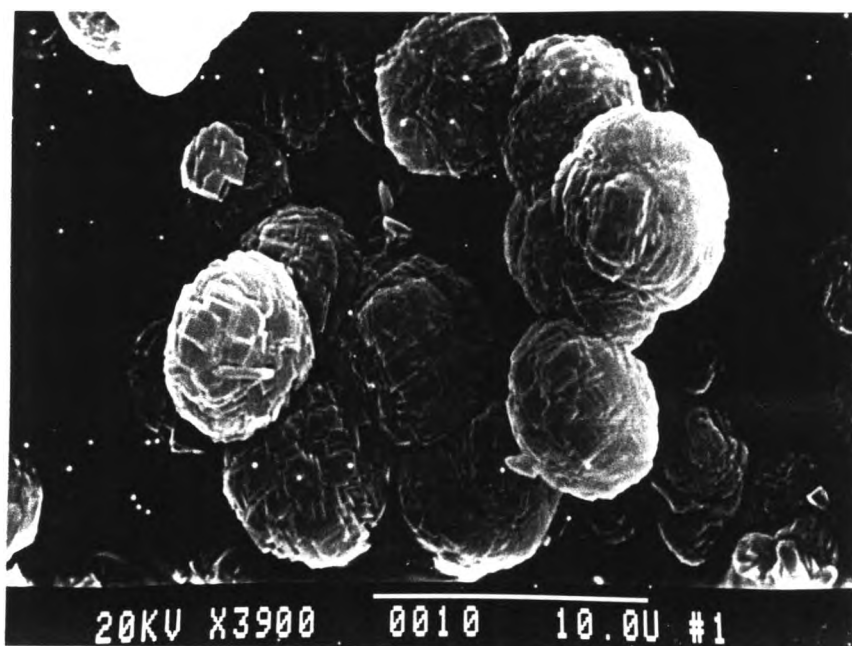


Figure 5.24 Comparison of pore size distribution between fresh and spent 35%Cu/Na-ZSM-5 after thermal decomposition reaction.

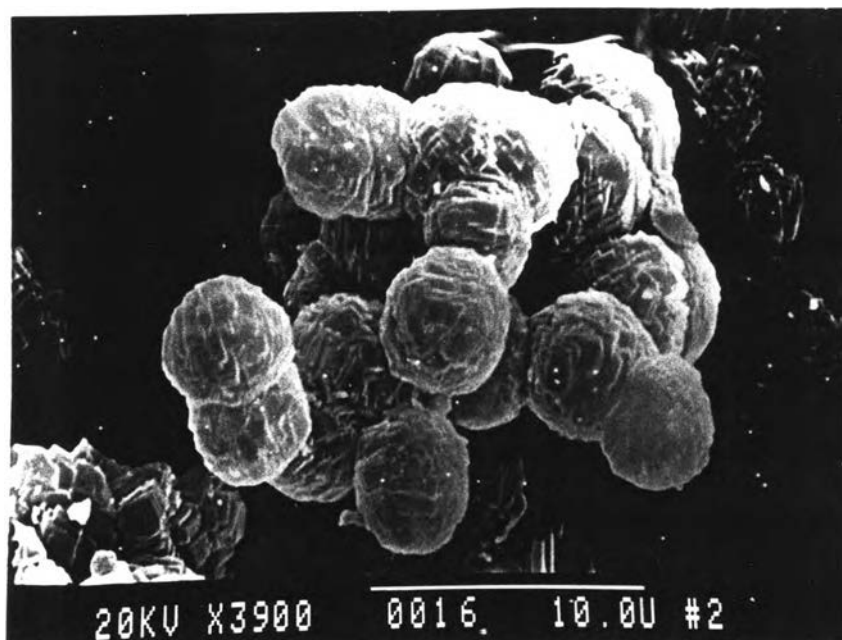
5.5.3 Morphology

SEM (Scanning Electron Microscope) photographs of Al- and Cu-silicate catalysts are shown in Figure 5.25. As shown, all of the catalysts were composed of roughly crystallized spherical particles. It was observed that the morphology of Cu-exchanged zeolite and Cu-silicate catalysts were very similar. This indicates that the metal loading do not change the shape of the crystals. In addition, the same morphology of H-ZSM-5 having different Si/Al ratio suggests that the ratio of Si/Al do not affect the morphology of the crystal. The result is in agreement with the above result as observed by XRD.

