CHAPTER V

RESULTS AND DISCUSSIONS

This thesis deals with studies on the selective catalytic reduction of NO by propane under excess oxygen conditions over Cu/ZSM-5 , Cu,Al-silicate and Cu/Cu,Al-silicate catalysts. The results and discussions of this study are as follows.

From thesis of J. Pincharoenthaworn [37], she found that Al content in catalyst had effect on NO reduction. In addition, Iwamoto et al. [24] reported that Cu ion-exchanged catalyst showed the lowest light-off temperature (the temperature at which a 50% conversion efficiency is reached with respect to the gas being converted). High activity of catalyst refers to the catalyst which has low light-off temperature for the considered reaction. Thus, to investigate this property of Cu,Al-silicate, which has both Cu, and Al in structure of ZSM-5, this catalyst was prepared by adding copper nitrate solution in stage of gel formation and synthesizing ZSM-5 (Al-silicate). First, the effect of copper content on Cu,Al-silicate for the reduction of NO by propane in an oxidizing atmosphere was examined. Second, Cu ion-exchanged was added into Cu,Al-silicate to investigate the effect of number of Cu ion-exchange on Cu,Al-silicate for NO reduction by propane in oxidizing atmosphere. Comparison of Cu/Na-Cu,Al-silicate and Cu ion-exchanged ZSM-5 (Cu/ZSM-5), which is the most frequently studied catalyst for the NO removal, was studied next. After that, effect of SO_2 on NO reduction over various catalysts was examined. Finally, coated Cu/Na-Cu,Al-silicate was studied.

5.1 Effect of Copper Content on Cu,Al-silicate Catalysts for the Selective Reduction of NO under the Reaction Condition of Excess Oxygen with a Small Amount of Propane.

The catalytic activities for NO reduction with propane and oxygen were investigated on Na-form, NH_4-form, and H-form of Cu,Al-silicate catalysts. The amount of copper content on Cu,Al-silicate was varied from 0.5 wt%-2.23 wt%. The copper content measured by atomic absorption spectroscopy (AAS) method is shown in Table 5.1. Moreover, Table 5.1 also summarises the light-off temperatures for NO reduction and C_3H_8 combustion of various Cu,Al-silicate catalysts. The effects of copper content in this study were categorized into three parts as follows:

5.1.1 Na-form of Cu,Al-silicate (Na-Cu,Al-silicate)

The dependency of the activities of Na-Cu,Al-silicate catalysts for NO and propane conversion in the temperature range 150-600 ^{0}C was reported in Figures 5.1, and 5.2, respectively. As shown in Figure 5.1, when Cu content in Na-Cu,Al-silicate was increased from 0.50 wt% to 0.71 wt%, the activity of Na-Cu,Al-silicate (Cu=0.71 wt%) increased and temperature window for NO reduction expanded to the high temperature side. Temperature window of Na-Cu,Al-silicate (Cu=1.91 wt%) still expanded to higher temperature but the light-off temperature slightly increased. However, NO conversion on Na-Cu,Al-silicate (Cu=1.91 wt%) was 63% at 550 ^{0}C which was higher than that of Na-

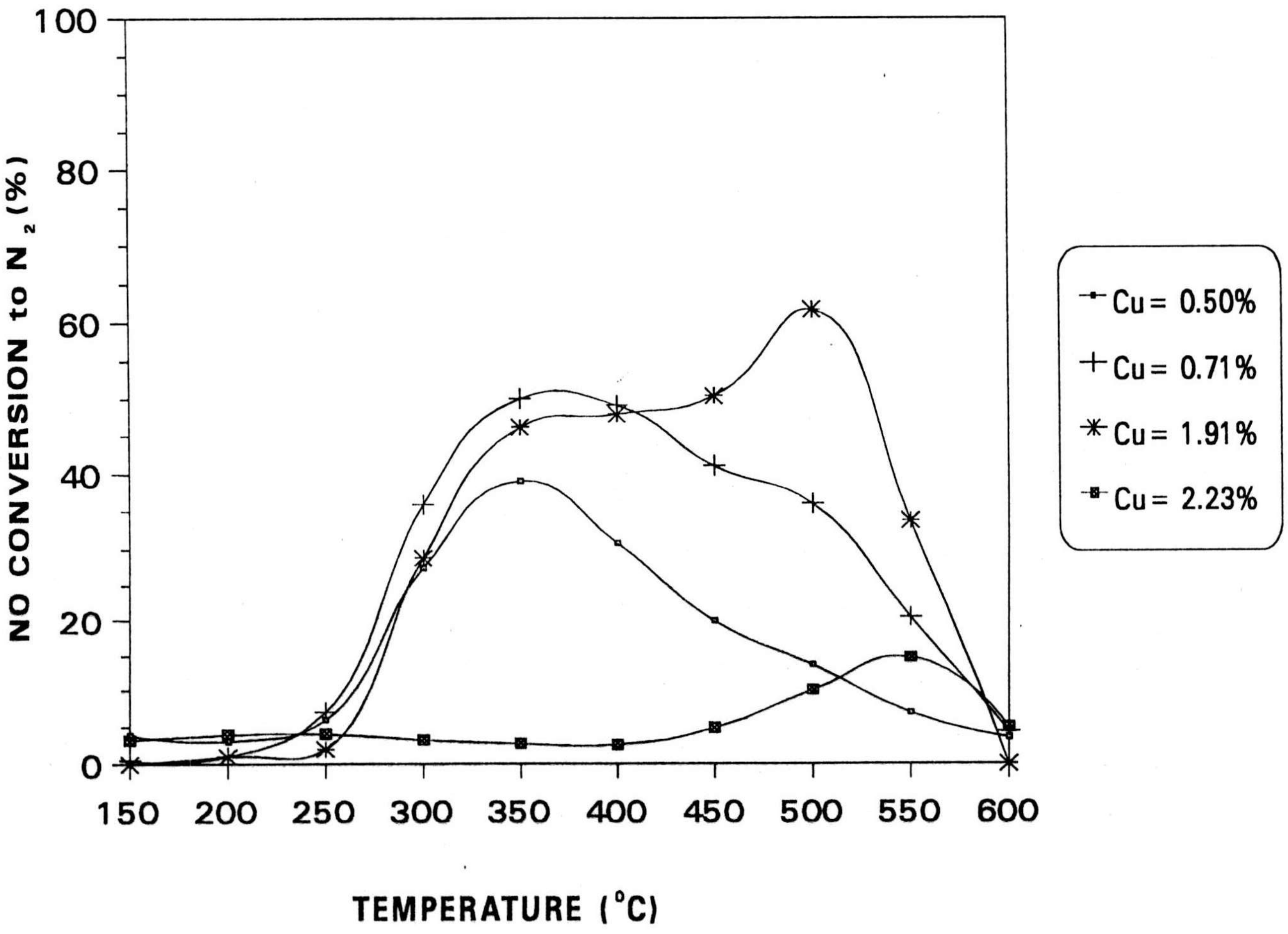

Figure 5.1 Effect of copper content in Na-Cu,Al-silicate on NO reduction.
1000 ppm NO, 10% O_2, 3000 ppm C_3H_8, and balanced He, GHSV 4000 h^{-1}

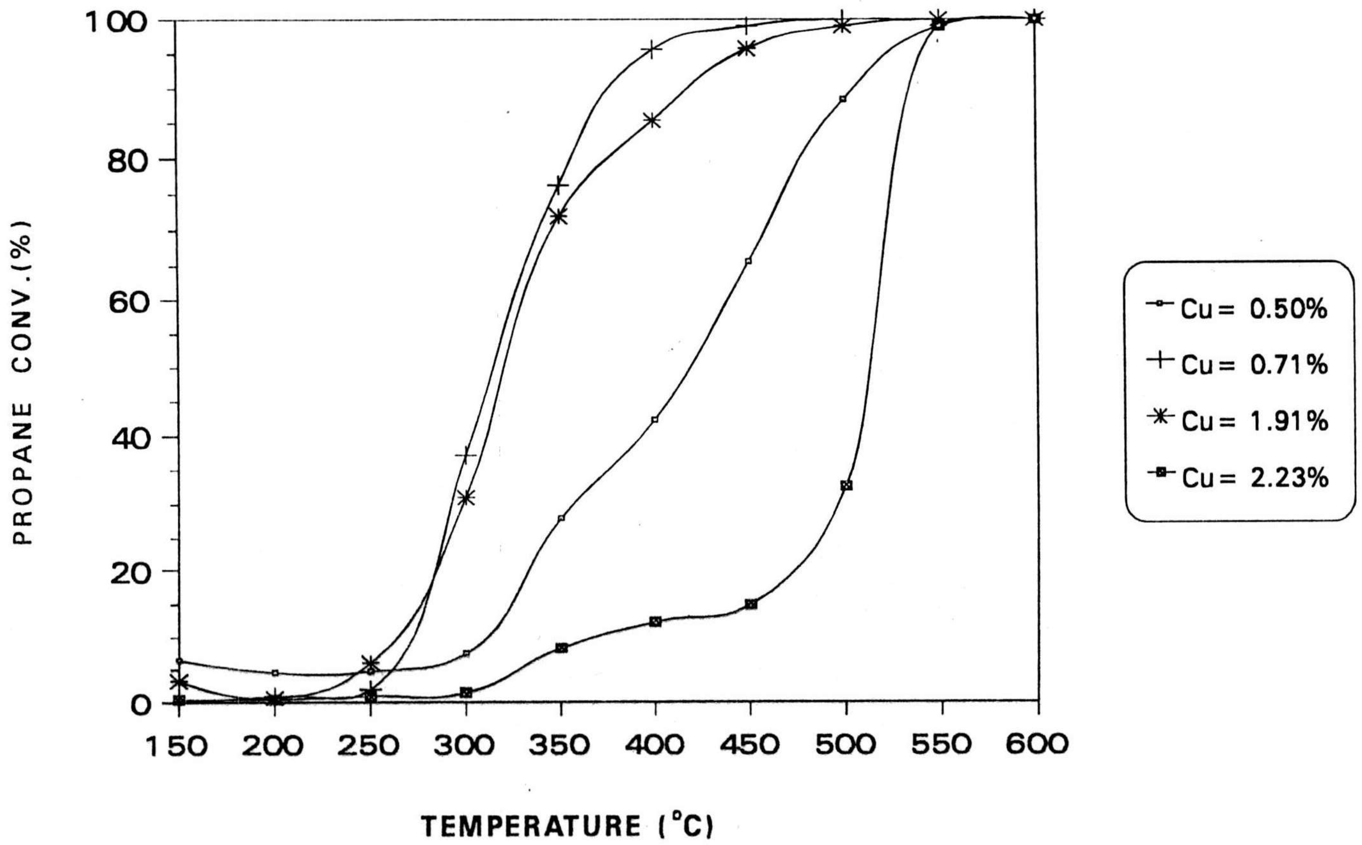

Figure 5.2 Temperature dependence of C_3H_8 conversion on Na-Cu,Al-silicate.
1000 ppm NO, 10% O_2, 3000 ppm C_3H_8, and balanced He, GHSV 4000 h^{-1}

Table 5.1 The light-off temperature of various catalysts

Catalyst	Copper content (wt.%)	Window* (°C)	Light-off temperature (°C)	
			NO conv.	C_3H_8 conv.
1. Na-form catalyst	0.50	-	-	420
(Na-Cu,Al-silicate)	0.71	55	345	310
	1.91	95	440	315
	2.23	-	-	515
2. NH_4-form catalyst	0.50	325	245	300
(NH_4-Cu,Al-silicate)	0.71	325	260	285
	1.91	303	255	265
	2.23	346	247	270
3. H-form catalyst	0.50	234	310	380
(H-Cu,Al-silicate)	0.71	303	285	320
	1.91	284	265	315
	2.23	311	285	315

* window (°C) measured at 50% NO conversion

Cu,Al-silicate (Cu=0.71%), which was 53% at 350 ^{0}C. When %Cu in Na-Cu,Al-silicate was increased to 2.23 wt%, the activity of this catalyst sharply dropped. This results indicated that the increase of Cu content on Na-Cu,Al-silicate could increase the catalytic activity of NO reduction, but upto a limit. Further increase in Cu loading dramatically suppressed the activity. In addition, the results of NO conversion as a function of reaction temperature showed that NO conversion increased rapidly at temperature range 250-300 ^{0}C and reached a maximum NO conversion at a temperature around 350 ^{0}C for Na-Cu,Al-silicate (Cu=0.50 and 0.71 wt%) or 550 ^{0}C for Na-Cu,Al-silicate (Cu=1.91 and 2.23 wt%) and then decreased at high temperature for each catalyst.

Effect of temperature on propane conversion of Na-Cu,Al-silicate, contrasted to the effect of temperature on NO conversion. Amount of C_3H_8 combustion sharply increased up to 100% when temperature gradually increased and remained there without any decrease. As shown in Figure 5.2, when %Cu in Na-Cu,Al-silicate were increased from 0.50% to 0.71%, C_3H_8 combustion was greatly improved. When Cu in Na-Cu,Al-silicate was increased to 1.91 wt%, C_3H_8 conversion slightly dropped and when Cu was increased to 2.23%, the activity of this catalyst for C_3H_8 combustion sharply dropped.

At low temperatures, propane selectively reacted with NO, thus NO conversion rapidly increased. However, at high temperature oxidation of propane by oxygen began to dominate the oxidation by NO. This phenomenon decreased NO conversion gradually, while conversion of propane did not drop. For higher temperature, almost all propane reacted with oxygen, thus left only a small amount to react with NO.

5.1.2 NH_4-form of Cu,Al-silicate (NH_4-Cu,Al-silicate)

Figures 5.3 and 5.4 show the catalytic activities for NO reduction and C_3H_8 combustion of NH_4-Cu,Al-silicate catalysts. Effect of copper content in NH_4-Cu,Al-silicate contrast to the case of Na-Cu,Al-silicate. From Figure 5.3, when Cu content was increased from 0.5 wt% to 1.91wt%, NO conversion significantly decreased, but when Cu content was increased to 2.23 wt%, the activity of NH_4-Cu,Al-silicate increased again. The effect of Cu content on the light-off temperature of these catalysts are similar to the results of the maximum NO conversion. Figure 5.4 showed that activity of propane conversion increased when copper content was increased in NH_4-Cu,Al-silicate. However, temperature dependence of NO conversion and propane conversion was similar to the case of Na-Cu,Al-silicate. NO conversion rapidly increased at lower temperature (200-300 ^{0}C) and gradually decreased at higher temperature and still constant at 100 % propane conversion. The reasons of this phenomenon were the same as that of Na-Cu,Al-silicate.

5.1.3 H-form of Cu,Al-silicate (H-Cu,Al-silicate)

The effect of copper content in H-Cu,Al-silicate for the reduction of gas containing NO, C_3H_8, and O_2 is depicted in Figures 5.5, and 5.6. When the amount of copper content in H-Cu,Al-silicate was increased from 0.50 wt% to 1.91 wt%, the activity of H-Cu,Al-silicate for NO reduction significantly increased as considered from light-off temperature. H-Cu,Al-silicate with Cu content of 2.23 wt% showed a slight increase of light-off temperature, and temperature window expanded to high temperature region. In addition, temperatures of maximum NO conversion of Cu 0.50 wt%, 0.71 wt%, 1.91 wt% and 2.23 wt%

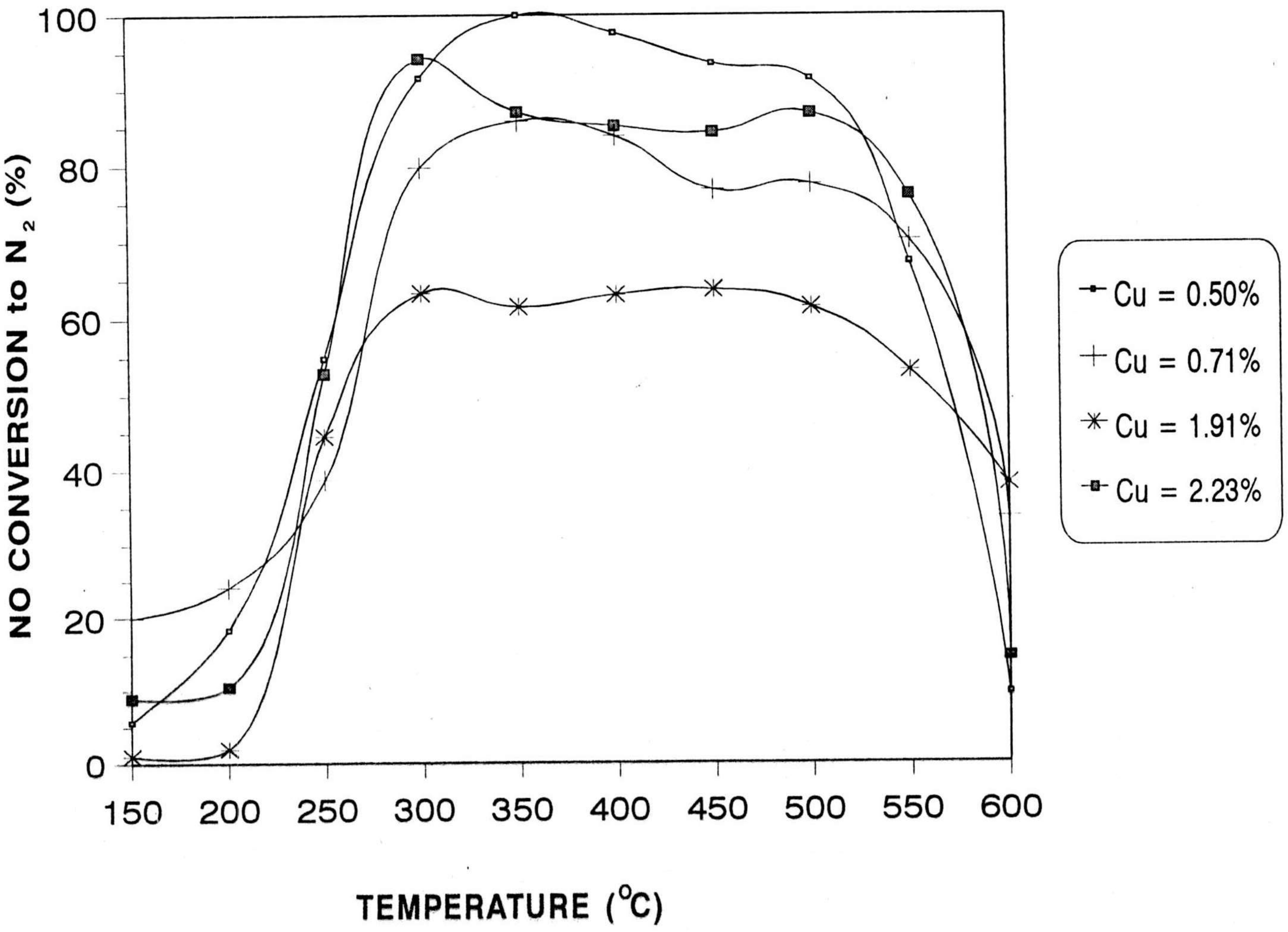

Figure 5.3 Effect of copper content in NH_4-Cu,Al-silicate on NO reduction.

