

CHAPTER IX
THE PERFORMANCE AND STABILITY OF
Cu ION-EXCHANGED Co-SILICATE FOR NITRIC OXIDE REMOVAL UNDER
HIGH THERMAL-TREATMENT

9.1 Introduction

As a result of the promotion of acid rain and urban smog formation which is a serious environmental problem, nitric oxide elimination has been studied so far. It is well known that nitric oxide can be reduced to nitrogen by the addition of a low concentration of hydrocarbon in the presence of oxygen.[1, 30, 132]. Regarding catalysts appropriate for nitric oxide removal, microporous crystalline catalysts such as zeolite have been extensively used. Metal ion exchanged zeolite was one of catalysts applied for nitric oxide elimination. Among of ion exchanged zeolites, copper ion exchanged MFI zeolite (Cu/MFI) is an suitable one for removal of nitric oxide in the presence of oxygen [9, 10]. Many researchers suggested that isolated copper species in the catalyst are active for nitric oxide removal [44, 57]. On the other hand, Co exchanged zeolites are reported as catalysts having hydrothermal stability [21, 82, 135]. However, according to its parent zeolite, such as thermal stability, the framework of MFI type zeolite can be easily sintered by high thermal condition and the coexistence of water vapor [44,-47]. Accordingly, metal ion exchanged MFI zeolites are limited for nitric oxide removal in practical use occupied by a wide range of temperature especially in high severe thermal condition. On the other hand, substitution of metals for Al in MFI structure zeolite is of great importance to exhibit higher thermal resistance. It can avoid the dislocation of alumina in the framework which was a cause of deactivation of MFI type zeolites under high severe condition [46, 136]. Inui et al. [48, 49, 137] proposed protonated cobalt incorporated silicate having MFI structure (H-Co-silicate) to be a powerful catalyst which can against the deterioration under severe condition at high temperature with water vapor. However, due to the difficulty of incorporating of cobalt into the framework, the activity on NO removal of H-Co-silicate is not too considerable. As a reason above, this chapter concerns about the activity on nitric oxide removal of copper ion exchanged cobalt incorporated silicate having MFI type structure (Cu/Co-silicate). Furthermore, the

activity on nitric oxide removal of H-Co-silicate and Cu/MFI were also compared. This study also concerns the stability of catalysts under high severe condition. Since it was found that the pretreatment is effective for nitric oxide removal of H-Co-silicate especially at the pretreatment temperature at 1,000°C [117, 138]. Therefore, the activity of catalysts pretreated at thermal-treatment condition of 1,000°C were investigated as well.

9.2 Experimental

9.2.1 Catalyst preparation

As-synthesized crystals were prepared by the rapid crystallization method [97]. For copper ion-exchanged MFI (Cu/MFI), the charge Si/Al atomic ratio was set at 50. Then, they were washed, dried over night, and heated at 540°C for 3.5 h in an air stream. They were subsequently ion-exchanged with an NH_4NO_3 aqueous solution and calcined at 540°C for 3.5 h in air. The obtained crystallites were designated as MFI materials. Loading of Cu on MFI zeolite was carried out twice by ion-exchange method at 80°C overnight using copper acetate as source. On the other hand, MFI zeolite whose Al content was substituted by Co, Co incorporated MFI zeolite, synthesized by the rapid crystallization method as same as Cu/MFI was supported by Prof. Inui's laboratory. The charge atomic ratio of Si/Co was set at 20. It was followed by the same procedure as mentioned above and designated as H-Co-silicate. Additionally, to accomplish copper ion-exchanged cobalt incorporated MFI zeolite (Cu/Co-silicate), Co incorporated MFI zeolite was ion-exchanged twice by copper acetate solution at 80°C overnight. It was washed, dried, and heated as mentioned above afterwards. On the other hand, some amount of MFI and Co incorporated MFI zeolite catalyst were pretreated at 1,000°C. Then, ion-exchange method using copper acetate was carried out 2 times in the same method. This step is to protect the transformation of copper species by thermal-treatment.