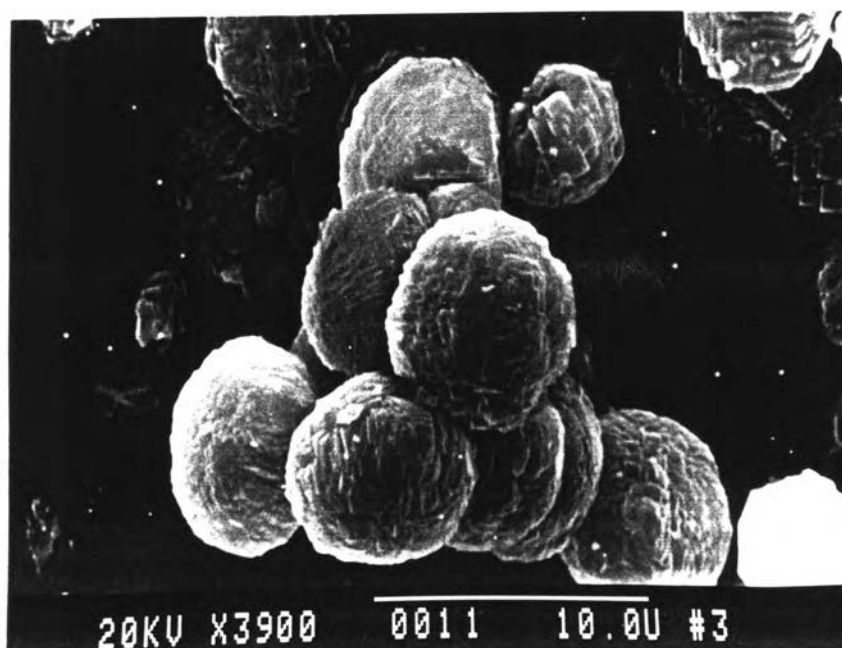


a) Na-ZSM-5

Figure 5.25 SEM photographs of metal loaded and non-loaded ZSM-5 and Cu-silicate.