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

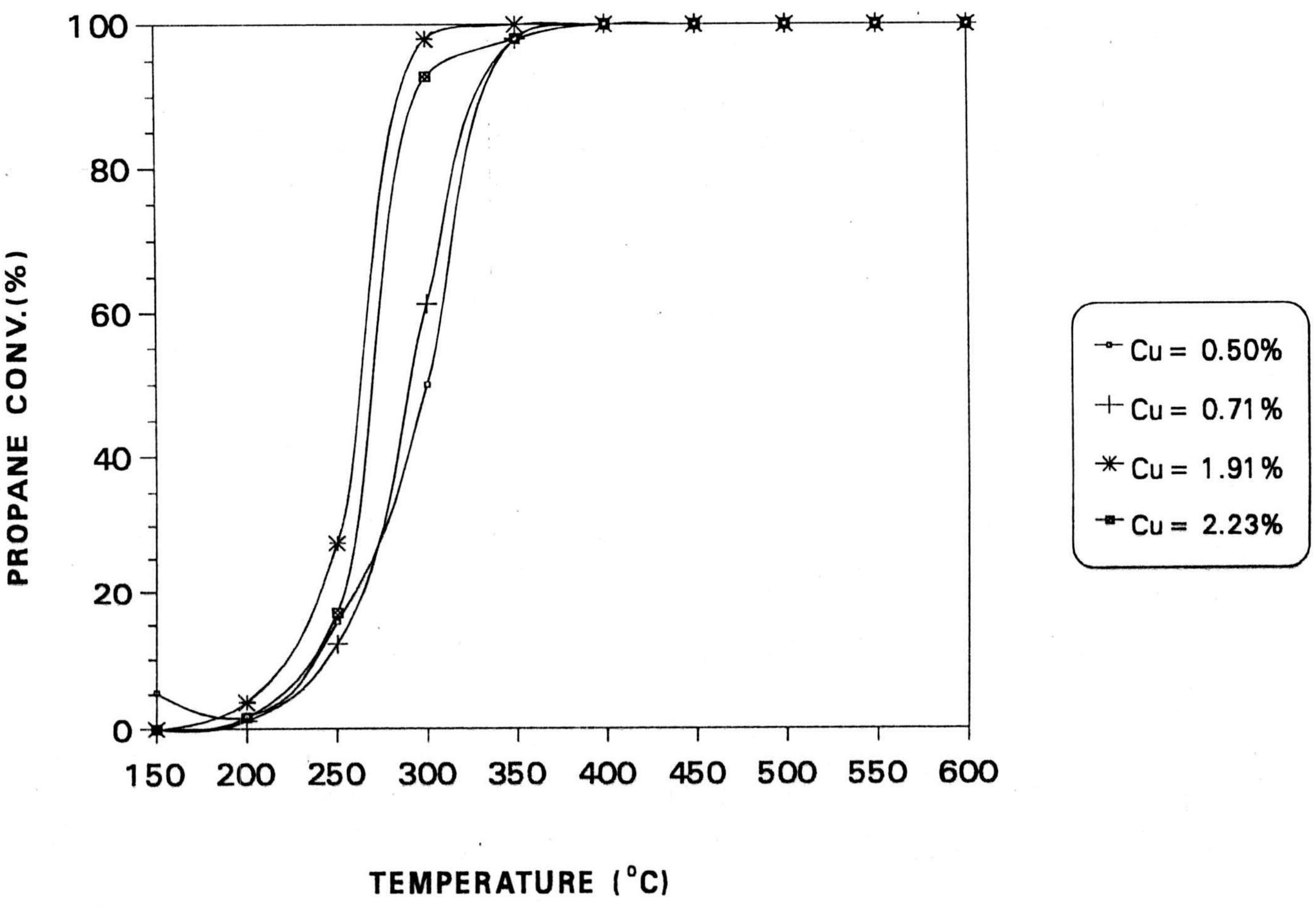

Figure 5.4 Temperature dependence of C_3H_8 conversion on NH_4-Cu,Al-silicate. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8 and balanced He, GHSV 4000 h^{-1}

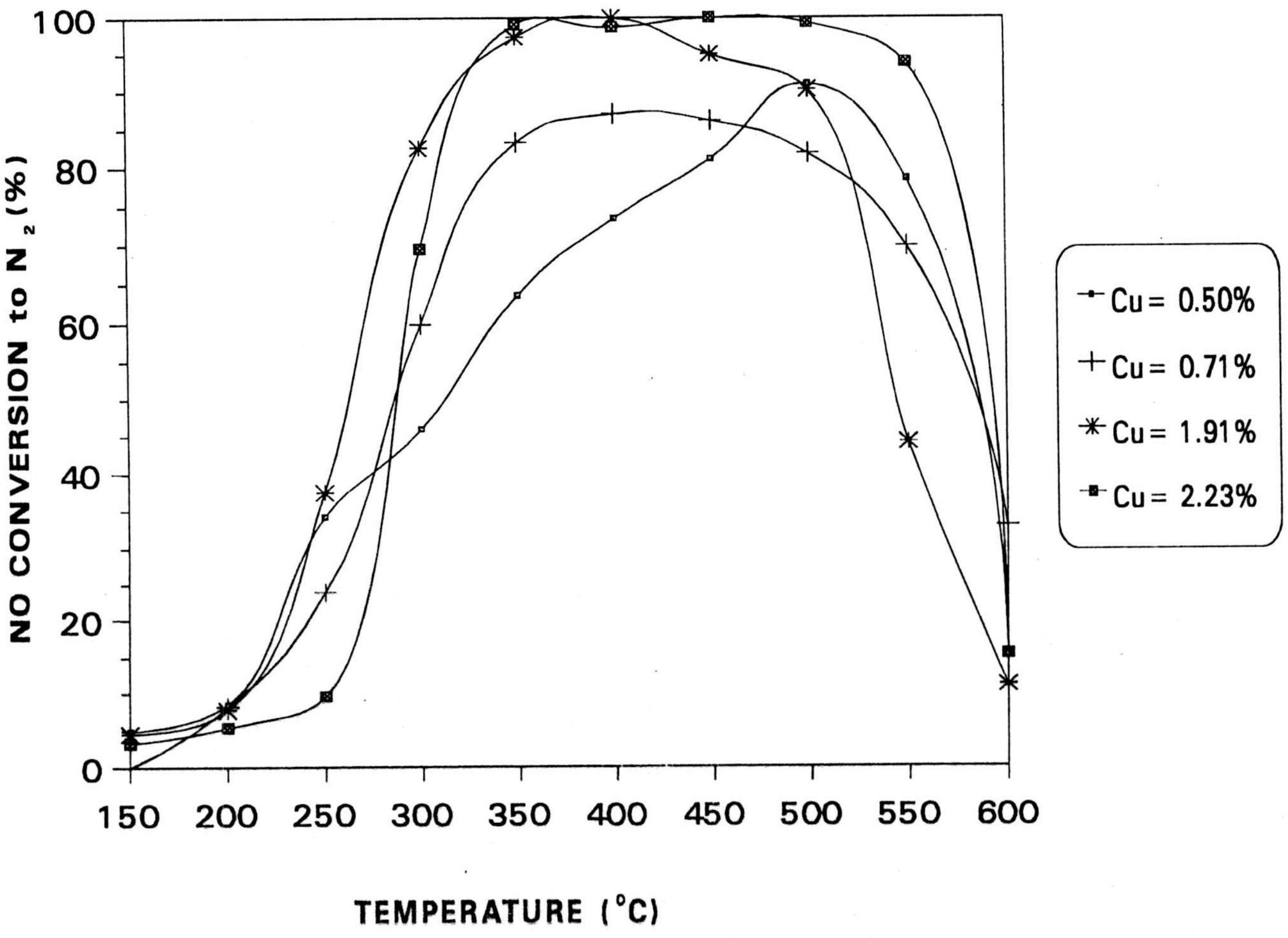

Figure 5.5 Effect of copper content in H-Cu,Al-silicate on NO reduction.

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

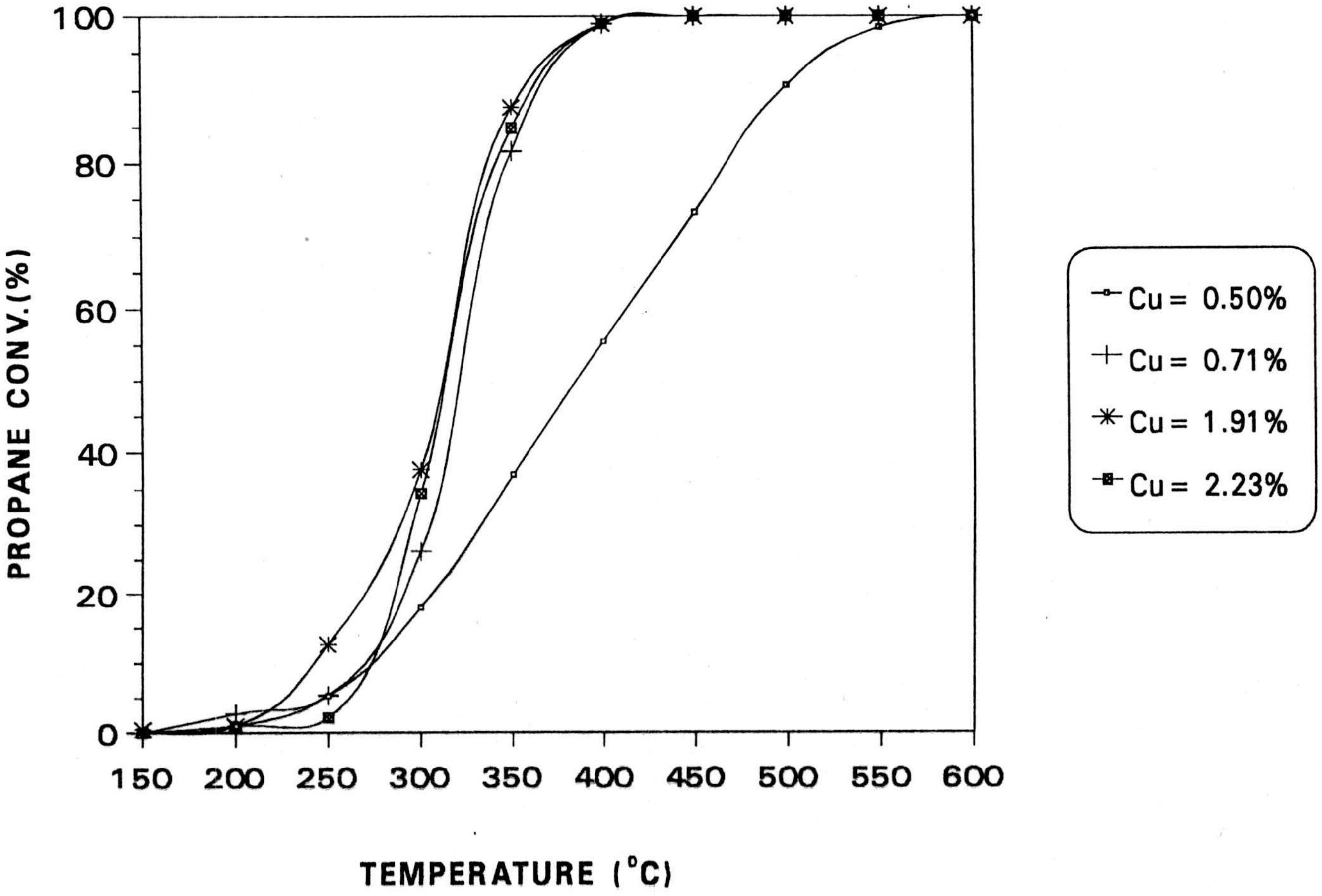

Figure 5.6 Temperature dependence of C_3H_8 conversion on H-Cu,Al-silicate. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8, and balanced He, GHSV 4000 h^{-1}

decreased from 500^{0}C (88% NO conversion), 400^{0}C (86% NO conversion) to, 400^{0}C (100% NO conversion), and 350^{0}C (100% NO conversion), respectively. The light off temperatures for both NO and propane conversion are shown in Table 5.1. In addition, H-Cu,Al-silicate with high copper content exhibited a broad temperature window of maximum NO conversion and a high light-off temperature.. It can be concluded that H-Cu,Al-silicate with higher copper content exhibits the lowest activity, but with a broader temperature window. This results indicated that the increase of copper content decreased temperature of maximum NO conversion, but the average of maximum NO conversion was higher than at lower copper content.

When three forms of high copper content Cu,Al-silicate were compared, it was found that NH_4-form of Cu,Al-silicate exhibited the lowest light off temperature, about 245 ^{0}C and H-form of Cu,Al-silicate showed higher light off temperature (285 ^{0}C). Moreover, NH_4-Cu,Al-silicate had wider temperature window of NO conversion. However, NH_4-form of zeolite is not stable at high temperature, because it can easily change to H-form. Consequently, NH_4-Cu,Al-silicate was not used in the next comparisons.

5.2 Effect of Number of Cu Ion-exchanged on Cu,Al-silicate for the Selective Reduction of NO by Propane in the Presence of Excess Oxygen

From the first section of this chapter, it was found that Cu,Al-silicate , with high copper content showed high NO conversion at high temperature. This indicated that Cu,Al-silicate is not an effective catalyst for NO reduction at relatively low temperature. Therefore, an effort was devoted to lower the light-off temperature. Copper exchanged into ZSM-5 greatly enhances the catalytic activity for reduction of NO at lower temperature [25]. To receive high Cu ion-exchanged in catalyst, the catalyst should be ion-exchanged for several times. Hence, this section reports the effect of Cu ion-exchange on both Na-form and H-form of Cu,Al-silicate for the reduction of NO in oxidizing atmosphere. To investigate effect of Cu ion-exchanged clearly, the catalysts which had the worst activity were chosen for this section.

5.2.1 Cu/Na-Cu,Al-silicate (Cu exchanged on Na-Cu,Al-silicate)

The effect of number of Cu-exchanged on Na-Cu,Al-silicate for the reaction of gas containing NO, C_3H_8, and O_2 is shown in Figures 5.8 and 5.9. The amount of copper contents on Cu/Na-Cu,Al-silicate catalysts measured by AAS methods are shown in Table 5.2. From Table 5.2, one can observe that increasing numbers of ion-exchange increased copper content on Cu/Na-Cu,Al-silicate catalysts. From Figure 5.7, Na-Cu,Al-silicate (Cu=2.23 wt%) showed low activity for NO removal. When a small amount of Cu was ion-exchanged (Cu=0.9 wt%), which prepared by ion exchanged 1 time, the activity greatly enhanced and up to maximum after the several ion-exchange. But further increase of copper content by Cu ion-exchange gradually decreased the activity

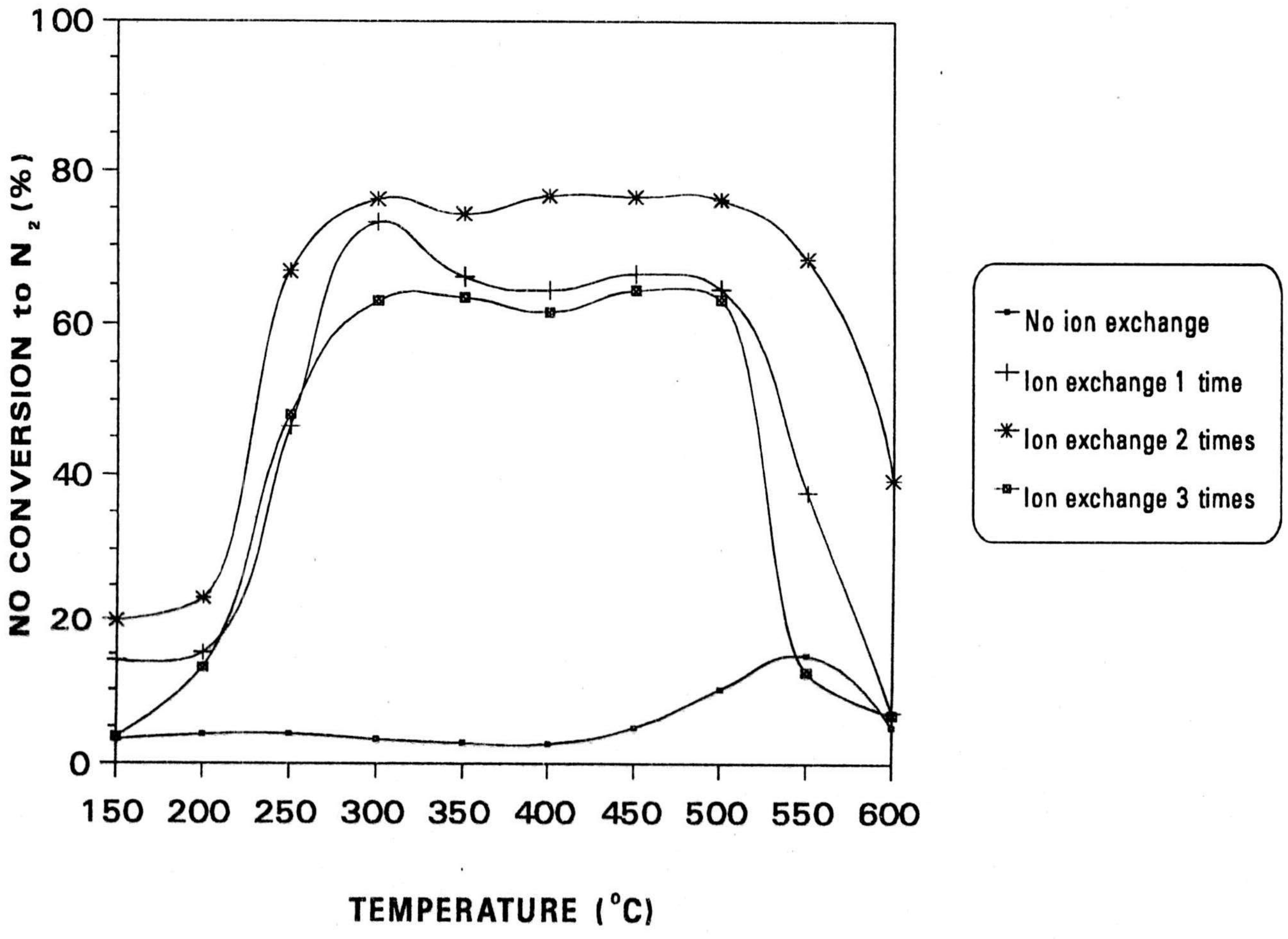

Figure 5.7 Effect of number of Cu ion-exchange in NO reduction on Na-Cu,Al-silicate. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8, and balanced He, GHSV 4000 h^{-1}