9.2.2 Thermal-treatment condition

To investigate the stability and activity of catalysts, catalysts were pretreated at high temperature. From ref. 138, it was summarized that H/Co-silicate has high optimum activity after thermal-treatment at 1,000°C. Therefore, catalysts were also pretreated at

1,000°C in the atmosphere of He in this study. First, catalysts were heated using a heating rate of 10°C/min from room temperature to 600°C and 1.67°C/min from 600°C to 1,000°C. When the temperature reached at 1,000°C, the catalysts were kept constant at that temperature for 30 min and cooled down to room temperature.

9.2.3 Reaction test

The catalytic activity was carried out using an ordinary flow microreactor under the atmospheric pressure. The catalyst powder was tabletted, crushed, and then sieved into 12-22 mesh to avoid the pressure drop. The catalyst was heated up in a He stream to 600°C with the heating rate of 10°C/min and maintained at that temperature for 30 min. Then, a feed gas composed of 1,000 ppm NO, 1,000 ppm n-C₈H₁₈, 2mol% O₂, 10mol% H₂O balanced with He was introduced with a GHSV of 30,000 h⁻¹. The reactants and products were analyzed by gas chromatographs (Chrompack, Micro GC CP 2000 with MS-5A and porapak Q column) 10 min after introducing feed gas. The reaction test was undertaken every 50°C with diminishing from 600°C to 200°C and followed by the same procedure mentioned above. The catalytic activity for nitric oxide reduction and n-octane combustion were investigated as the amount of N₂ and carbon oxides (CO_x; CO₂+CO) produced, respectively.

9.2.4 Characterization

X-ray diffraction patterns recorded by an X-ray refractometer, Shimadzu XD-D1, with Ni-filtered CuK α radiation were analyzed. Inductively Coupled Plasma analysis (ICP SHIMADZU ICPS-1000 II) and Shimadzu Flow Sorb II 2300 using liquid nitrogen as a probe molecule, respectively measured the bulk composition and BET surface area of sample. IR spectra of self - supporting wafer made of mixture of KBr and sample were also recorded by Nicolet model Impact 400 to study MFI crystallinity of the catalyst. To investigate the surface morphology of catalysts, Scanning Electron Microscope Model JSM-6400 was operated. ²⁹Si MAS NMR analysis was adopted using JEOL 270 SGX. UV-visible spectra were also analyzed by Shimadzu MPS-2000 spectrometer installed with a multi-purpose reflectometry attachment, RTA-2000 using BaSO₄ as a reflectance standard. Moreover, the X - band spectra characteristic of Cu²⁺ were recorded at liquid nitrogen temperature with a JEOL model JES-RE 2X

spectrometer equipped with a JEOL microwave power 0.1 mW. For ESR measurement, an exact weight of catalyst was calcined at 500°C for 2 h to remove adsorb species.

9.3 Results and discussion

9.3.1 Influence of high thermal-treatment on NO and n-octane conversions

To compare the activity of catalysts easily, NO and n-octane conversions of 200%Cu/MFI, Cu/Co-silicate and H-Co-silicate are illustrated in Figures 9.1a, 9.1b, and 9.1c, respectively. It can be shown that without pretreatment, 200%Cu/MFI exhibits highest activity for conversion of NO to N₂. Nevertheless, 200%Cu/MFI pretreated at 1,000°C significantly loses the activity for both NO and n-octane conversions. The effect of high thermal-treatment deactivating the catalytic performance of 200%Cu/MFI was already discussed before. In contrast, the activities for NO conversion of Cu/Co-silicate and H/Co-silicate are higher than those without pretreatment. Kagawa et al. and Dangsawai et al. [117, 138] found the similar trend of the catalytic activity of H/Co-silicate enhanced by high temperature pretreatment. Cu/Co-silicate promotes higher conversion of NO to N₂ than H-Co-silicate enormously in the condition of without pretreatment. However, the activity for NO conversion of Cu/Co-silicate pretreated at 1,000°C over the whole range of reaction temperature is not different significantly from that of H-Co-silicate pretreated at 1,000°C. The advantage is that Cu/Co-silicate pretreated at 1,000°C exhibits NO conversion at lower temperature than H-Co-silicate pretreated at 1,000°C. The optimum reaction temperature of Cu/Co-silicate pretreated at 1,000°C lower by 50°C relative to that of H-Co-silicate pretreated at 1,000°C. In order to clarify the effect of high thermal-treatment condition on the catalyst, the characterizations in both physical and chemical were carried out.