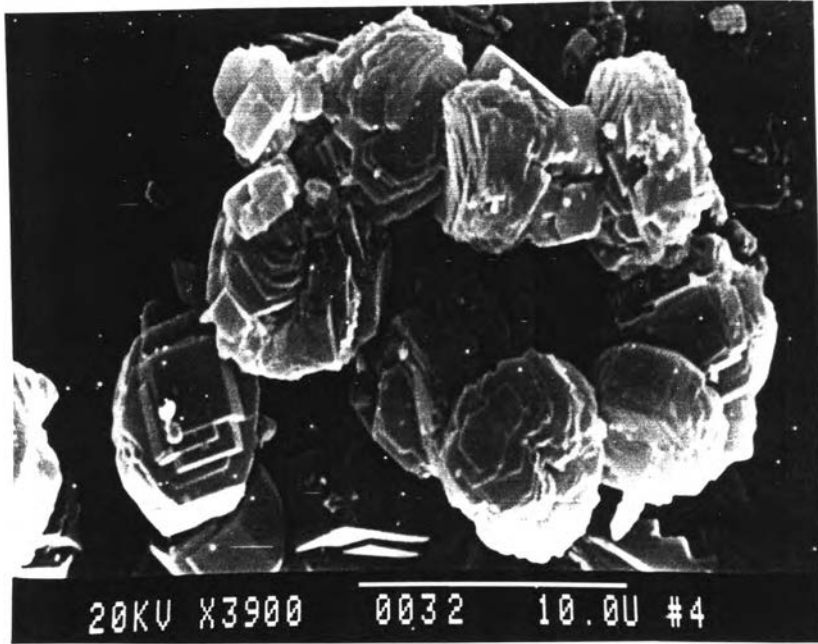


b) 35%Cu/Na-ZSM-5

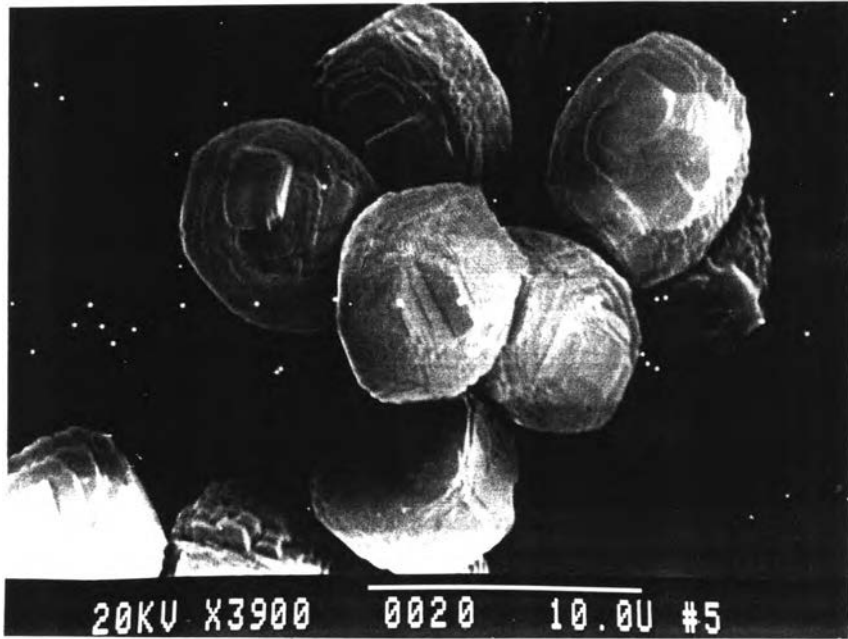


c) 0.2%Cu/Na-ZSM-5

Figure 5.25 continued.