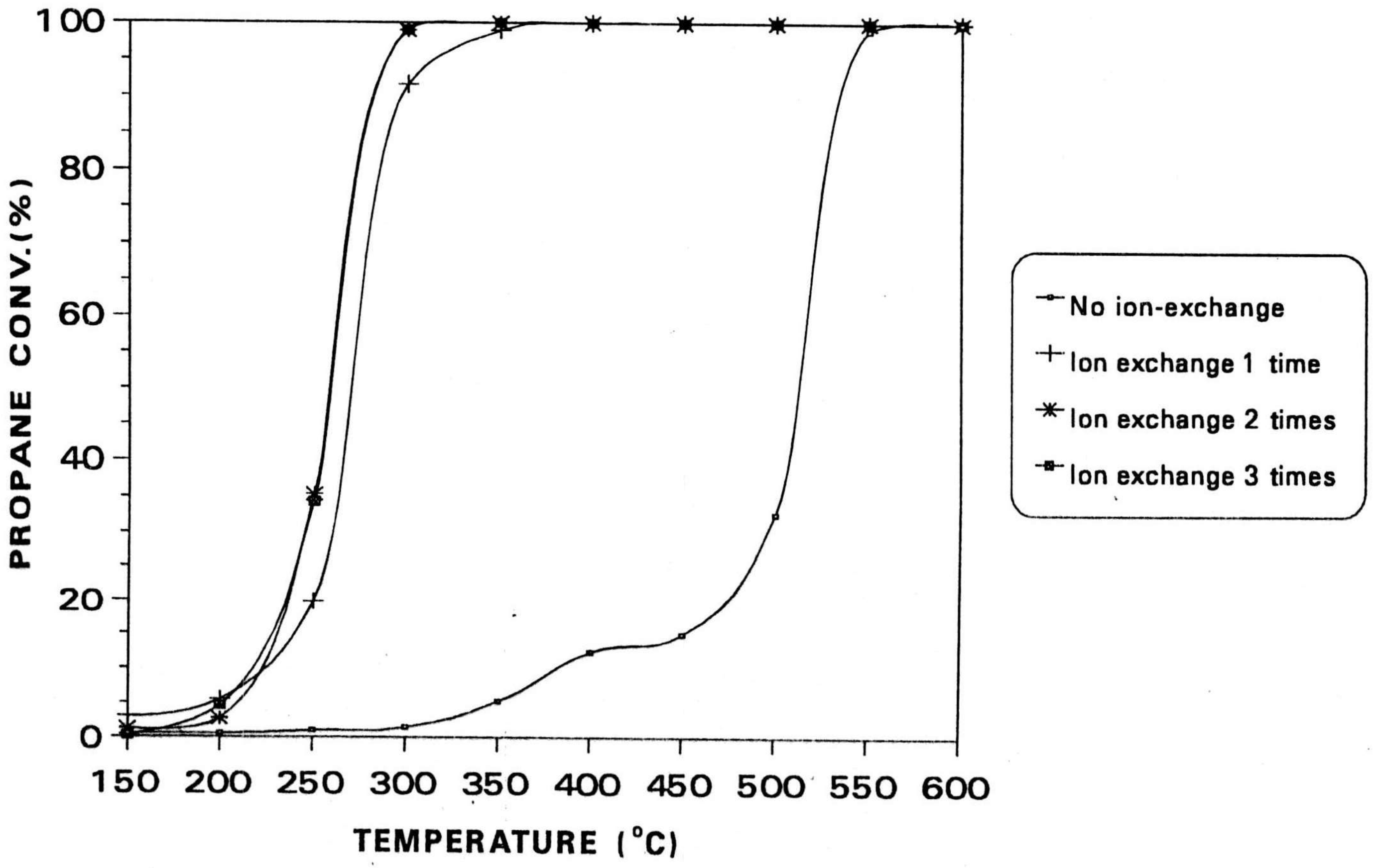

Figure 5.8 Temperature dependence of C_3H_8 conversion on Cu/Na-Cu,Al-silicate. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8, and balanced He, GHSV 4000 h^{-1}

of the catalyst. The light-off temperatures of copper ion-exchanged in Na-Cu,Al-silicate (Cu in structure = 2.23 wt%) for 0.90 wt%, 2.35 wt%, and 2.44 wt% were 250 ^{0}C, 230 ^{0}C, and 250 ^{0}C, respectively. Temperature windows at 50% NO conversion for 0.9 wt%, 2.35 wt%, and 2.44 wt% were 270 ^{0}C, 350 ^{0}C, and 258 ^{0}C, respectively. The results revealed that increment of number of Cu ion exchange increased activity of NO reduction , but ion-exchange more than 2 times decreased activity of this reaction.

From the results of propane conversion (Figure 5.8), it was found that Cu ion-exchanged also greatly improved activity of propane combustion. When 0.9 wt% of copper was ion-exchanged, amount of propane combustion rapidly increased. But when the copper content were 2.35-2.44 wt%, the activity of propane combustion slightly changed. After that, Cu ion-exchanged procedure was used with H-Cu,Al-silicate.

Table 5.2 Copper content by Cu ion exchange in Na-Cu,Al-silicate, which Cu in structure equal 2.23 wt.%.

Cu/Na-Cu,Al-silicate number of ion exchange	% Cu loading by Cu exchanged
ion exchange 1 time	0.9
ion exchange 2 times	2.35
ion exchange 3 times	2.44

5.2.2 Cu/H-Cu,Al-silicate (Cu exchanged on H-Cu,Al-silicate)

Effect of number of Cu ion-exchange on Cu/H-Cu,Al-silicate for the selective reduction of NO with the presence of propane and oxygen is illustrated in Figure 5.9 and combustion of propane is depicted in Figure 5.10. The amount of copper contents on Cu/H-Cu,Al-silicate catalyst measured by AAS method is shown in Table 5.3. Figure 5.9 showed that H-Cu,Al-silicate (Cu in structure = 0.46 wt%) had low activity for NO reduction. Amount of copper content by Cu ion-exchanged increased with increment of number of Cu ion-exchange. Cu/H-Cu,Al-silicate (ion-exchange 1 time) showed lower light-off temperature, but slightly decreased maximum NO conversion. When copper from ion-exchange increased from 1.61 wt% to 1.78 wt%, light-off temperature slightly decreased, however temperature window of NO conversion expanded. When %Cu content by ion-exchange was 2.83 wt%, which was after 3 times of Cu ion-exchanged, activity of the catalyst significantly decreased. It was observed that the increment of number of ion exchange would increase the activity for NO conversion, but Cu ion exchange more than 2 times would decrease this activity. This is consistent with the case of Cu/Na-Cu,Al-silicate catalysts.

For propane conversion (Figure 5.10), when copper content was 1.91 wt%, it was observed that the activity of propane conversion greatly increased. However, at higher copper content, the activity of these catalysts was slightly affected. This indicated that copper ion-exchanged on H-Cu,Al-silicate could increase activity but with the expense of lower maximum NO conversion.

Cu ion-exchanged on both Na-form and H-form of Cu,Al-silicate could enhance activity. This indicated that Cu ion-exchanged could improve the

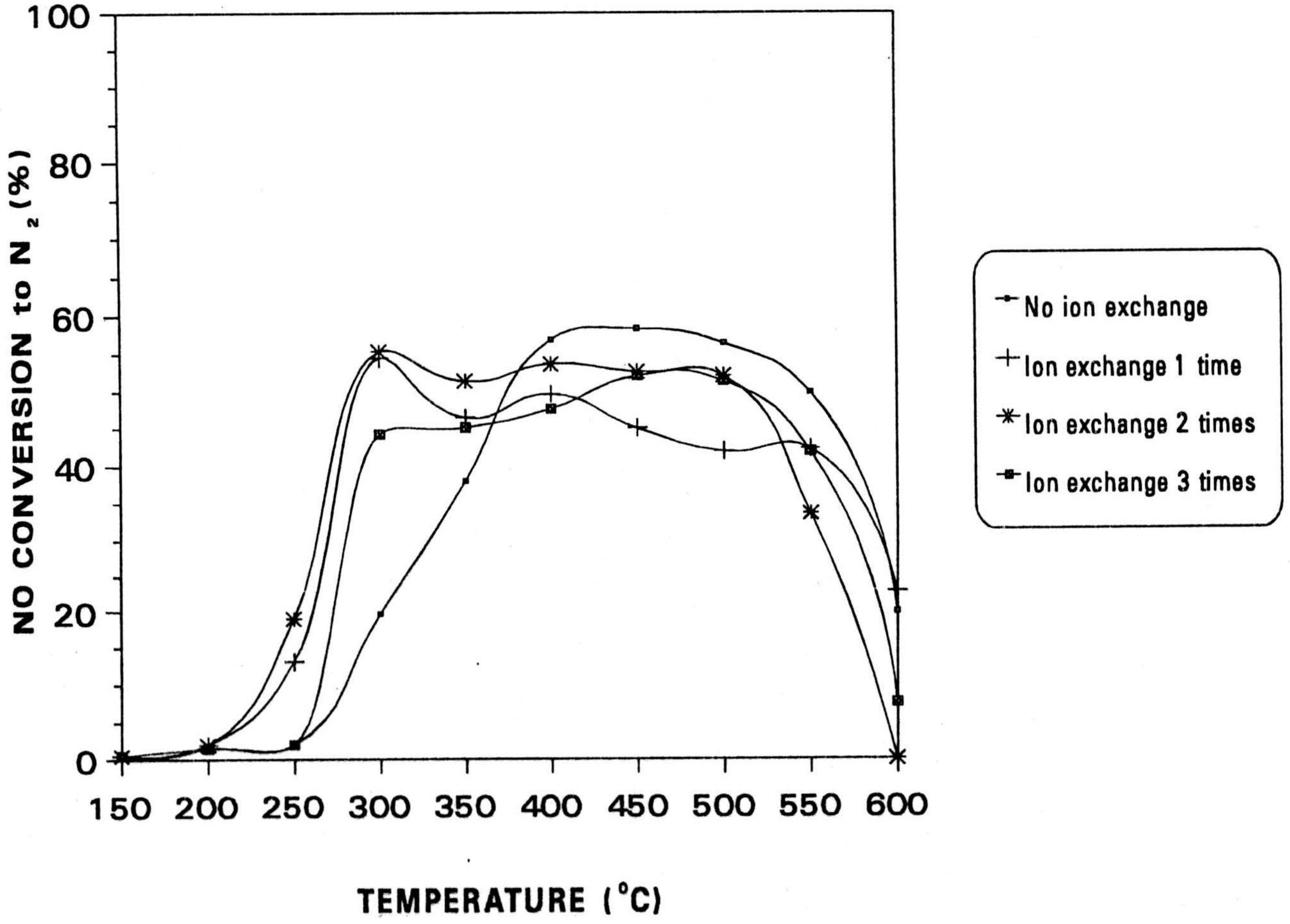

Figure 5.9 Effect of number of Cu ion-exchange in NO reduction on H-Cu,Al-silicate.
1000 ppm NO, 10% O_2, 3000 ppm C_3H_8 and balanced He, GHSV 4000 h^{-1}

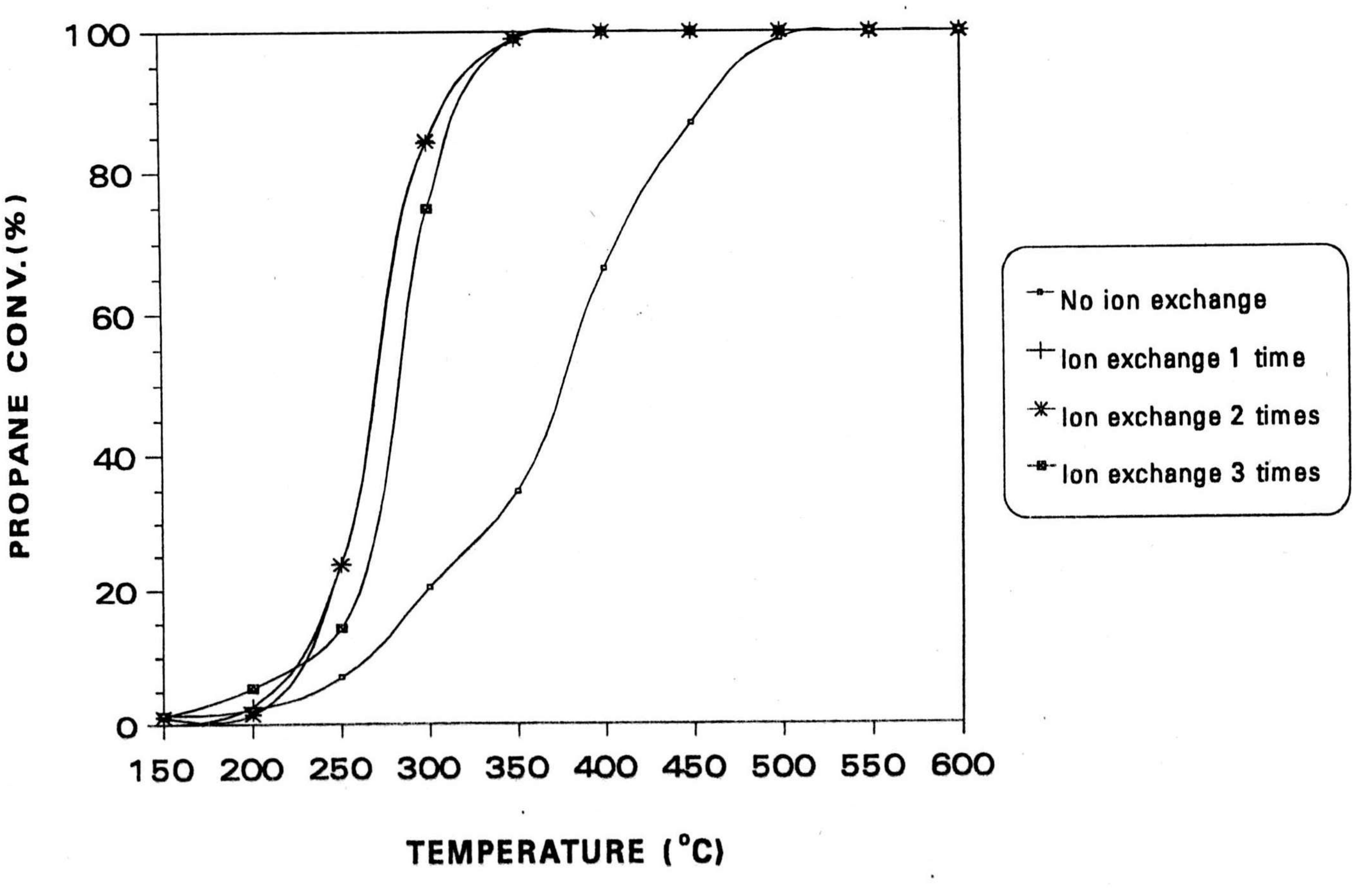

Figure 5.10 Temperature dependence of C_3H_8 conversion on Cu/H-Cu,Al-silicate.
1000 ppm NO, 10% O_2, 3000 ppm C_3H_8, and balanced He, GHSV 4000 h^{-1}

activity of NO reduction, which considered from lowering of light-off temperature. However, it had a limit. When Cu was ion-exchanged too much, the activity gradually decreased. This agrees with previous results obtained by Campa et. al.[28]. They found that "over excessively" ion-exchanged Cu/ZSM-5 exhibited low NO conversion to nitrogen. They suggested that it was due to formation of Cu_xO_y microcluster on surface.

Table 5.3 Copper content by Cu ion exchange in H-Cu,Al-silicate, which Cu in structure equal 0.46 wt.%.

Cu/H-Cu,Al-silicate number of ion exchange	% Cu loading by Cu exchanged
ion exchange 1 time	1.61
ion exchange 2 times	1.78
ion exchange 3 times	2.83

5.3 Comparison of the Catalytic Activity among Cu/Na-ZSM-5, and Cu/Na-Cu,Al-silicate for the Selective Reduction of NO by Propane in Oxidizing Atmosphere

In order to compare the selective catalytic reduction of NO by propane in an excess oxygen atmosphere, Cu/Na-Cu,Al-silicate and Cu/Na-ZSM-5 catalysts were examined in the same condition. Cu/Na-ZSM-5 (Japan) was the catalyst which received from another laboratory. Cu/Na-ZSM-5 was prepared in this laboratory, and Cu/Na-Cu,Al-silicate was the novel catalyst which was firstly prepared in this research. The results of NO to N_2 conversion and C_3H_8 conversion as a function of the reaction temperature are shown in Figures 5.11 and 5.12, respectively. The amount of copper contents on Cu-exchanged, and both Cu-exchanged and incorporated are measured by AAS method. The amounts of Cu in catalysts by ion-exchange are summarized in Table 5.4. Results shown in Figures 5.11 and 5.12 showed that the capabilities to convert propane of these catalysts were the same, but the capabilities of NO reduction of these catalysts were different. Cu/Na-ZSM-5 could ion-exchange only 2.73 wt% Cu, which was less than Cu/Na-ZSM-5 (Japan), and had lower maximum NO conversion. Light-off temperature of Cu/Na-Cu,Al-silicate was slightly higher than that of both catalysts, but Cu/Na-Cu,Al-silicate had wider temperature for NO reduction. Temperature windows of Cu/Na-ZSM-5 (Japan), Cu/Na-ZSM-5, and Cu/Na-Cu,Al-silicate were 294 ^{0}C, 320 ^{0}C, and 380 ^{0}C, respectively. From section 5.1 it was found that ion-exchanged copper enhanced the activity of Cu,Al-silicate. Consequently, Cu/Na-Cu,Al-silicate, the catalyst with both copper ion-exchanged and incorporated, showed both the advantages of Cu-exchanged