9.3.2 Characterization of Cu/Co-silicate and compared catalysts with and without thermal-treatment

9.3.2.1 Physical characterizations of catalysts

Table 9.1 shows the physical data of catalysts including the crystallinity, bulk composition and surface area of catalysts. Now we also study the crystallinity of catalysts by IR method. The crystallinity of zeolite can be considered as the relative ratio of IR band at 550 to 450 cm⁻¹ (I_{550}/I_{450}). IR band at 550 cm⁻¹ is typical of the vibration of 5-membered oxygen rings and that at 450 cm⁻¹ is typical of the internal vibration of TO₄

Fig.5.19a 200%Cu/MFI

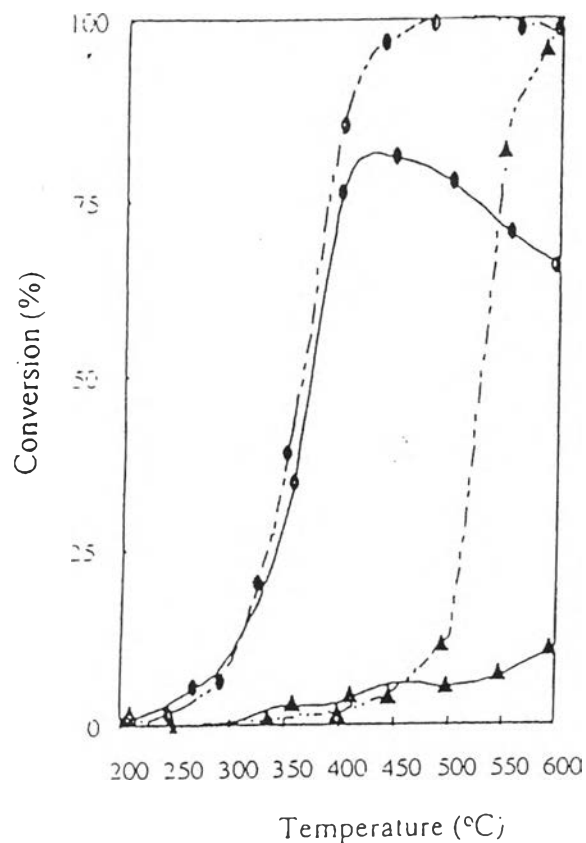


Fig.5.19b Cu/Co-silicate

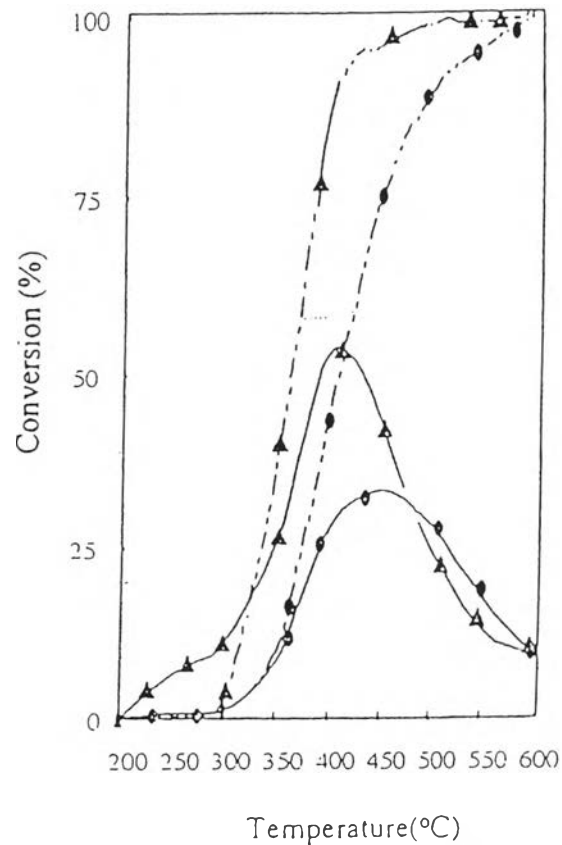


Fig.5.19c H-Co-silicate

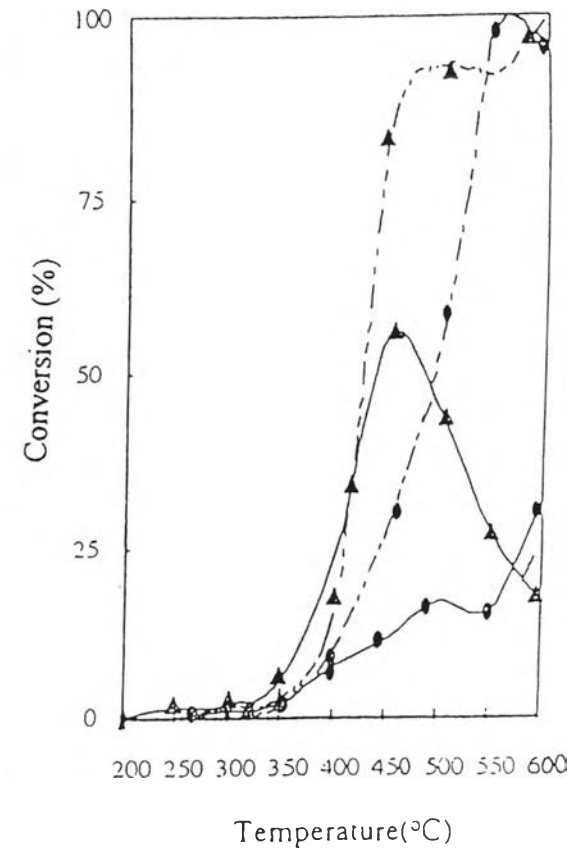


Figure 9.1 NO and n-octane conversions of 200%Cu/MFI, Cu/Co-silicate and H-Co-silicate with and without pretreatment at 1,000°C. Symbols: darkened line: NO conversion to N_2 (%), dotted line: n-octane conversion to $CO_x(CO_2+CO)$ (%); circle symbol: without pretreatment; triangle symbol: with pretreatment at 1,000°C. Feed gas: NO 1,000 ppm, n- C_8H_{18} 1,000 ppm, O_2 2%, H_2O 10%, He balance, GHSV 30,000 h^{-1}

units [49, 117]. XRD and I_{550}/I_{450} values of all catalysts without pretreatment showed high crystallinity. After thermal-treatment at 1,000°C, the frameworks of Cu/Co-silicate and H-Co-silicate are gradually changed while that of framework of 200%Cu/MFI is damaged remarkably. The data from BET method also confirm high stability of surface area of Cu/Co-silicate and H-Co-silicate in contrast with 200%Cu/MFI. Therefore, it can be summarized that metallosilicate catalyst can resist the deactivation better than metal ion-exchanged catalyst also supported by Inui [110]. For bulk composition data by ICP method, it was shown that the amount copper and cobalt in the catalysts without pretreatment are not different enormously from those in the catalysts with thermal-treatment. It can be concluded that there is no loss of metal species such as evaporation of metal due to high thermal-treatment.