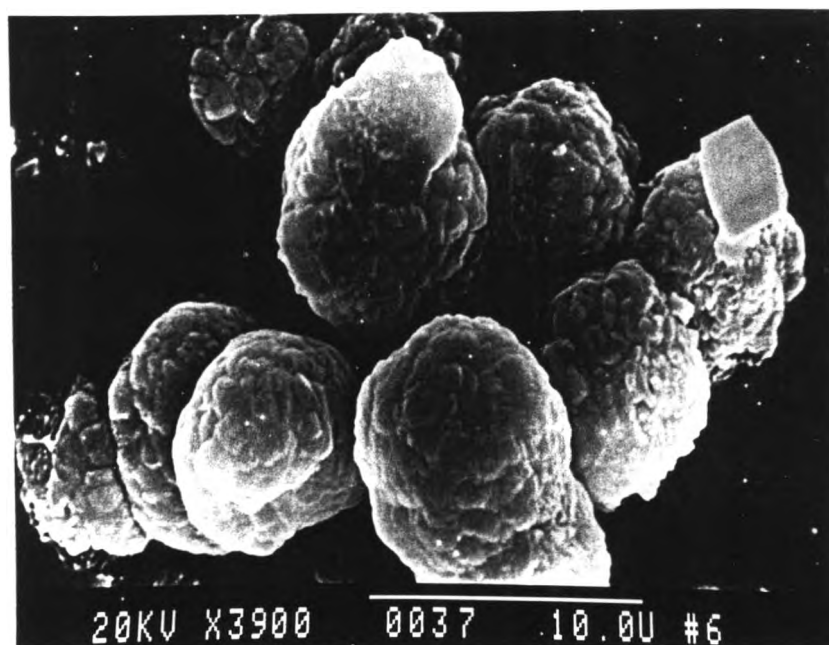


d) 0.25%Cu/Na-silicalite

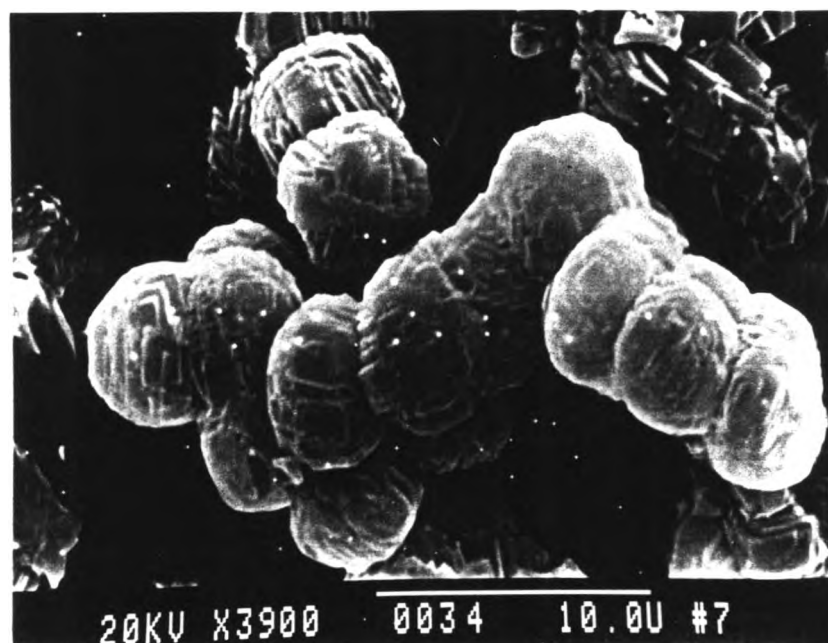


e) Na-Cu-silicate

Figure 5.25 continued.

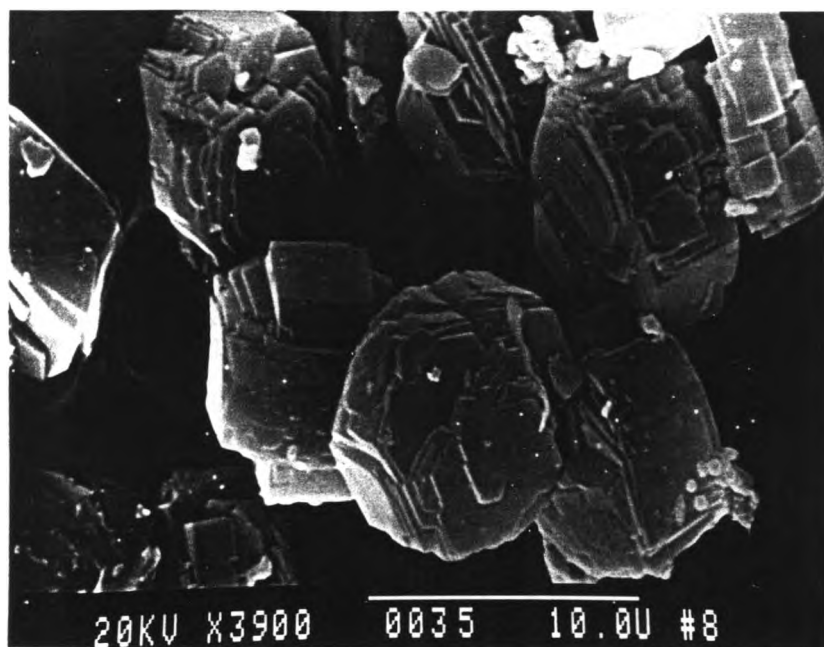


f) H-ZSM-5 Si/Al=20



g) H-ZSM-5 Si/Al=50

Figure 5.25 continued.