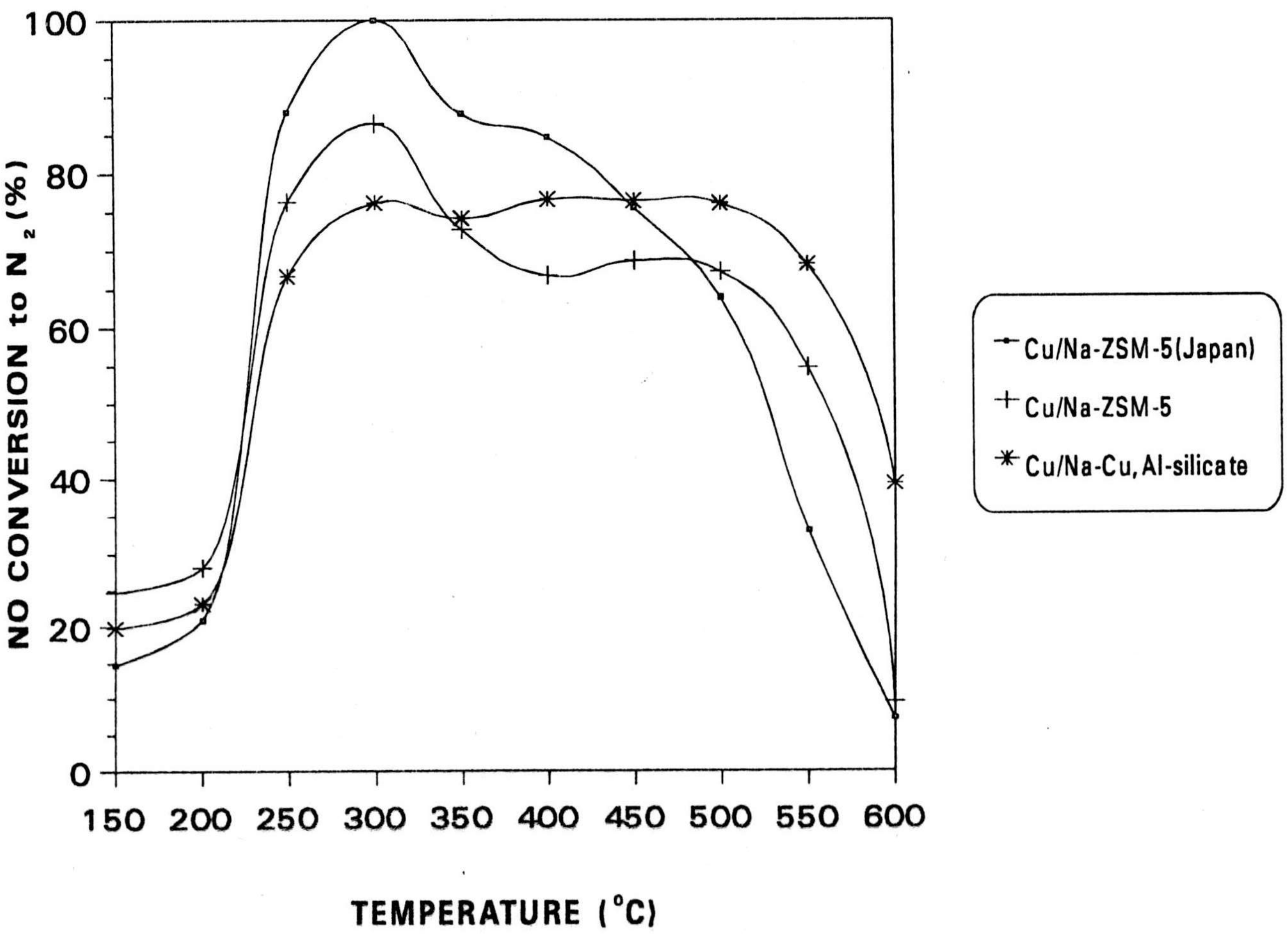

Figure 5.11 Comparison of NO conversion between Cu/Na-ZSM-5 and Cu/Na-Cu,Al-silicate catalysts. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8 and balanced He, GHSV 4000 h^{-1}

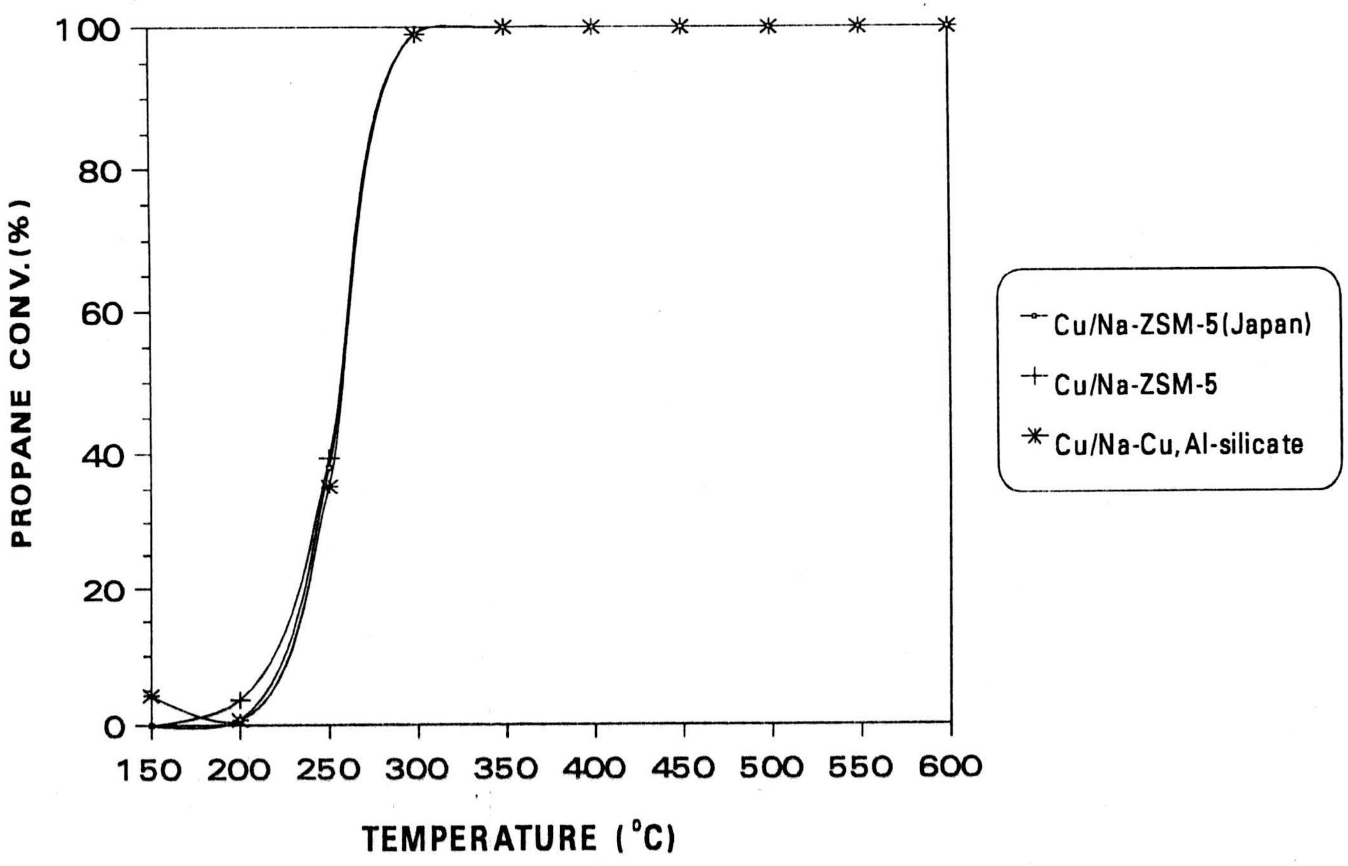

Figure 5.12 Temperature dependence of C_3H_8 conversion on Cu/Na-ZSM-5 and Cu/Na-Cu,Al-silicate. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8, and balanced He, GHSV 4000 h^{-1}

and Cu-incorporated catalysts. This result demonstrated that Cu/Na-Cu,Al-silicate was a potential catalyst for NO removal in oxidizing atmosphere.

Figure 5.13 shows the comparison of NO reduction by propane in the presence of oxygen between Cu/Na-ZSM-5 and Cu/Na-ZSM-5 which was added CuO (Cu=2.23%) to investigate the effect of deposited copper on Cu/Na-ZSM-5. The light-off temperatures of Cu/Na-ZSM-5 and Cu/Na-ZSM-5 with CuO (Cu=2.23 wt%) were 250 °C, and 280 °C, respectively. The result had revealed that deposited copper caused decrement of activity and did not improve temperature window. From this result, it was clearly that Cu in Cu/Cu,Al-silicate was not deposited copper.

Table 5.4 Copper content by ion-exchange in various catalysts

Catalysts	% Cu loading
	by Cu exchanged
Cu/Na-ZSM-5 (Japan)	4.05
Cu/Na-ZSM-5	2.73
Cu/Na-Cu,Al-sil.	2.35

The reactions in this research composed of two parallel reactions, i.e., NO reduction by C_3H_8 and C_3H_8 combustion by O_2, both occur simultaneously

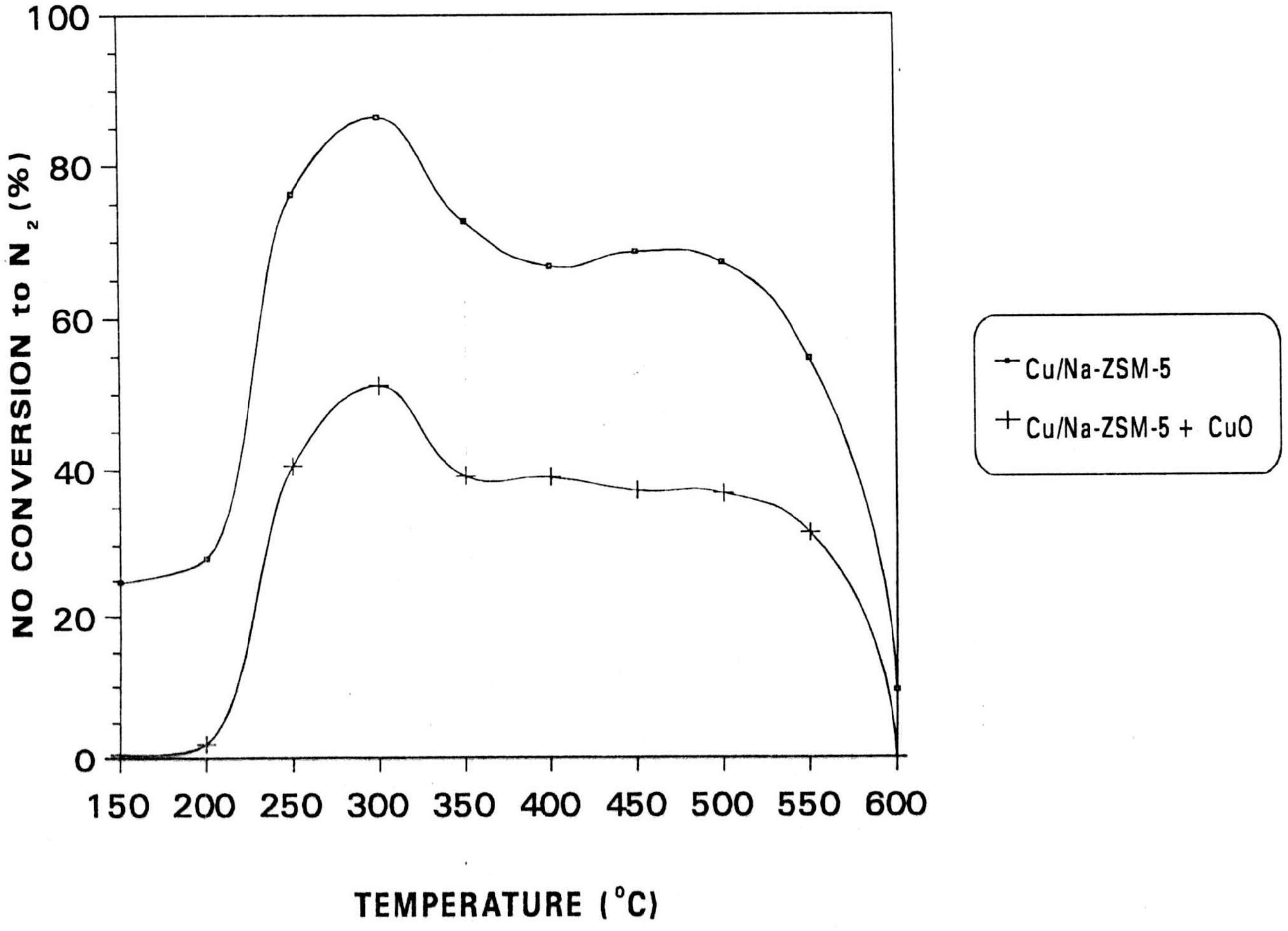

Figure 5.13 Comparison of NO conversion between Cu/Na-ZSM-5 and Cu/Na-ZSM-5 with CuO. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8 and balanced He, GHSV 4000 h^{-1}

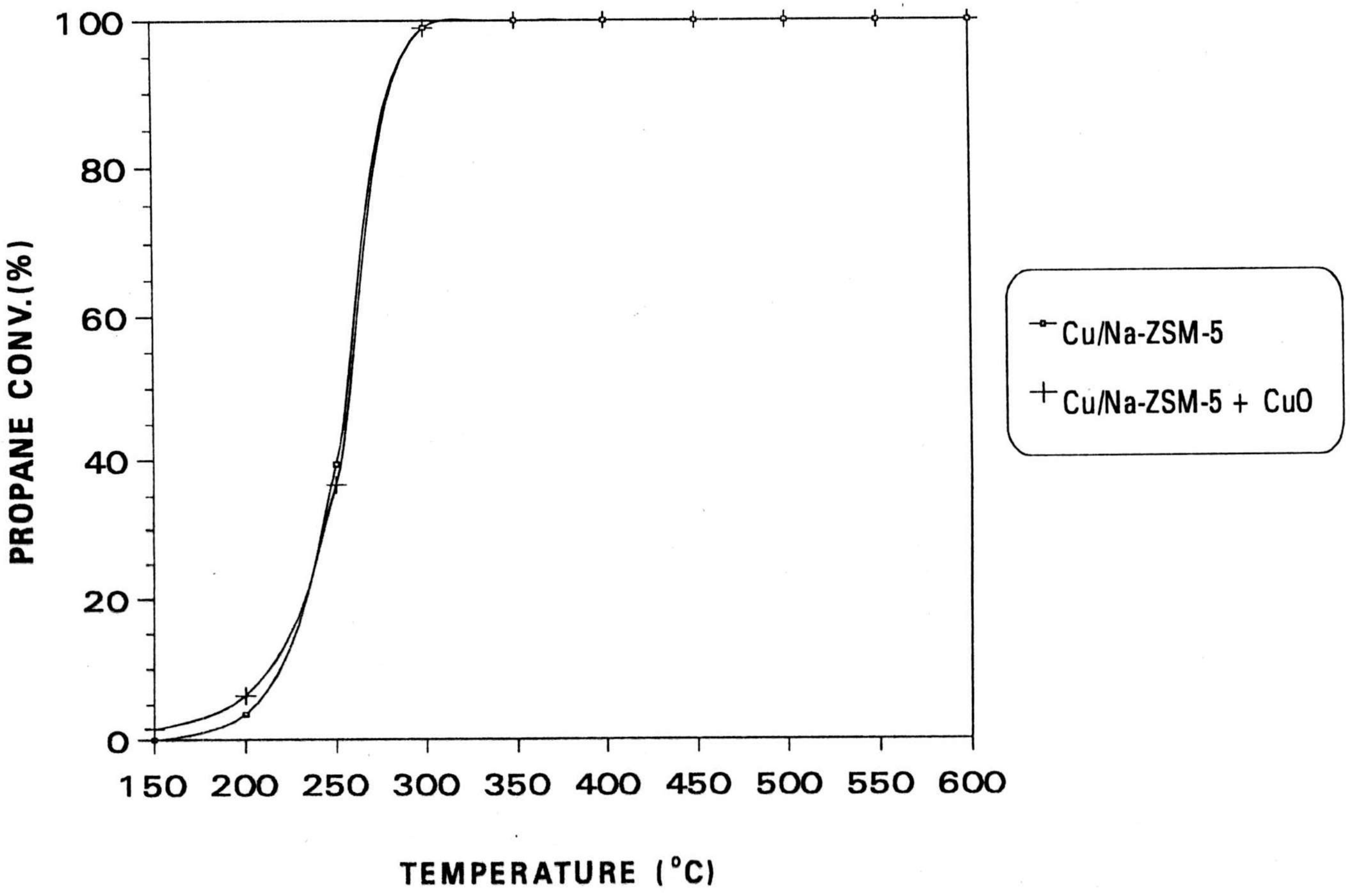

Figure 5.14 Temperature dependence of C_3H_8 conversion on Cu/Na-ZSM-5 and Cu/Na-ZSM-5 with CuO. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8 and balanced He , GHSV 4000 h^{-1}

during a reaction run. NO conversion is proportional to the C_3H_8 concentration in the catalyst bed [3], thus the enhancement of NO conversion over Cu,Al-silicate with high copper content at elevated temperature may be the result of decreasing C_3H_8 combustion rate. The results revealed that temperature of complete propane combustion shifted from 300 ^{0}C (for Cu/Na-ZSM-5) to 400 ^{0}C (for H-Cu,Al-silicate, Cu=2.23%) as shown in Figures 5.12 and 5.6, respectively. Consequently, broad temperature may be due to propane available for NO reduction. The same results were obtained by Yogo [62]. They found that Ga/ZSM-5 showed high activity in a wide range of reaction temperature. The complete combustion of propane on Cu/ZSM-5 was lower than Ga/ZSM-5. Because of the high ability of Cu/ZSM-5 for the oxidation of propane, it would limit the reaction of NO convert to N_2 in the presence of excess oxygen. The ability of Ga/ZSM-5 catalyst for the oxidation of propane was so moderate that high efficiency was attained for the reaction of propane with NO. Moreover, Li and Armor[35], who studied NO reduction by CH_4 over Co/ZSM-5 when there was SO_2 in feed, suggested that SO_2 inhibited the CH_4 combustion rate, thus it showed high conversion at high temperature.

5.4 Effect of SO_2 Addition on NO Reduction by Propane in the Presence of Excess Oxygen

One of the major problems of NO removal is source of fuel for diesel engine both in vehicle and stationary engine. The fuel of this engine always composed of surphur. As the fuel was combusted, SO_2 was emitted to the exhaust gas. Thus, in this section the influence of SO_2 content (300 ppm) in the feed gas on the catalytic performance of Cu/Na-ZSM-5 and Cu/Na-Cu,Al-silicate was investigated over wide range of temperature.