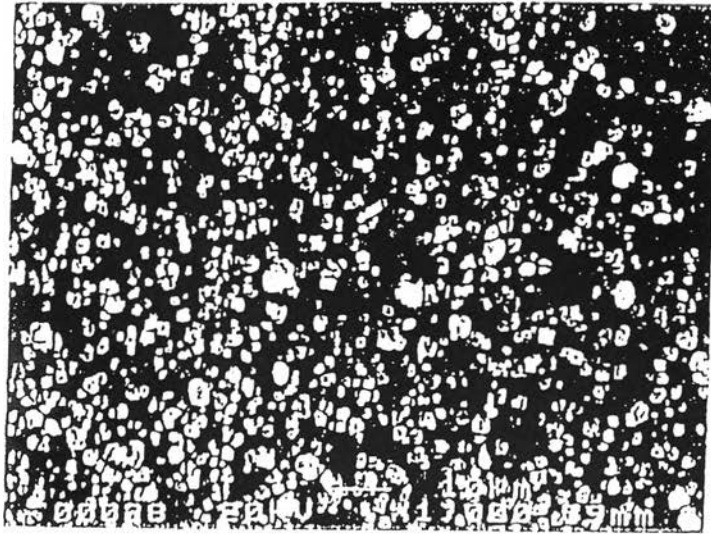
9.3.2.2 Techniques for characterization of Cu/Co-silicates

Scanning electron micrographs of catalysts are shown in Figures 9.2, 9.3, and 9.4 for 200%Cu/MFIs, Cu/Co-silicates, and H-Co-silicates, respectively. Crystallite distributions of Cu/Co-silicate with and without thermal-treatment at 1,000°C are similar. As for 200%Cu/MFI, the pretreated one showed less well-dispersed crystallite morphology than the other without pretreatment did. And the crystallite morphology in both shape and size of some parts of 200%Cu/MFI pretreated at 1,000°C are destroyed. For the characterizations of both 200%Cu/MFI and H-Co-silicate with and without thermal-treatment at 1,000°C, we already discussed as mentioned above. Moreover, for Cu/Co-silicates the state of Cu and Co species was studied by ESR method. As shown in Figures 9.5 and 9.6 demonstrate ESR spectra of the catalysts with and without thermal-treatment at 1,000°C. High spin Co^{2+} species can be detected at g factor around 5.8 [88, 120, 121] and Cu^{2+} species are also observed at about the range of 2,000-3,000 G [126, 127]. ESR features characteristic of high spin Co^{2+} of H-Co-silicate resembles to that of Cu/Co-silicate. As compared with both Cu/Co-silicate and H-Co-silicate without pretreatment, the intensities of high spin Co^{2+} spectra of both catalysts with thermal-treatment at 1,000°C decrease although there are the remnants. Furthermore, the signal of high spin Co^{2+} spectra of both pretreated catalysts became broadened relative to both same catalyst without pretreatment. These ESR spectra of H-Co-silicates were already discussed above. By using the results as illustrated above, it can be suggested that

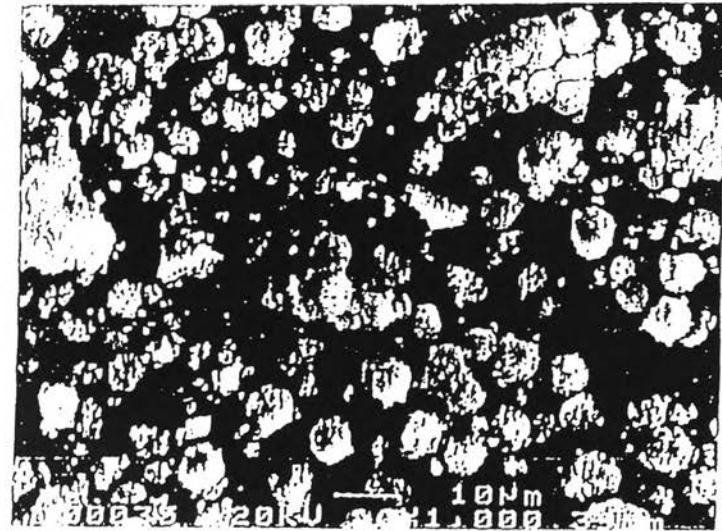
Table 9.1 Data for bulk compositions, BET surface area and crystallinity of 200%Cu/MFI, H-Co-silicate and Cu/Co-silicate with and without thermal-treatment at 1,000°C

Catalyst	Pretreatment condition (°C)	Content of metal		BET surface area (m ² /g)	Crystallinity ^a (%)	I ₅₅₀ /I ₄₅₀ ratio
		Si/Co	Si/Cu			
200%Cu/MFI	without pretreatment	-	51	360	100	0.80
	1,000	-	56	120	32	0.61
H-Co-silicate	without pretreatment	257	-	350	98	0.77
	1,000	258	-	400	92	0.76
Cu/Co-silicate	without pretreatment	258	236	390	100	0.80
	1,000	258	291	410	90	0.78