h) H-ZSM-5 Si/Al=3200

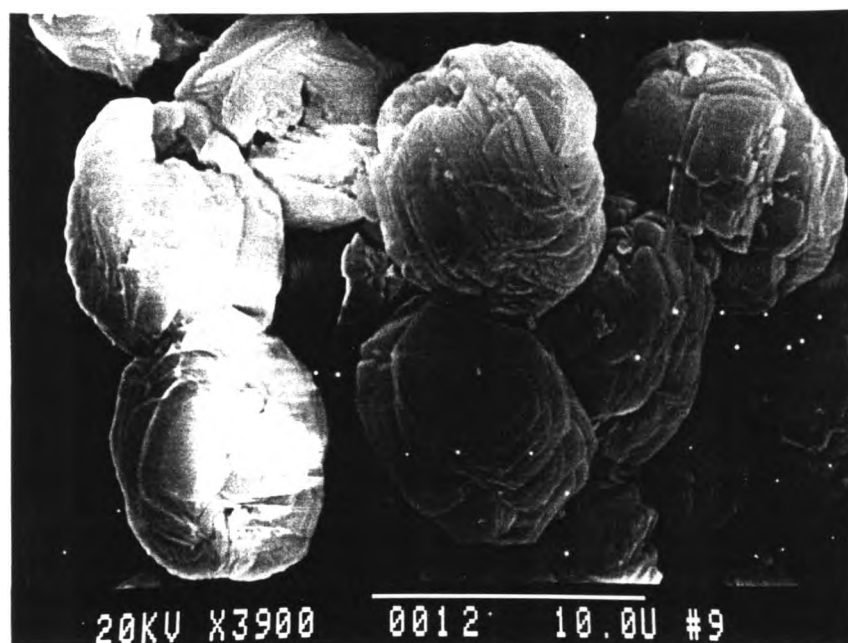
i) H-ZSM-5 Si/Al= ∞

Figure 5.25 continued.

5.5.4 FT-IR Spectroscopy

IR spectra of the catalysts are shown in Figure 5.26. All of the spectra showed the IR bands of ZSM-5 structure at about 450, 550, 800, 1100, and 1225 cm^{-1} that conformed to XRD patterns of the catalysts. Moreover, the IR spectrum of Na-Cu-silicate also showed the band at about 1050 cm^{-1} that can be suggested as Cu-O-Si band.

5.5.5 Temperature Programmed Desorption of Carbon Dioxide

The CO_2 TPD profiles for the catalysts are shown in Figure 5.27. It was observed that only Cu-exchanged ZSM-5 catalysts having copper content more than 1 wt.% exhibited a sharp peak of CO_2 at temperature about 250-300 °C. The higher copper loading in Cu/Na-ZSM-5 showed the higher CO_2 desorption peak. On the contrary, Cu-incorporated catalysts as Cu-silicate and Cu-Al-silicate and the catalysts with copper content less than 1 wt.% as H-ZSM-5 and 0.2%Cu/Na-ZSM-5 showed no desorption peaks up to 500 °C. This indicates that an isolated copper ion site located in a zeolite cavity can adsorb CO_2 . The results of NO reduction with propane over Cu/Na-ZSM-5 indicated that the catalyst with higher copper content showed higher catalytic activity for NO reduction by propane as shown in Figure 5.12. Whether the increment of catalytic activity relates to the adsorption of CO_2 of the isolated copper ion site or not needs further study. In addition, it was found that the relationship between cumulative CO_2 desorption and the amount of copper ion-exchange (wt.%) was non linear as shown in Figure 5.28.