Figures 5.15 and 5.16 show the catalytic activity for NO reduction and C_3H_8 combustion of Cu/Na-ZSM-5 and Cu/Na-Cu,Al-silicate catalysts with SO_2 addition in the temperature range of 150-600^{0}C. It was observed that with the presence of SO_2 the NO conversion to N_2 over Cu/Na-ZSM-5 were depressed drastically all over the range of temperature, while propane conversion to CO_2 was slightly depressed. Cu/Na-Cu,Al-silicate catalyst also shows similar result. For example, the conversion of NO into N_2 was 54 percent for Cu/Na-ZSM-5 and 52 percent for Cu/Na-Cu,Al-silicate at 300^{0}C in the presence of SO_2, while it was 86 and 76 percent in its absence, respectively. This indicates that on Cu/Na-ZSM-5 and Cu/Na-Cu,Al-silicate SO_2 severely hinder the performance. The effect of addition of SO_2 was similar to that reported by Iwamoto et al.[36]. They suggested that the decrement of catalytic activity would be due to change of state of copper ion by the adsorption of SO_2. However, this is a reversible process. In addition, Teraoka et al.[63] suggested that SO_2 competes with NO for the adsorption sites and prevent the catalytic reduction of NO. A slight decrease of propane conversion with SO_2 in feed gas could not explain why propane conversion was slightly affected by SO_2 gas. This result could suggest

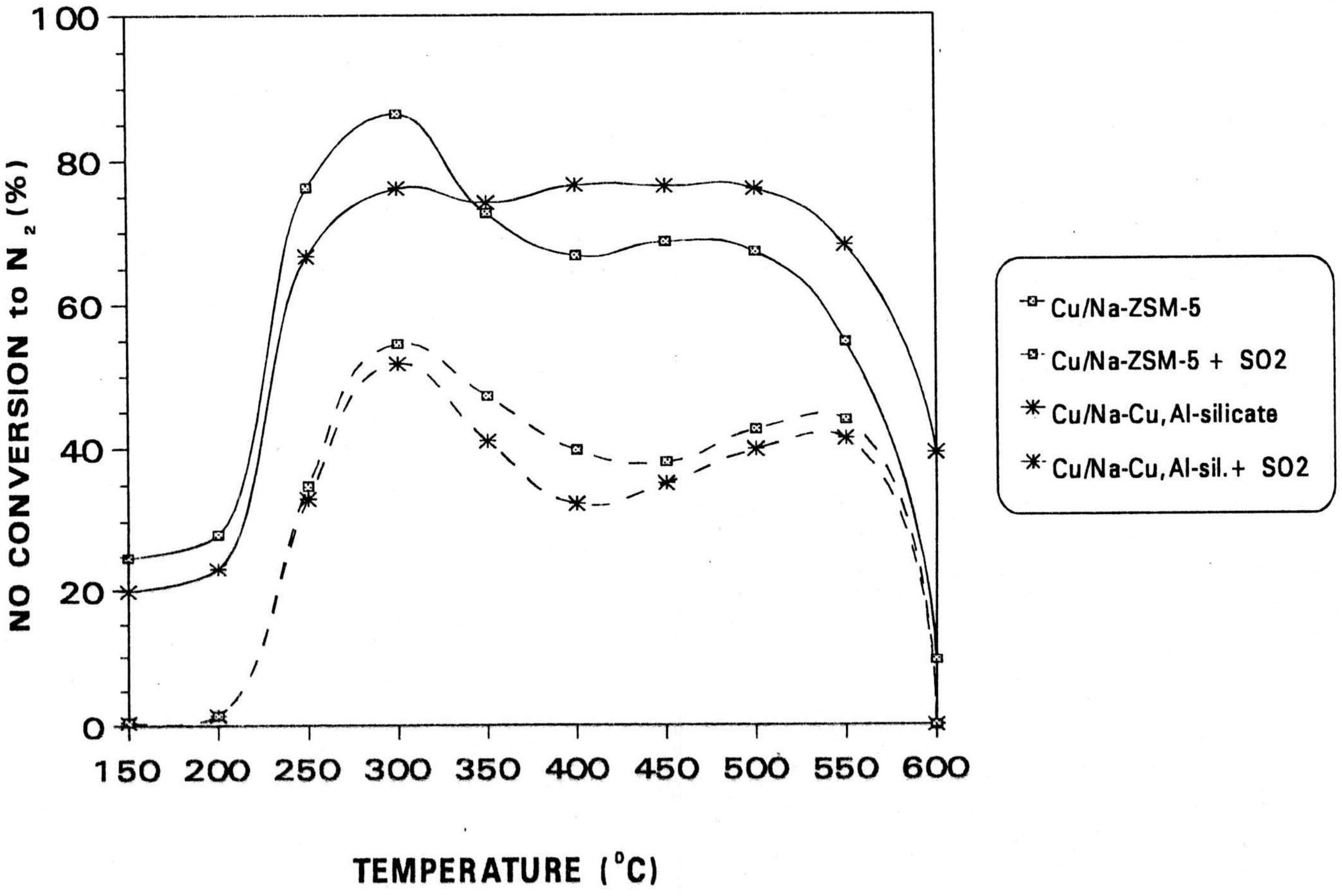

Figure 5.15 Effect of SO_2 in NO reduction on Cu/Na-ZSM-5 and Cu/Na-Cu,Al-silicate. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8 SO_2 300 ppm, and balanced He, GHSV 4000 h^{-1}

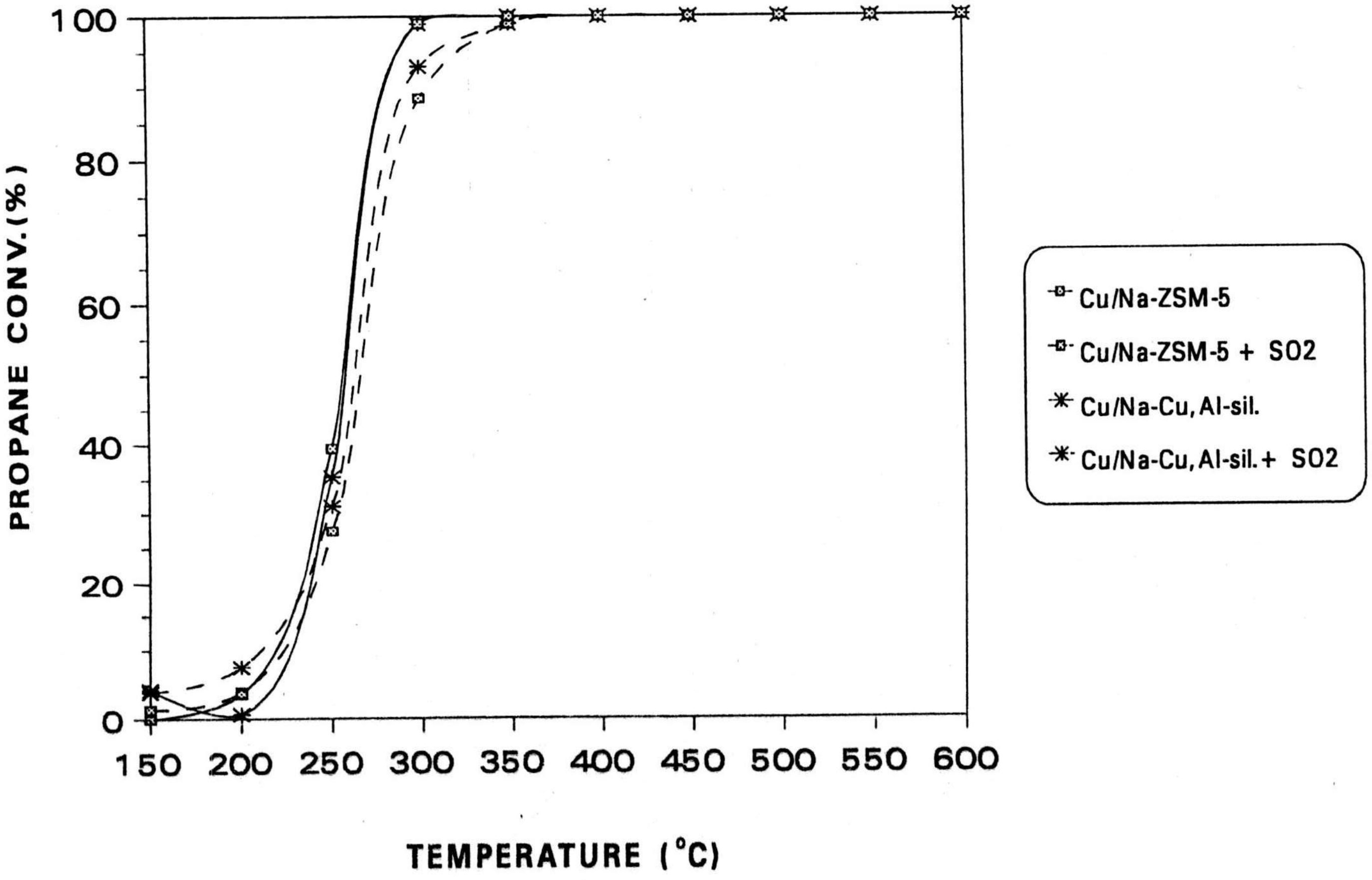

Figure 5.16 Temperature dependence of C_3H_8 conversion on Cu/Na-ZSM-5 and Cu/Na-Cu,Al-silicate. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8, SO_2 300 ppm, and balanced He, GHSV 4000 h^{-1}

that combustion of propane by oxygen may be reacted in gas phase, thus adsorbed SO_2 on active site did not depress activity of propane conversion.

5.5 Effect of Coated Cu/Na-Cu,Al-silicate on Monolith

Advantages of monolith substrate are the low pressure drop associated with high flow rates, resistance to crack due to thermal shock and high mechanical integrity. For these reasons, coated Cu/Na-Cu, Al-silicate on monolith was studied. The ratio of Cu/Na-Cu,Al-silicate to Al_2O_3 was changed in order to investigate its effect on activity for NO reduction. In addition, comparison of coated catalyst and pelleted catalyst with the same weight of Cu/Na-Cu,Al-silicate also was studied.

5.5.1 Effect of ratio of Cu/Na-Cu,Al-silicate to Al_2O_3 on Monolith

The results of NO to N_2 conversion and C_3H_8 conversion as a function of the reaction temperature are shown in Figures 5.17 and 5.18, respectively. As shown in Figure 5.17, only alumina on monolith, NO conversion of this catalyst was high at elevated temperature. The maximum NO conversion of Al_2O_3 on monolith was 65% at 500 ^{0}C. When added the zeolite, which is Cu/Na-Cu,Al-silicate, coated on monolith, it was found that the zeolite greatly enhanced activity of NO reduction, and propane combustion. When Cu/Na-Cu,Al-silicate : Al_2O_3 ratio was increased from 50:50 to 70:30, it found that activities increased a little. The data suggested that the ratio of Cu/Na-Cu,Al-silicate to Al_2O_3 in the range from 50:50 to 70:30 did not have a significant effect for NO reduction in the presence of propane and oxygen.

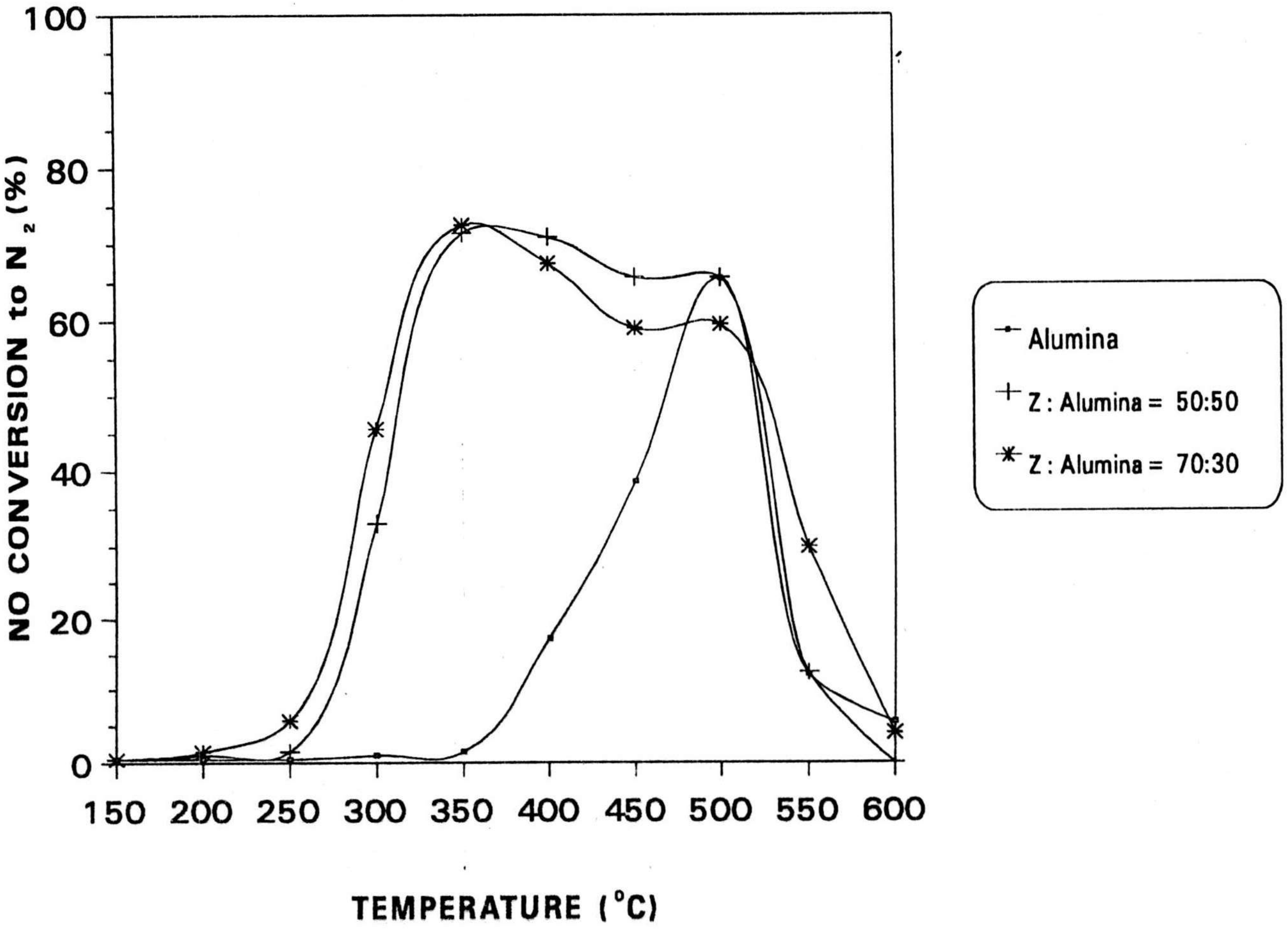

Figure 5.17 Effect of coated Cu/Na-Cu,Al-silicate on monolith in NO reduction.

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

Z = Cu/Na-Cu,Al-silicate

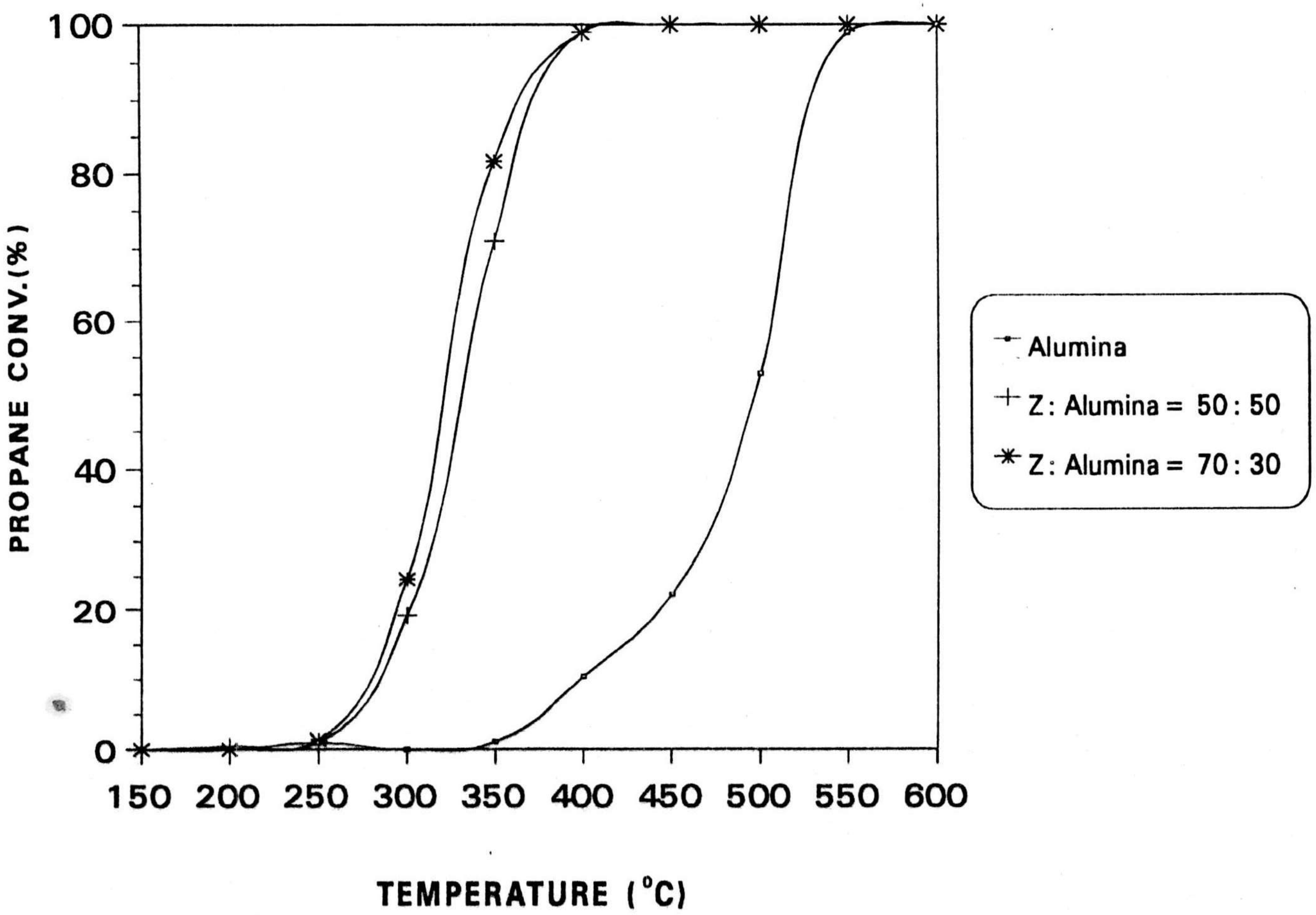

Figure 5.18 Temperature dependence of C_3H_8 conversion coated Cu/Na-Cu,Al-silicate on monolith. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8 and balanced He , Z = Cu/Na-Cu,Al-silicate

5.5.2 Comparison of Activity for NO Reduction on Pelleted Catalyst and Coated Catalyst on Monolith with the same WHSV

Figures 5.19 and 5.20 show the catalytic activity for NO reduction and C_3H_8 combustion over coated catalyst on monolith and pelleted catalyst with the same weight of Cu/Na-Cu,Al-silicate. The light-off temperature of coated catalyst on monolith and pelleted catalyst were 312 ^{0}C and 380 ^{0}C, respectively. In addition, coated catalyst on monolith had higher maximum NO conversion and wider temperature windows than pelleted catalyst. The results have revealed that coated Cu/Na-Cu,Al-silicate exhibited higher NO conversion than pelleted Cu/Na-Cu,Al-silicate. The enhancement of catalytic activity by coating catalyst on a monolitic material may be due to a change in mass transfer effect. However, results of NO conversion and propane conversion as a function of the reaction temperature were similar to the catalysts, which was reported in previous section. Examples of the same phenomena were decreasing of activity of NO conversion at high temperature and still complete propane combustion at high temperature. Therefore , the reason of this phenomena could explain in the same way in previous sections.