^a Intensities are referenced to diffraction line at 23.5° 2θ

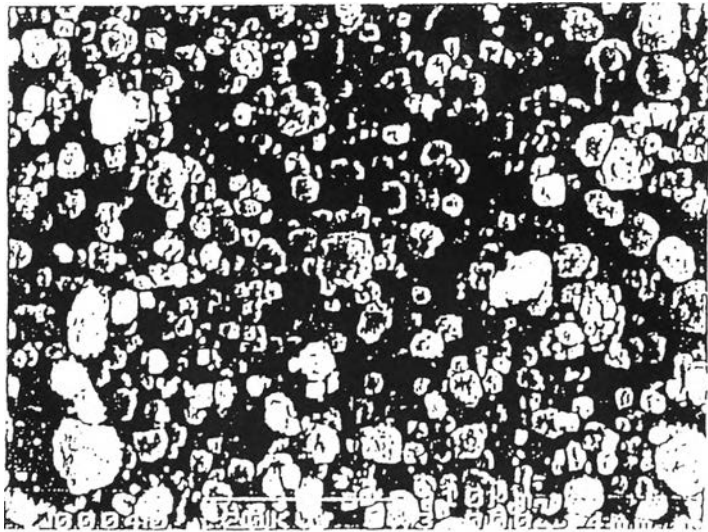


a)

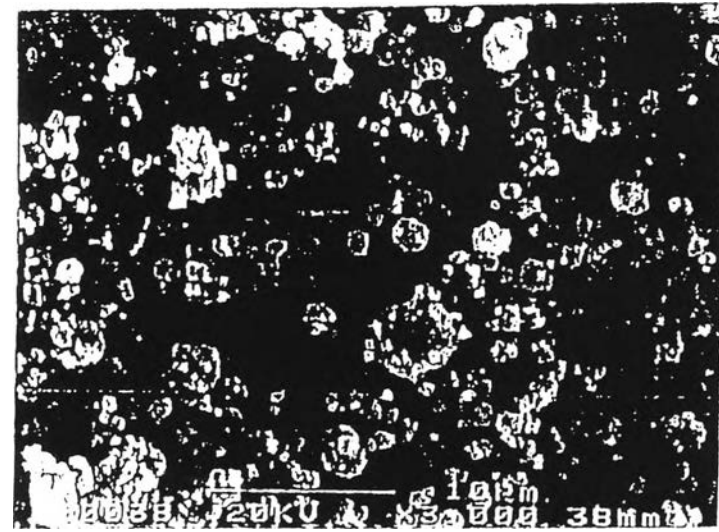


b)

Figure 9.2 Scanning electron micrographs of 200%Cu/MFI
a) without pretreatment, with pretreatment at 1,000°C

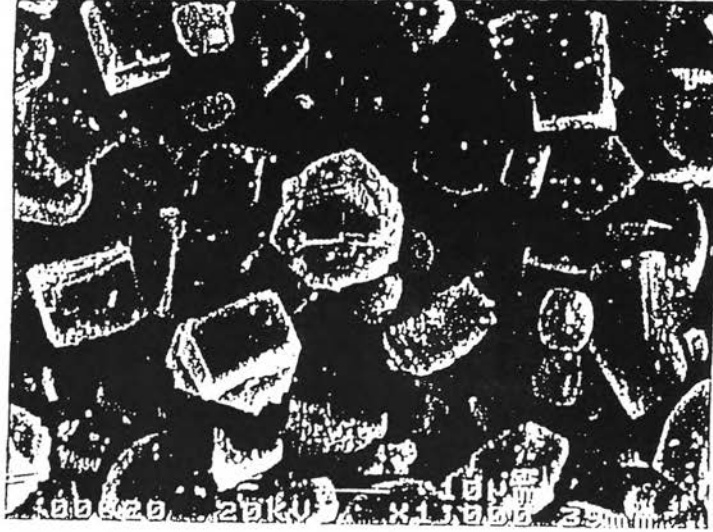


c)