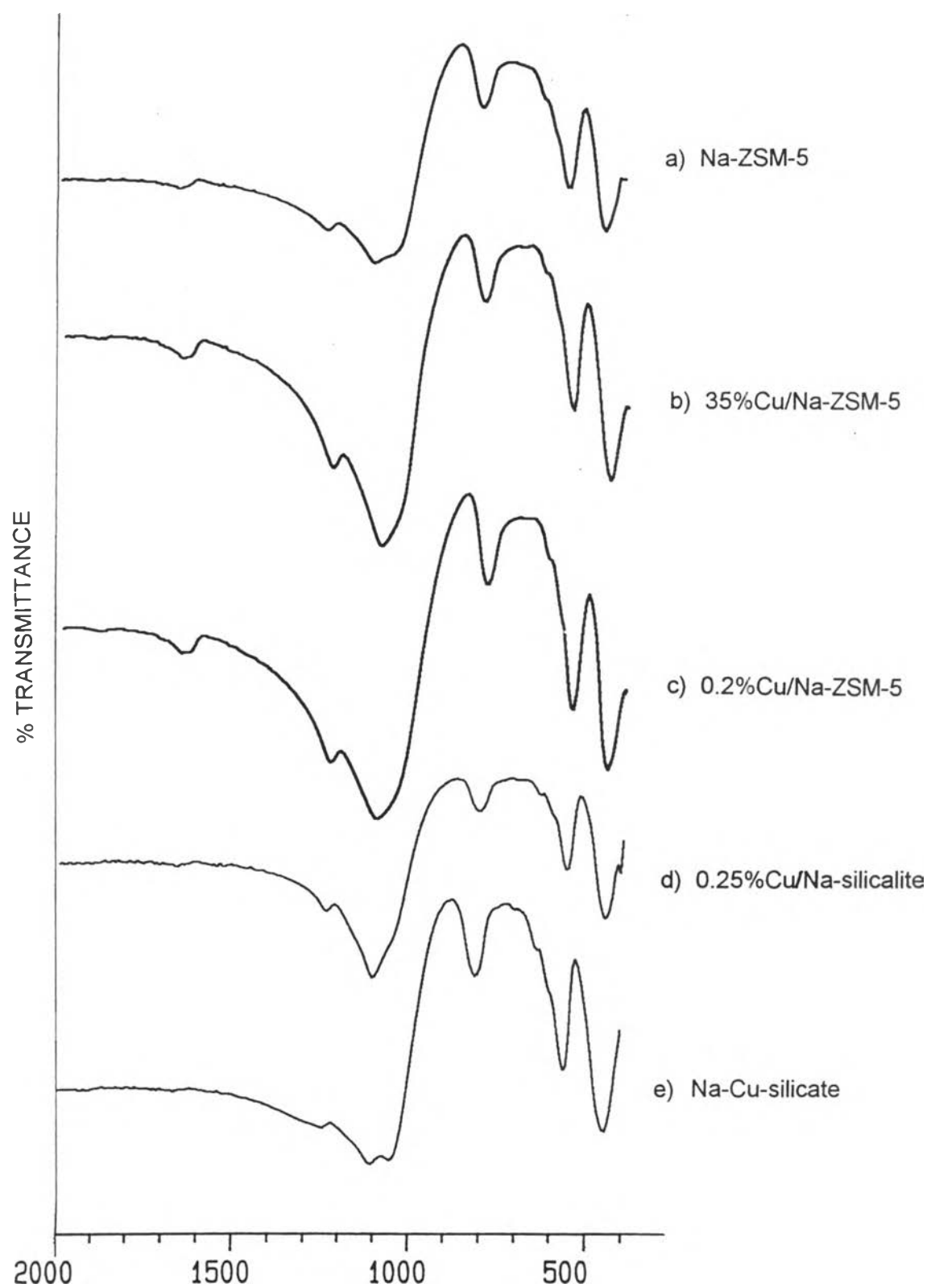


Figure 5.26 IR spectra of the catalysts.