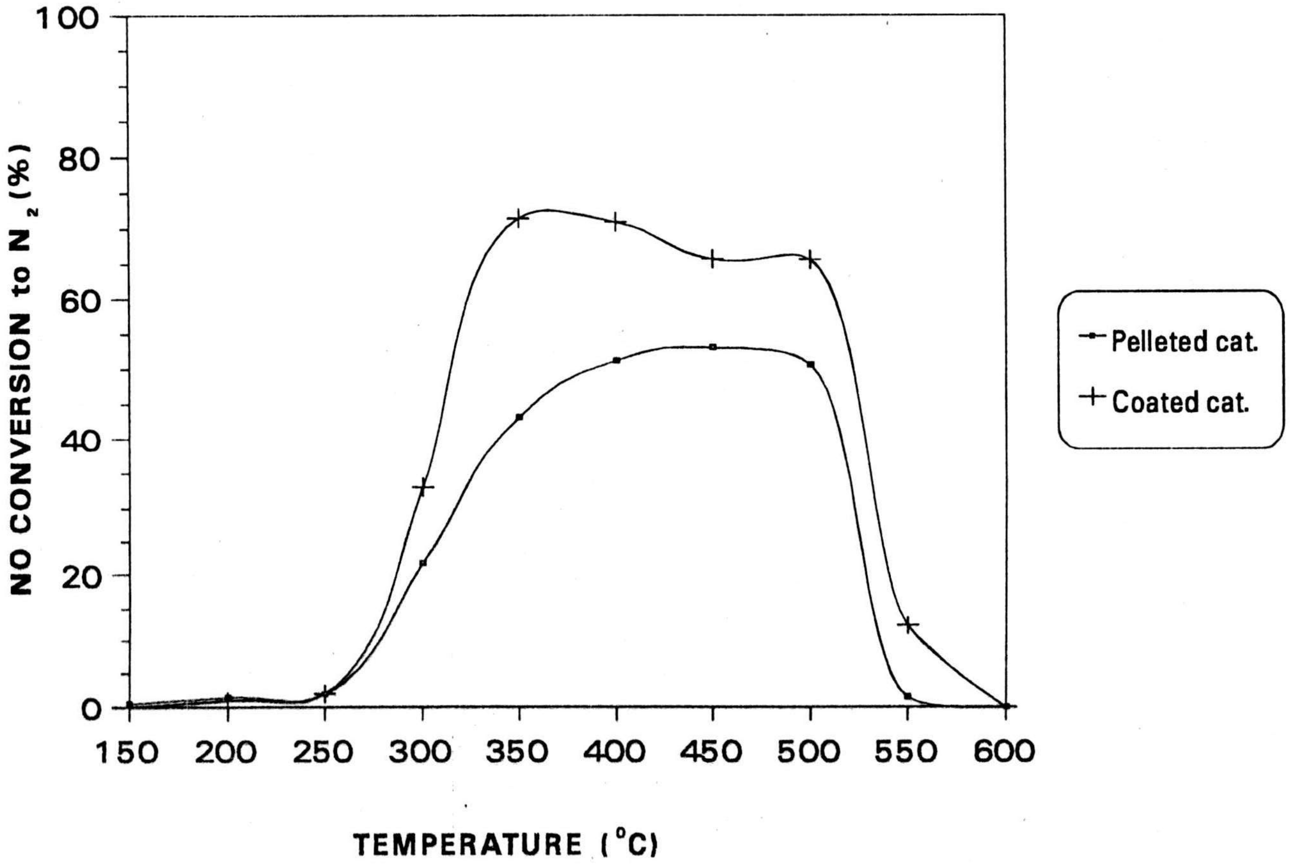

Figure 5.19 Comparison of NO conversion between coated catalyst on monolith and pelleted catalyst. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8 and balanced He

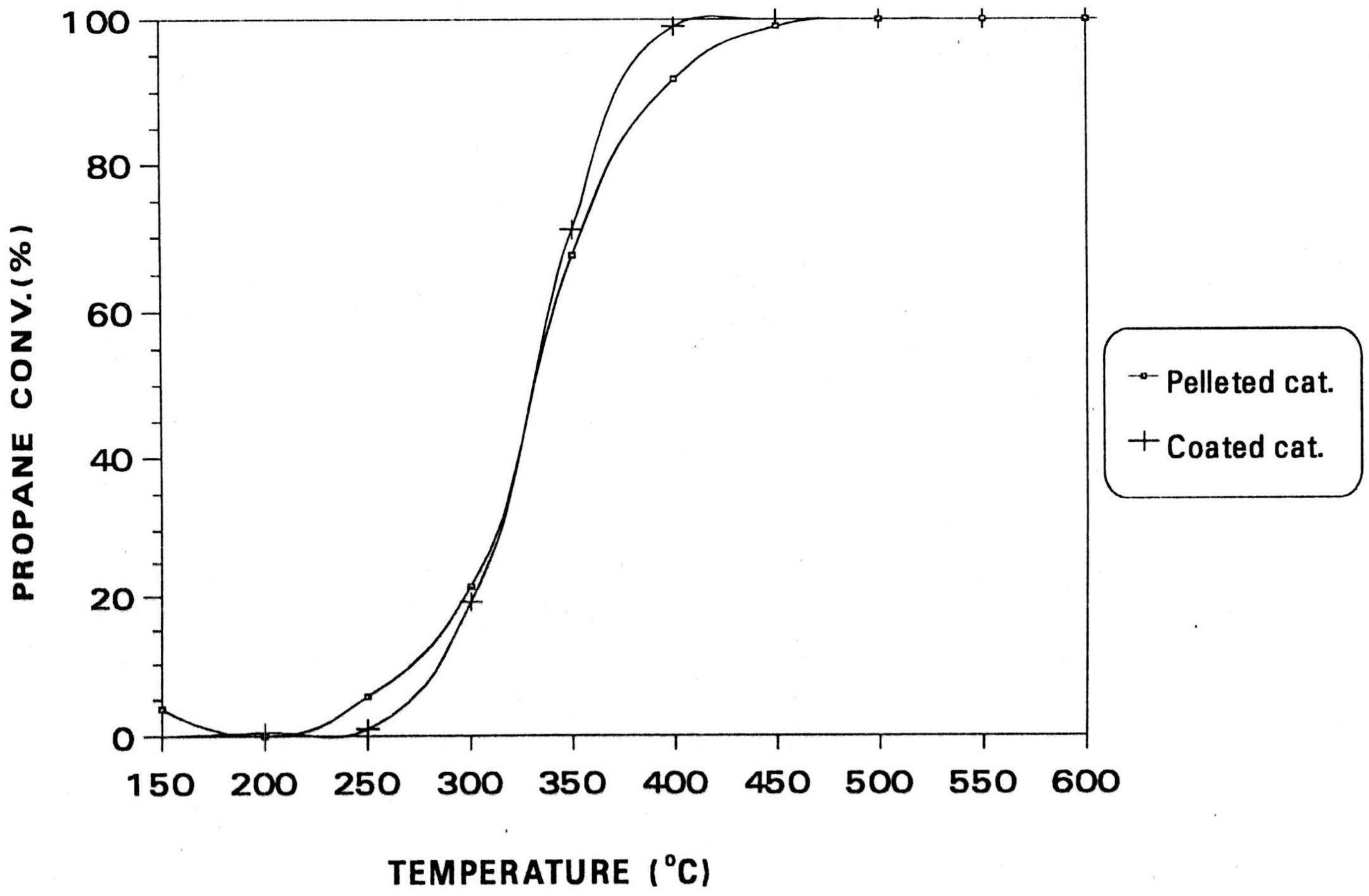

Figure 5.20 Temperature dependence of C_3H_8 conversion on coated Cu/Na-Cu,Al-silicate on monolith and pelleted Cu/Na-Cu,Al-silicate catalyst. 1000 ppm NO, 10% O_2, 3000 ppm C_3H_8 and balanced He

5.6 Characterization of the Catalyst

5.6.1 X-ray Diffraction Pattern

X-ray diffraction patterns for the prepared catalysts and those of H-ZSM-5 of Mobil Oil Corporation are shown in Figure 5.21. As shown in Figure 5.21, it was found that various forms of Cu,Al-silicate catalysts (Na, NH_4, and H-form) had the same XRD patterns. In addition, the XRD patterns of Cu,Al-silicate with various copper content and Cu,Al-silicate with adding Cu ion-exchange did not show any change of their crystalline patterns. The XRD peak of copper oxides was not observed. Thus, copper may be highly dispersed in the structure of crystal. Moreover, all of the patterns of these catalysts prepared in this laboratory by rapid crystallization method were almost similar to that of ZSM-5 of Mobil Oil Corporation [60]. This indicated that the prepared catalysts also had the pentasil pore-opening structure - the same crystalline structure as ZSM-5.

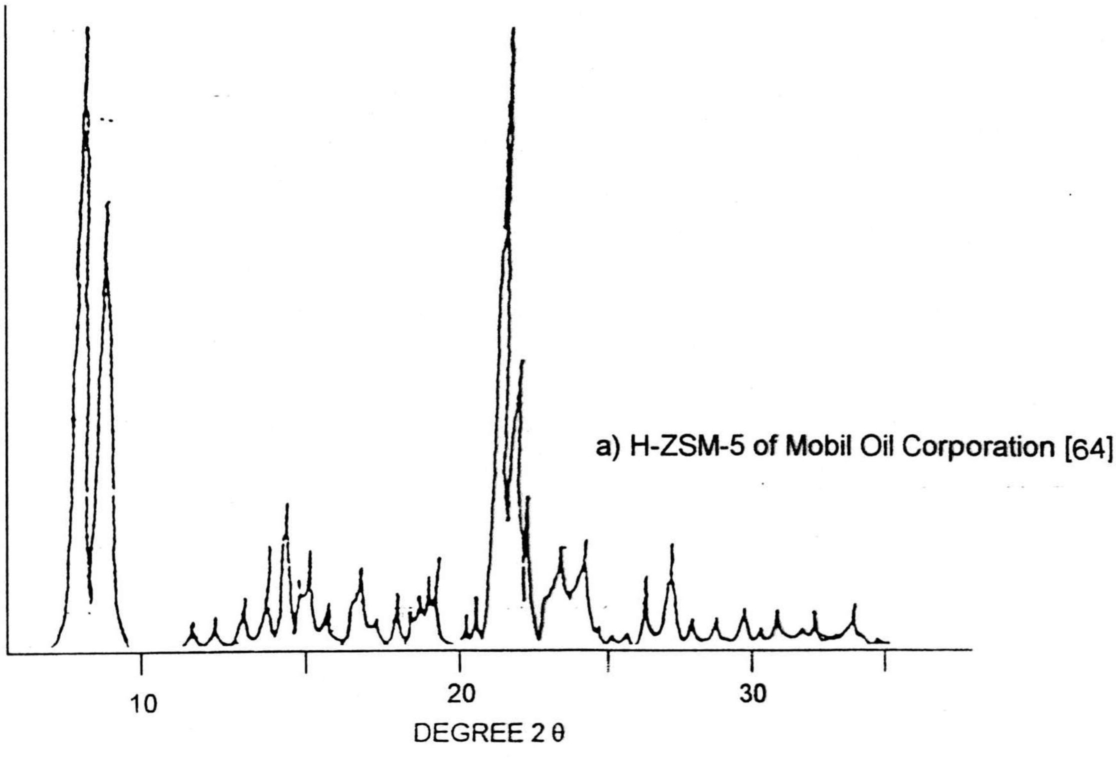

Figure 5.21 X-ray Diffraction Patterns for

a) H-ZSM-5 of Mobil Oil Corporation [64].

b) Cu,Al-silicate

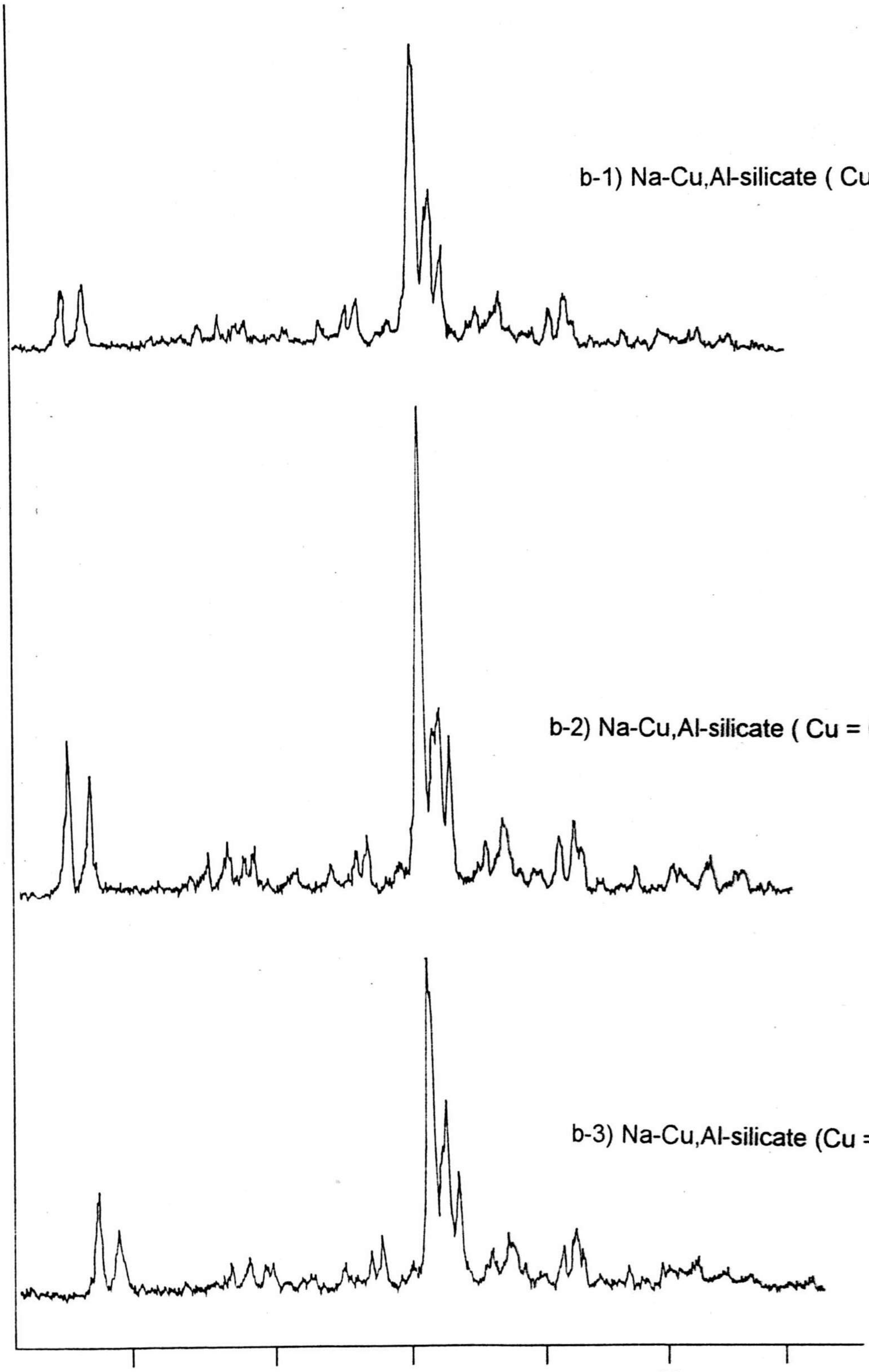

Figure 5.21 continued.

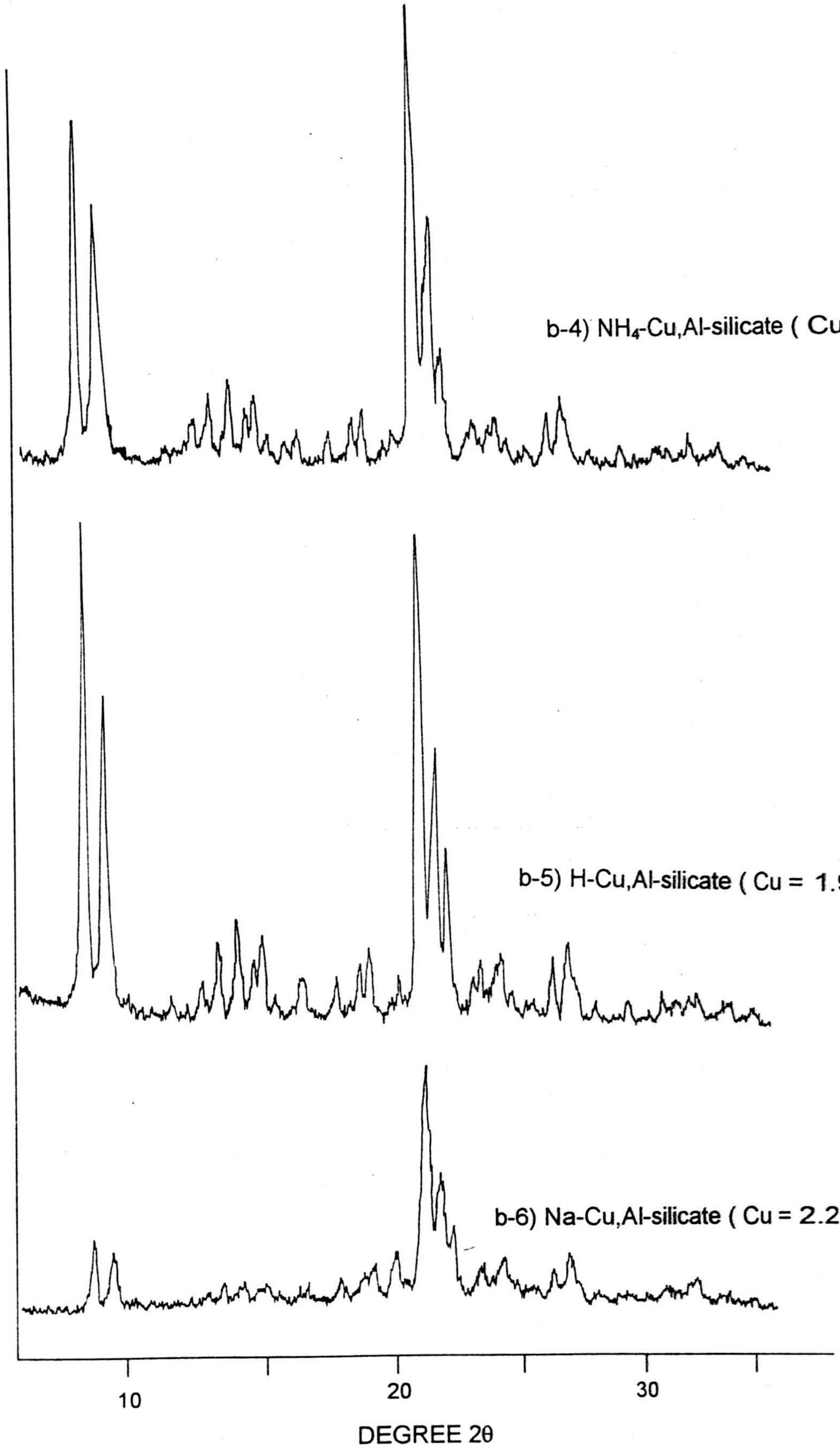

Figure 5.21 continued.