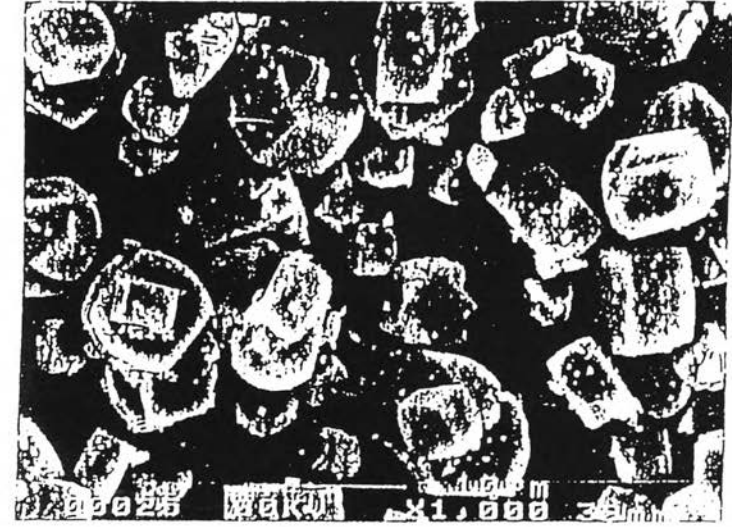


d)

Figure 9.3 Scanning electron micrographs of Cu/Co-silicate
c) without pretreatment, d) with pretreatment at 1,000°C



e)



f)

Figure 9.4 Scanning electron micrographs of H-Co-silicate
e) without pretreatment, f) with pretreatment at 1,000°C

thermal-treatment at 1,000°C causes migration of some parts of cobalt in the framework to the external sites. As for characterization of Cu^{2+} species, ESR spectra of 200%Cu/MFI and Cu/Co-silicate with and without thermal-treatment were investigated and depicted in Figure 9.6. Relative to Cu^{2+} spectra of both 200%Cu/MFI and Cu/Co-silicate without pretreatment, ESR spectra representative of Cu^{2+} species of both pretreated catalysts diminish and become broaden. For 200%Cu/MFI, thermal-treatment at 1000°C was carried out after ion exchange by copper source. It can be suggested that not only the loss of framework crystallinity occurred as mentioned before, but the loss of active Cu^{2+} species also happened for 200%Cu/MFI pretreated at 1,000°C. On the other hand, for Cu/Co-silicate, ion exchange by copper source was performed after thermal-treatment at 1,000°C of H-Co-silicate in order to avoid the loss of Cu^{2+} sites by pretreatment. Nevertheless, the intensity of ESR spectra indicative of Cu^{2+} of Cu/Co-silicate pretreated at 1,000°C is lower than that of Cu/Co-silicate. This can be suggested that the pretreatment at 1,000°C has some effects on the state of copper loaded. It can be implied that the amount of Cu^{2+} existed on Cu/Co-silicate pretreated at 1,000°C was less than that located on Cu/Co-silicate without pretreatment. The results indicate that the activity of Cu/Co-silicate pretreated at 1,000°C is mainly caused by cobalt species including parts of cobalt excluded from the framework. It may be possible that the large amount of Cu introduced on pretreated H-Co-silicate is the Cu^{1+} species which not promoting effective nitric oxide conversion in SCR reaction.

To clarify the suggestion, NO decomposition was also studied on the catalyst. Figure 9.7 shows NO conversion to N_2 for NO decomposition of Cu/Co-silicates. It was shown that Cu/Co-silicate pretreated at 1,000°C provides high decomposition of NO than Cu/Co-silicate without pretreatment. From the study of Iwamoto et al. [9, 10], they found that the Cu^{+1} species are active for NO decomposition. From these results, it can be implied that the large amount of Cu on pretreated H-Co-silicate is Cu^{+1} .