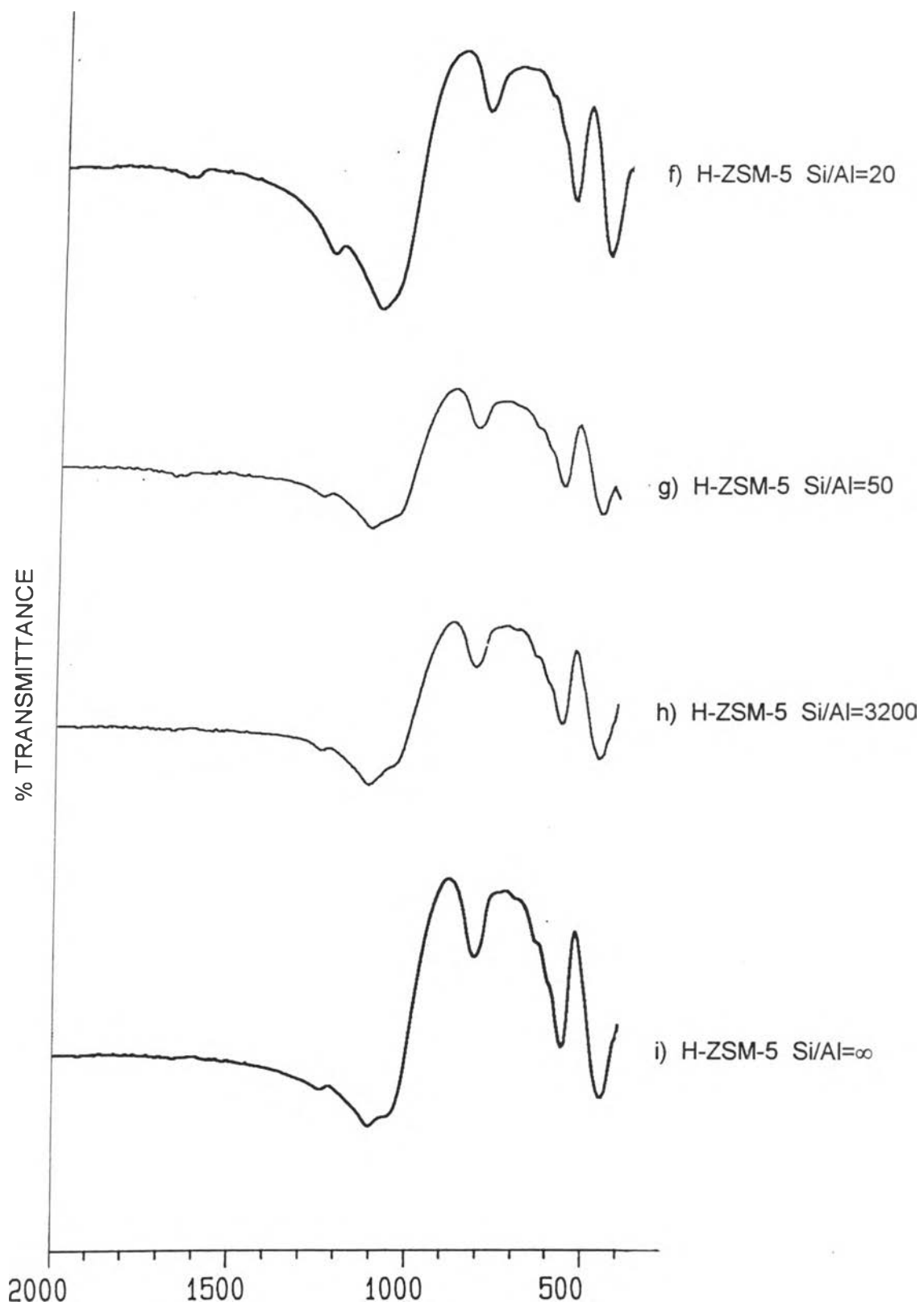


Figure 5.26 continued.