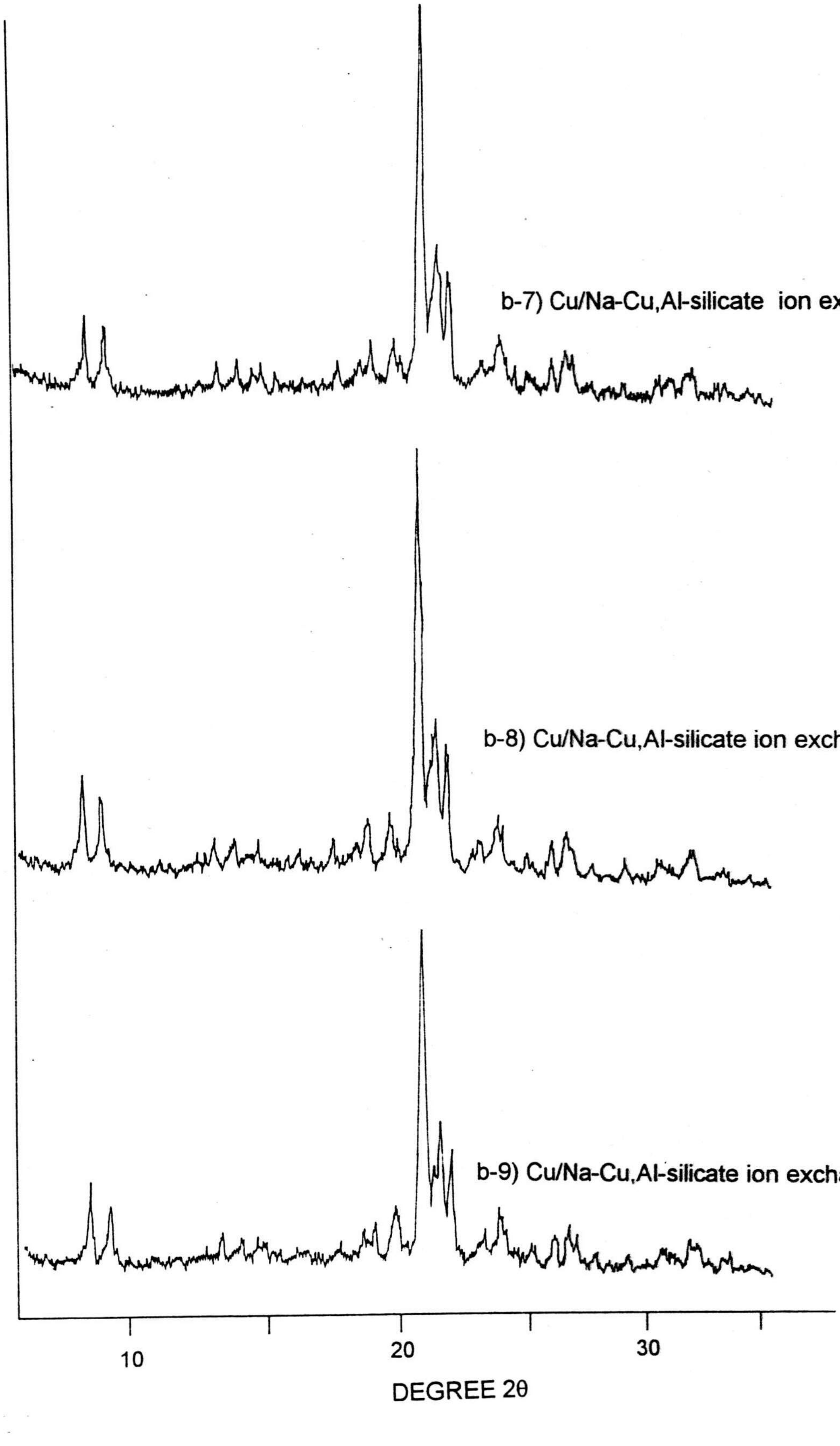

Figure 5.21 continued.

5.6.2 Specific Surface Area and Pore Size Distribution

BET surface areas of the catalysts used in the present work are shown in Figure 5.22. Figure 5.22 illustrated that BET surface areas of Cu,Al-silicate catalysts with various copper content were slightly different. This result indicated that Cu loading can little change BET surface area. However, forms of cation of Cu, Al-silicate greatly affected BET surface area. The orders of BET surface area were as follows; H-Cu,Al-silicate > NH_4-Cu,Al-silicate > Na-Cu,Al-silicate.

Pore size distributions of Cu,Al-silicate with various copper content and different forms of cation are shown in Figures 5.23-5.29. For the effect of Cu loading on Cu,Al-silicate, it was found that when copper content was increased, pore size distribution curve was lower than that of lower copper content, especially in cases of NH_4-form and H-form of Cu,Al-silicate. In addition, pore size distribution curves of Cu,Al-silicate with different forms of cation depicted various height of curves. This results were consistent with the BET surface areas such that the order of the height of pore size distribution curves were as follows; H-form > NH_4-form > Na-form of Cu,Al-silicate. It may be due to the size of cation. H^+ is the smallest cation, thus it has the highest surface areas and pore volume.

It may be concluded that the forms of cation on Cu,Al-silicate greater affects BET surface areas and pore size distribution than that of copper loading on Cu,Al-silicate.

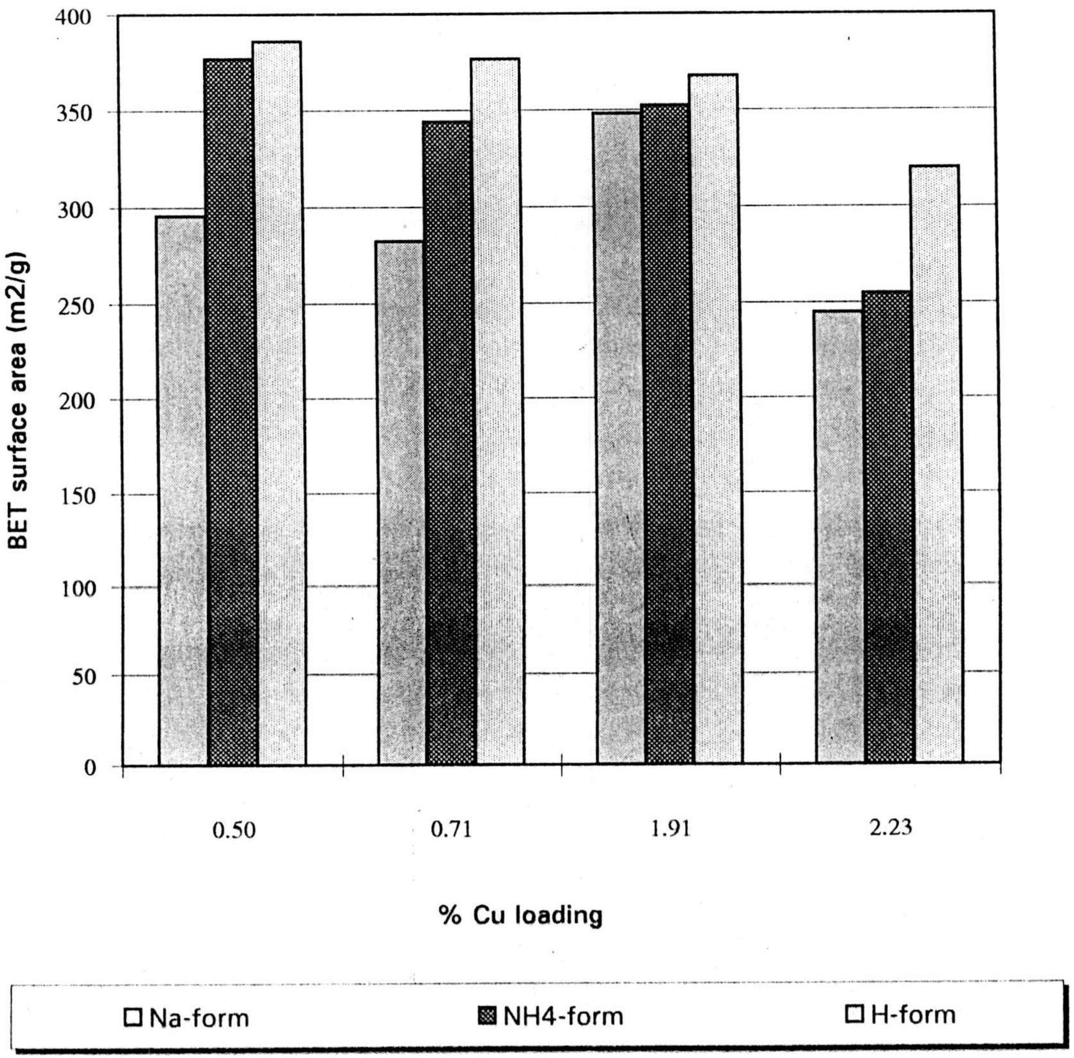

Figure 5.22 BET surface areas of Cu,Al-silicate catalysts.

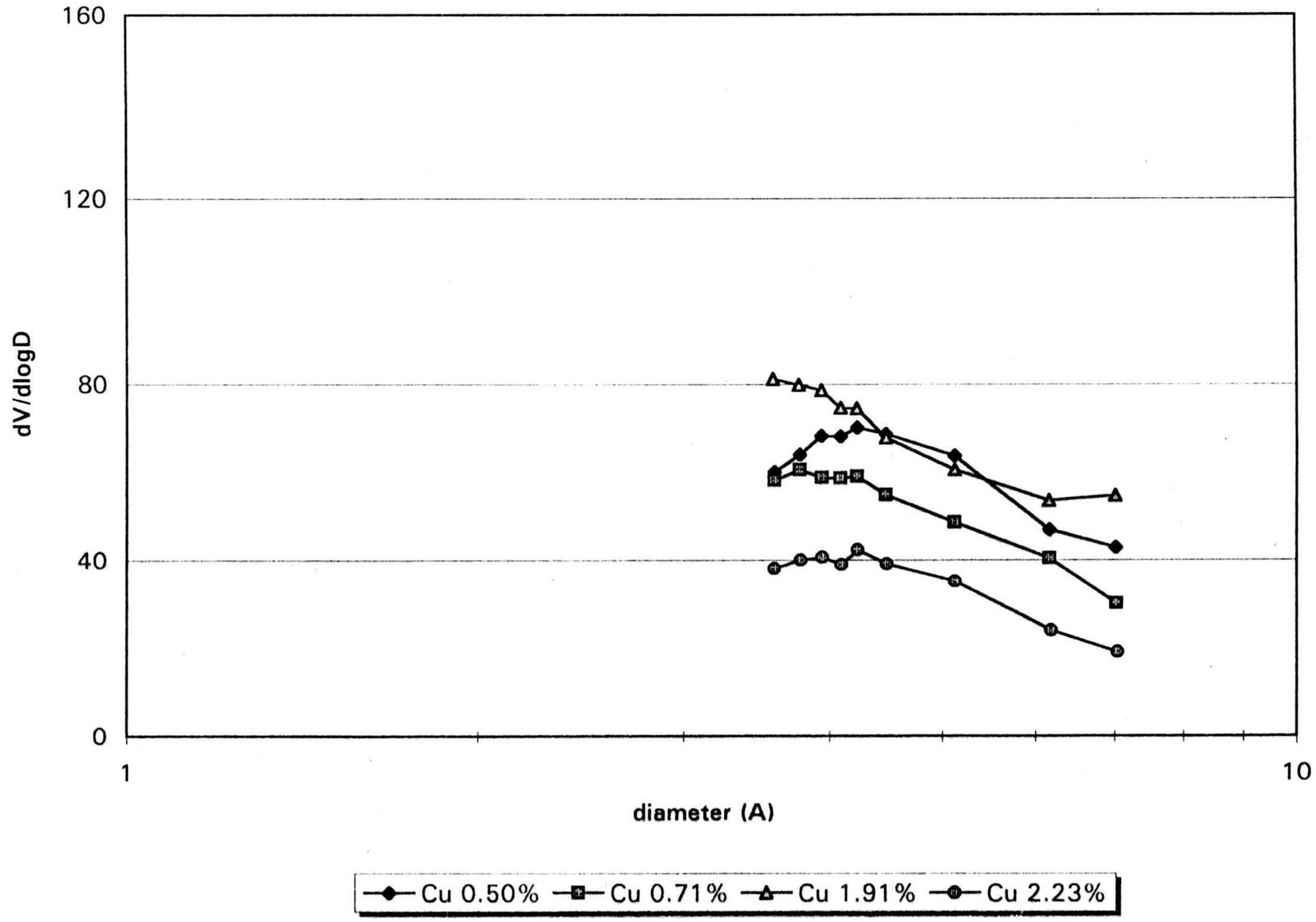

Figure 5.23 Pore size distribution of Na-Cu,Al-silicate with various copper content.

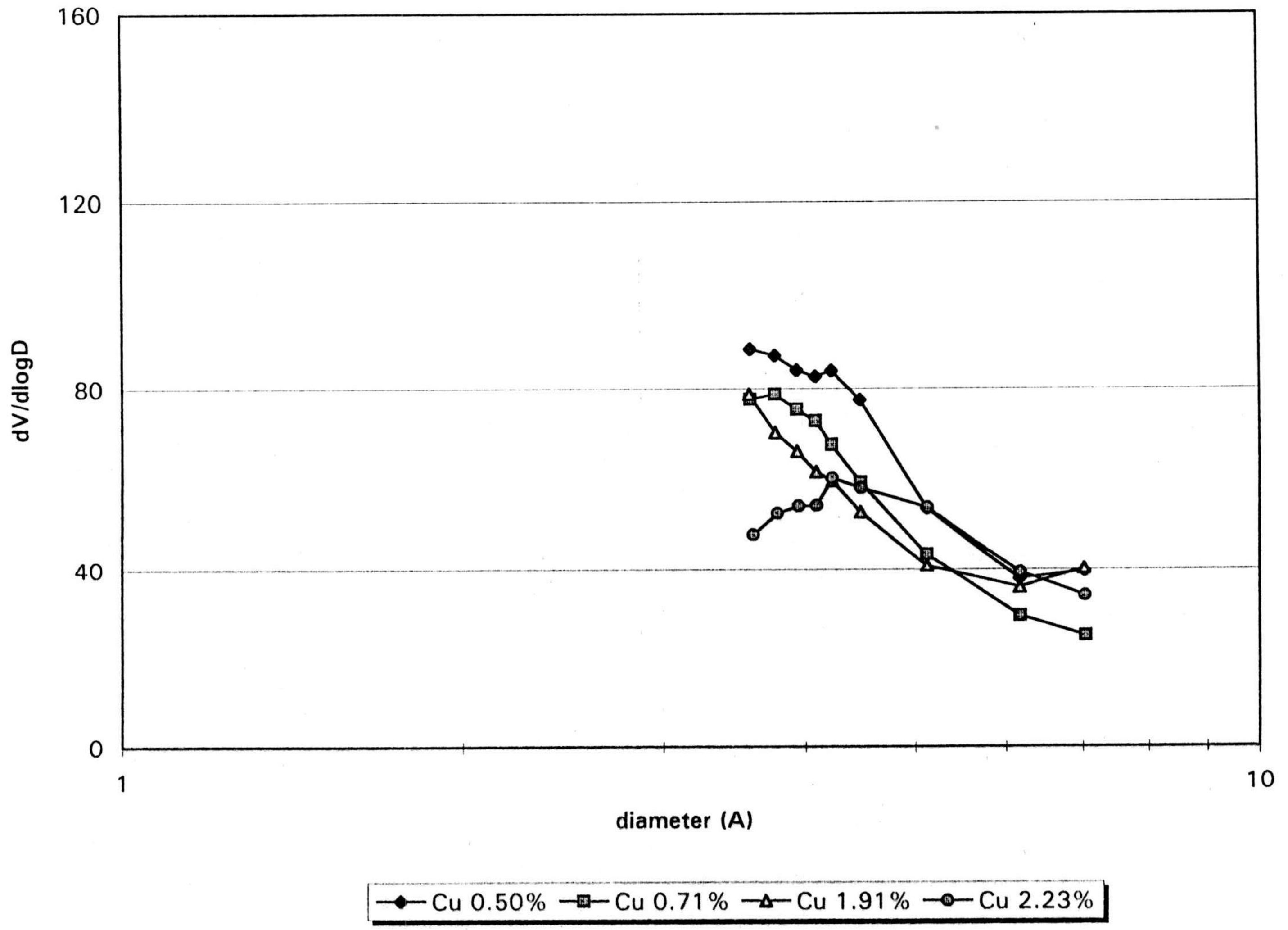

Figure 5.24 Pore size distribution of NH_4-Cu,Al-silicate with various copper content.