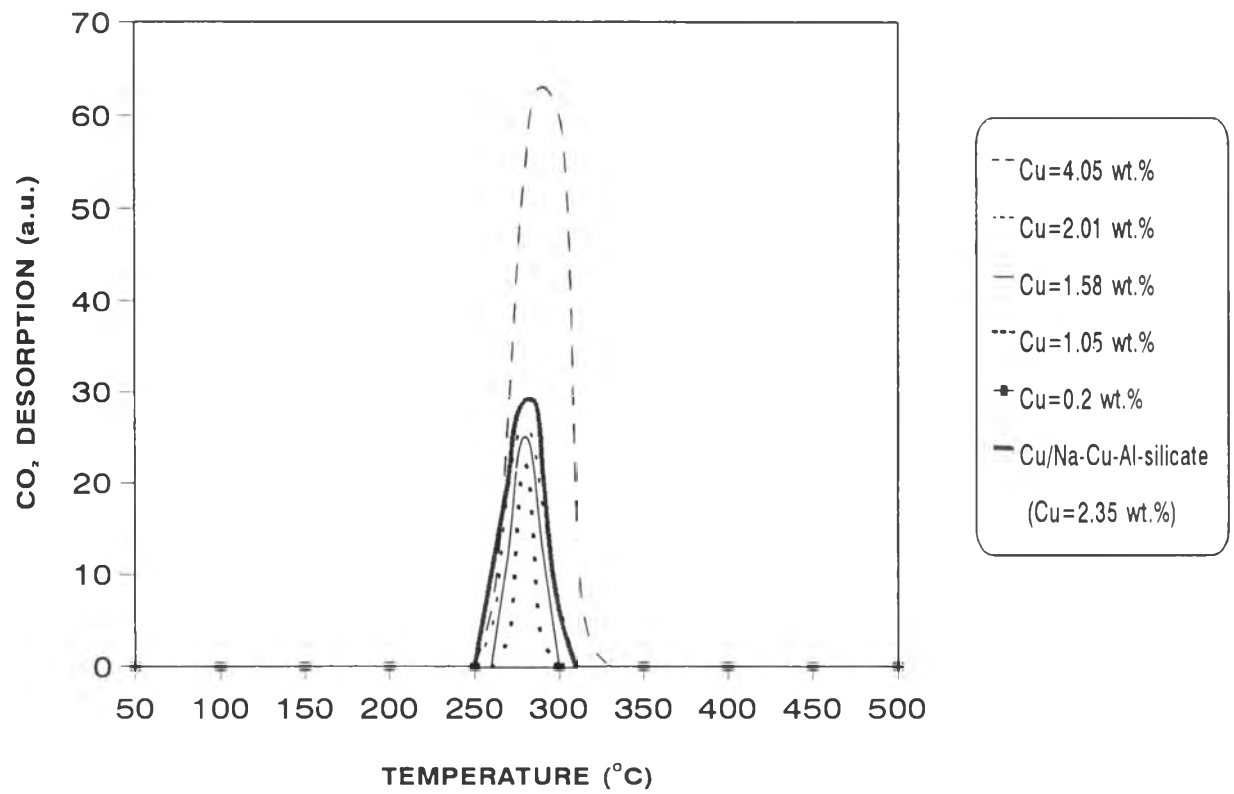


Figure 5.28 Copper content dependence of cumulative CO₂ desorption.

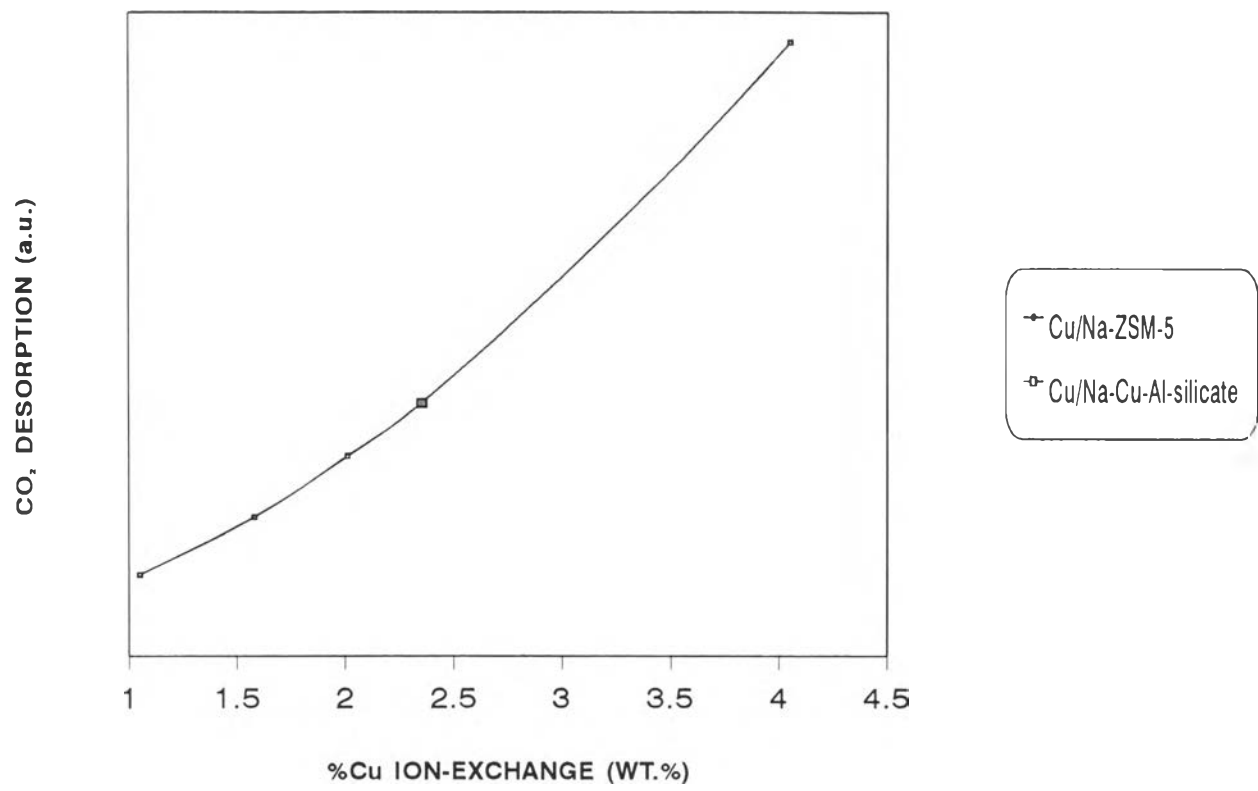


Figure 5.27 CO₂ TPD profiles for various Cu-exchanged zeolite catalysts.