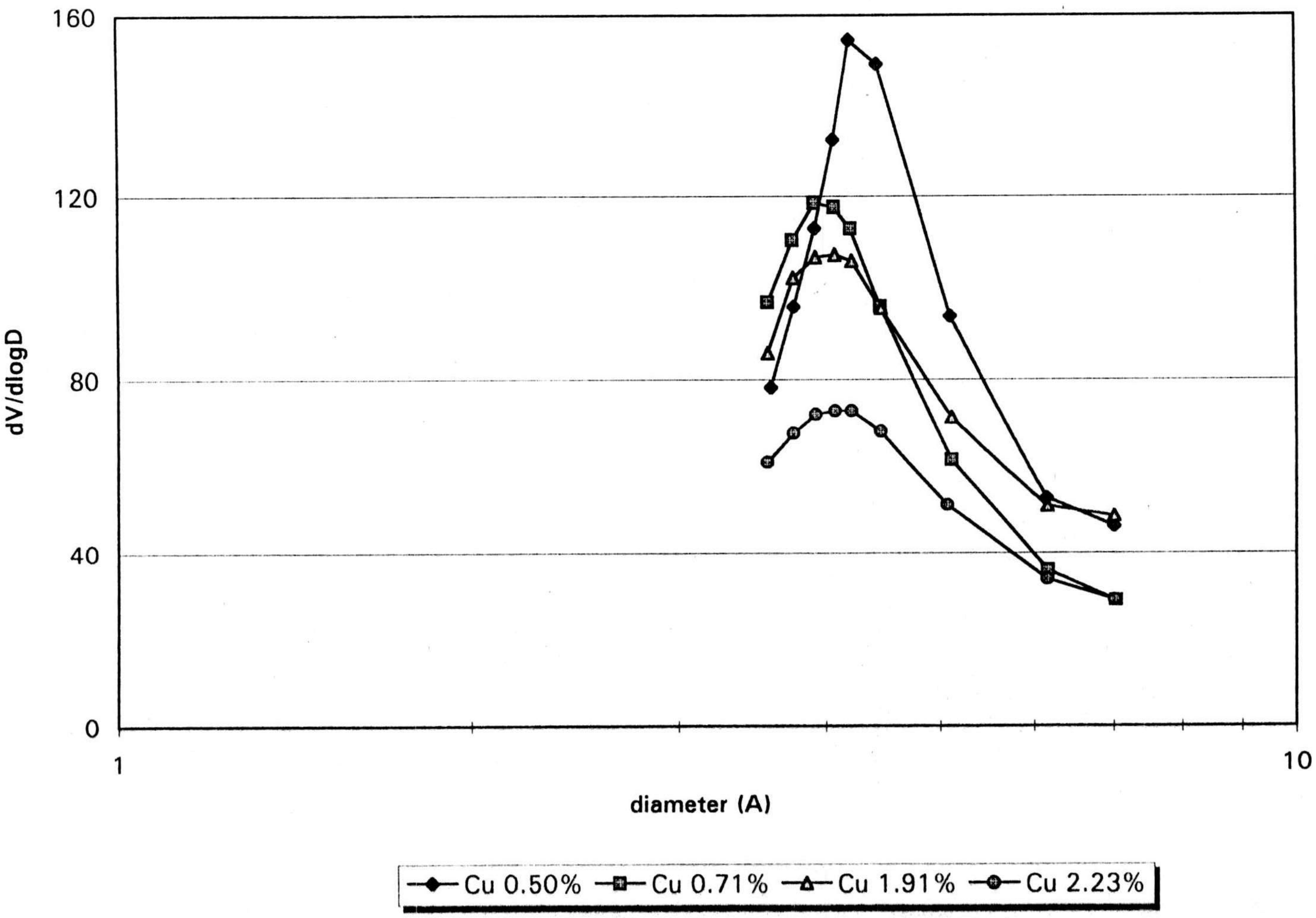

Figure 5.25 Pore size distribution of H-Cu,Al-silicate with various copper content.

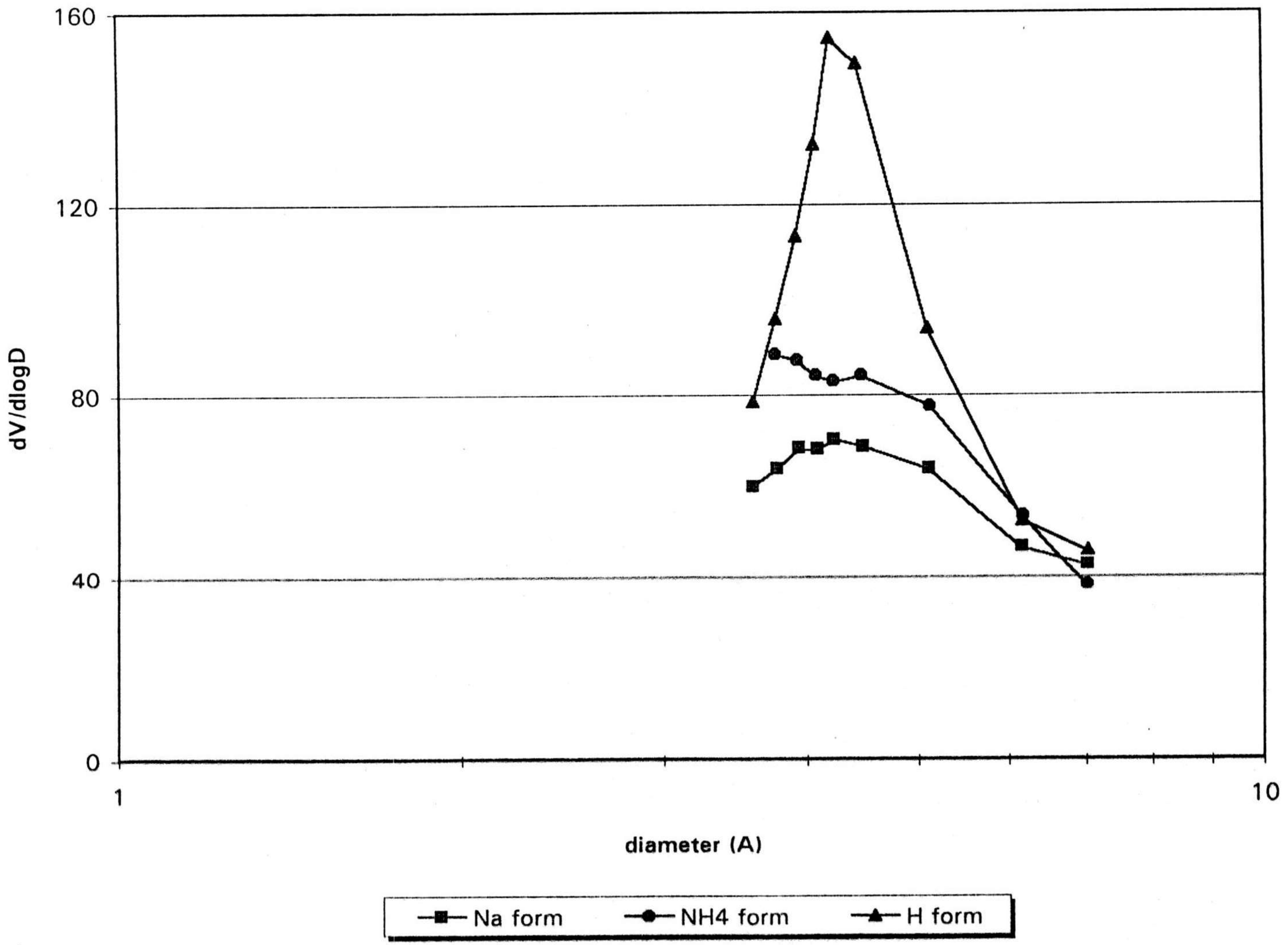

Figure 5.26 Pore size distribution of forms of cation of Cu,Al-silicate (Cu=0.50% wt)

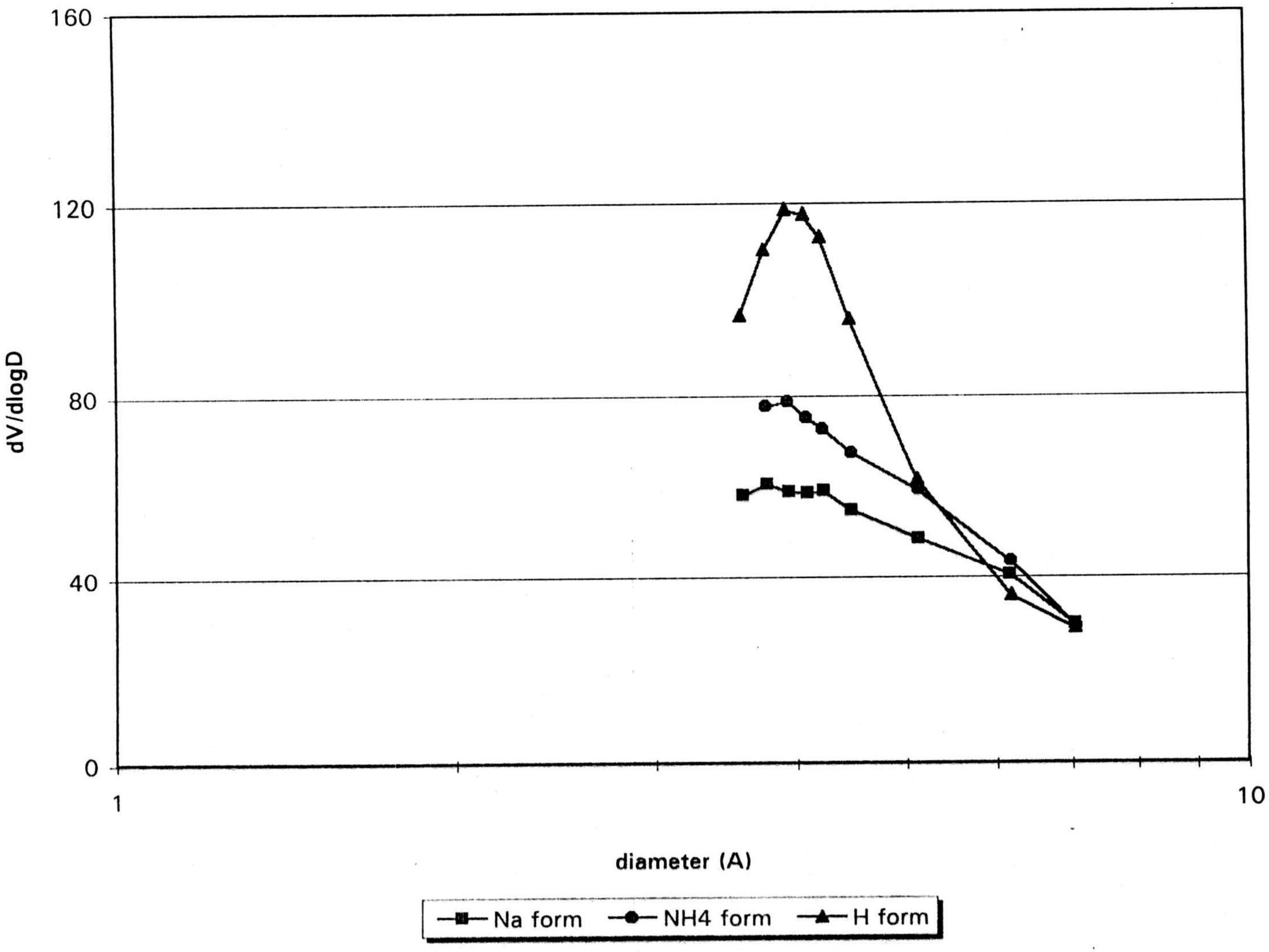

Figure 5.27 Pore size distribution of forms of cation of Cu,Al-silicate (Cu=0.71% wt)

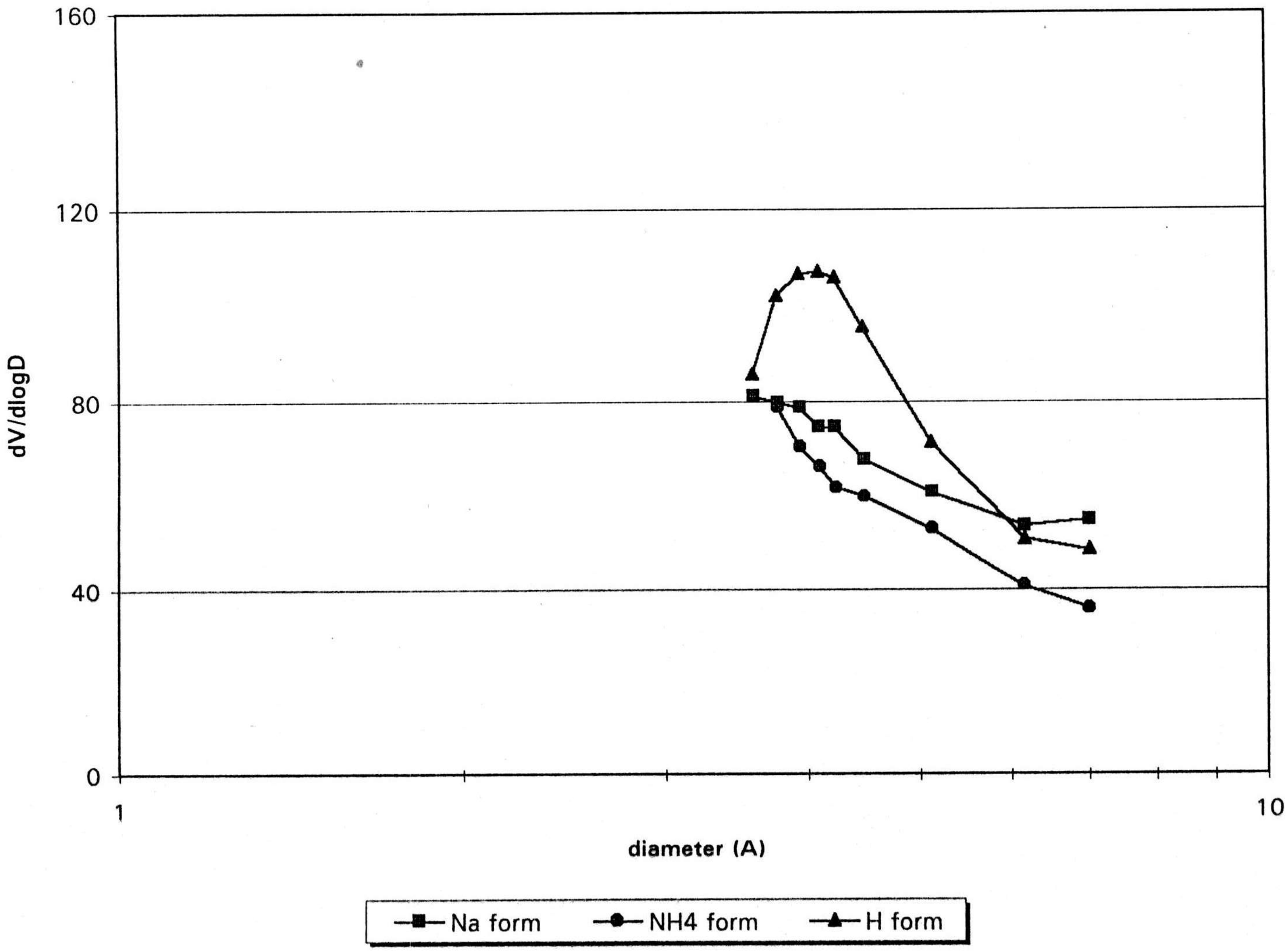

Figure 5.28 Pore size distribution of forms of cation of Cu,Al-silicate (Cu=1.91% wt)

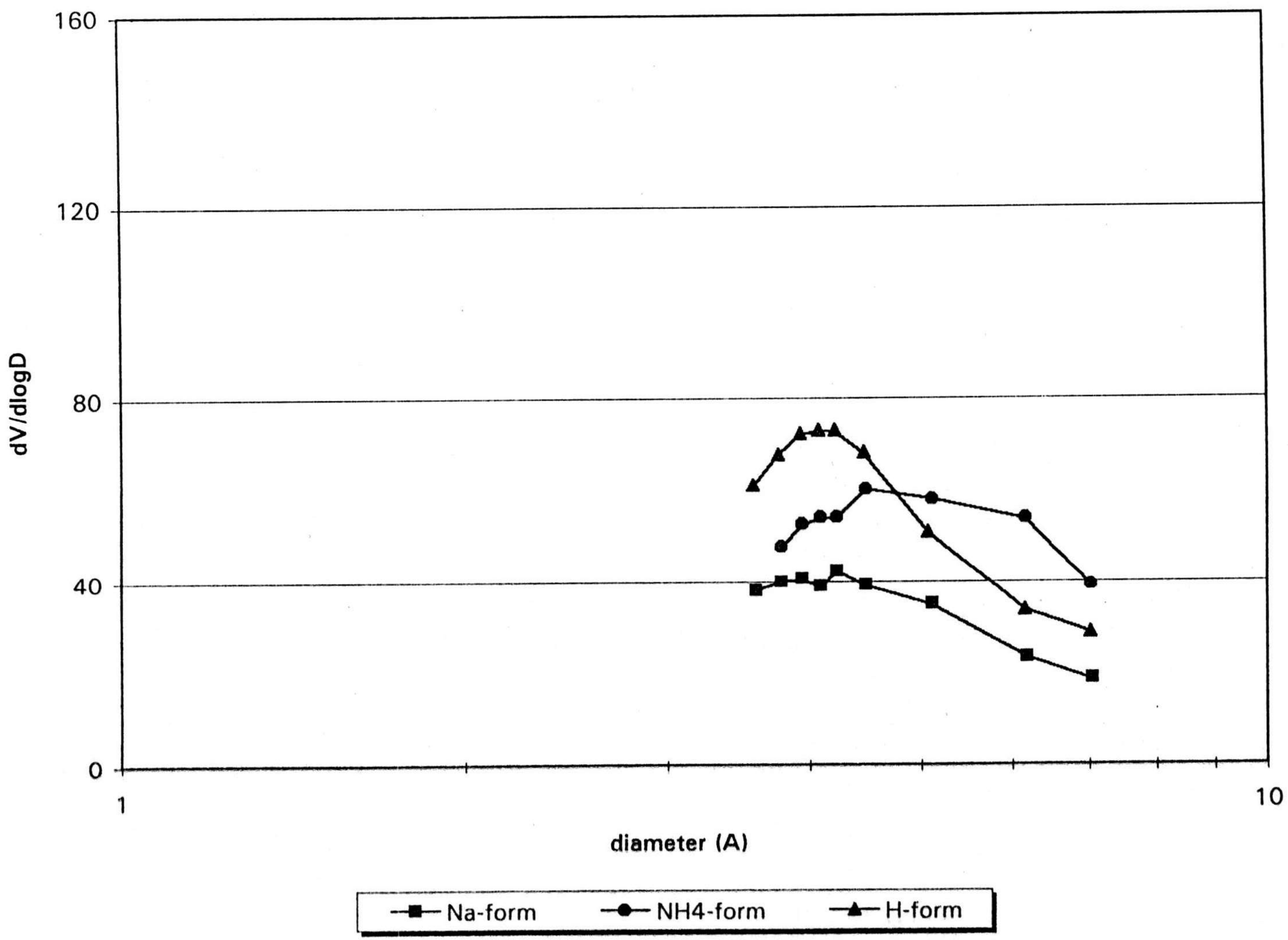

Figure 5.29 Pore size distribution of forms of cation of Cu,Al-silicate (Cu=2.23% wt)