9.3.3 The stability of catalysts for NO conversion against 10mol% H_2O at the reaction temperature of 400°C

Figure 9.8 shows the stability of 200%Cu/MFI, Cu/Co-silicate and H-Co-silicate at the reaction temperature of 400°C, the optimum temperature for conversion of NO to

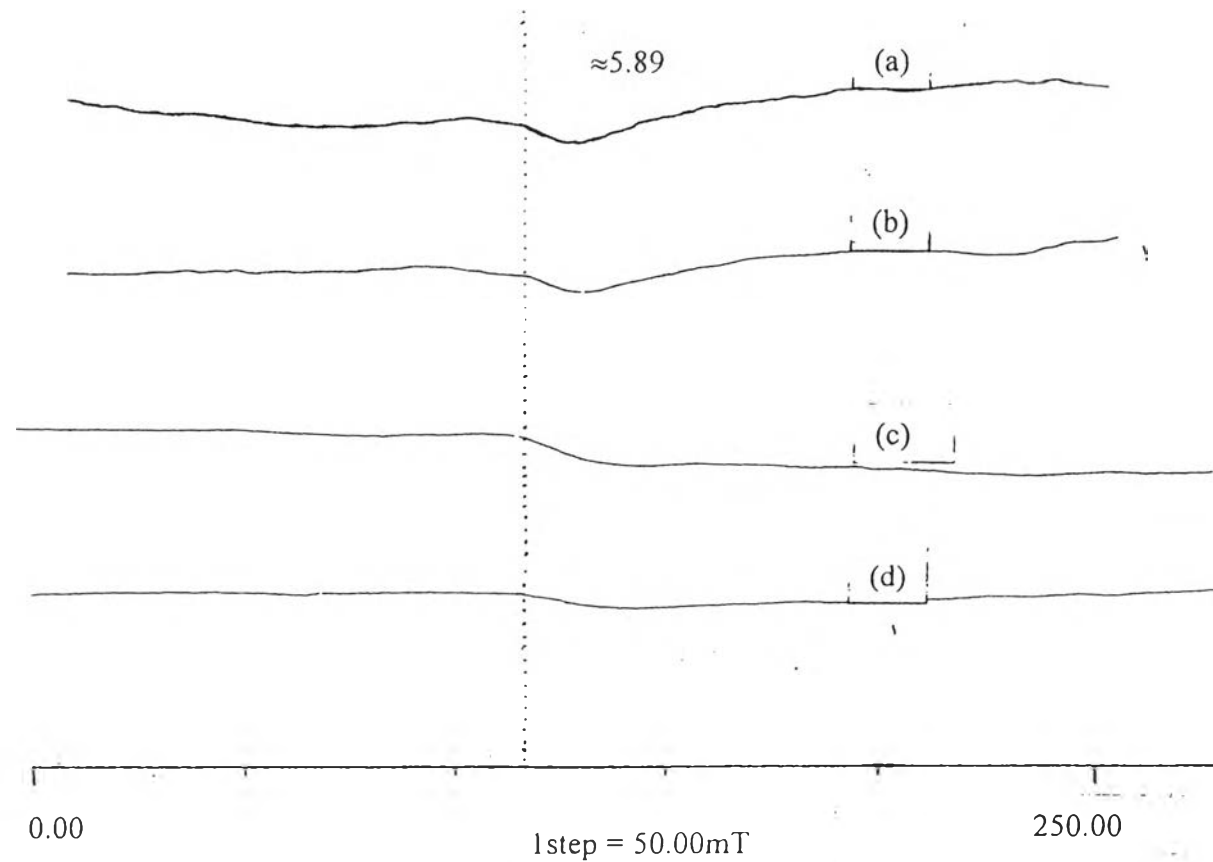


Figure 9.5 ESR spectra of high spin Co^{2+} of H-Co-silicate and Cu/Co-silicate with and without pretreatment at $1,000^\circ\text{C}$. a) H-Co-silicate without pretreatment; b) H-Co-silicate pretreated at $1,000^\circ\text{C}$, c) Cu/Co-silicate without pretreatment, d) Cu/Co-silicate pretreated at $1,000^\circ\text{C}$

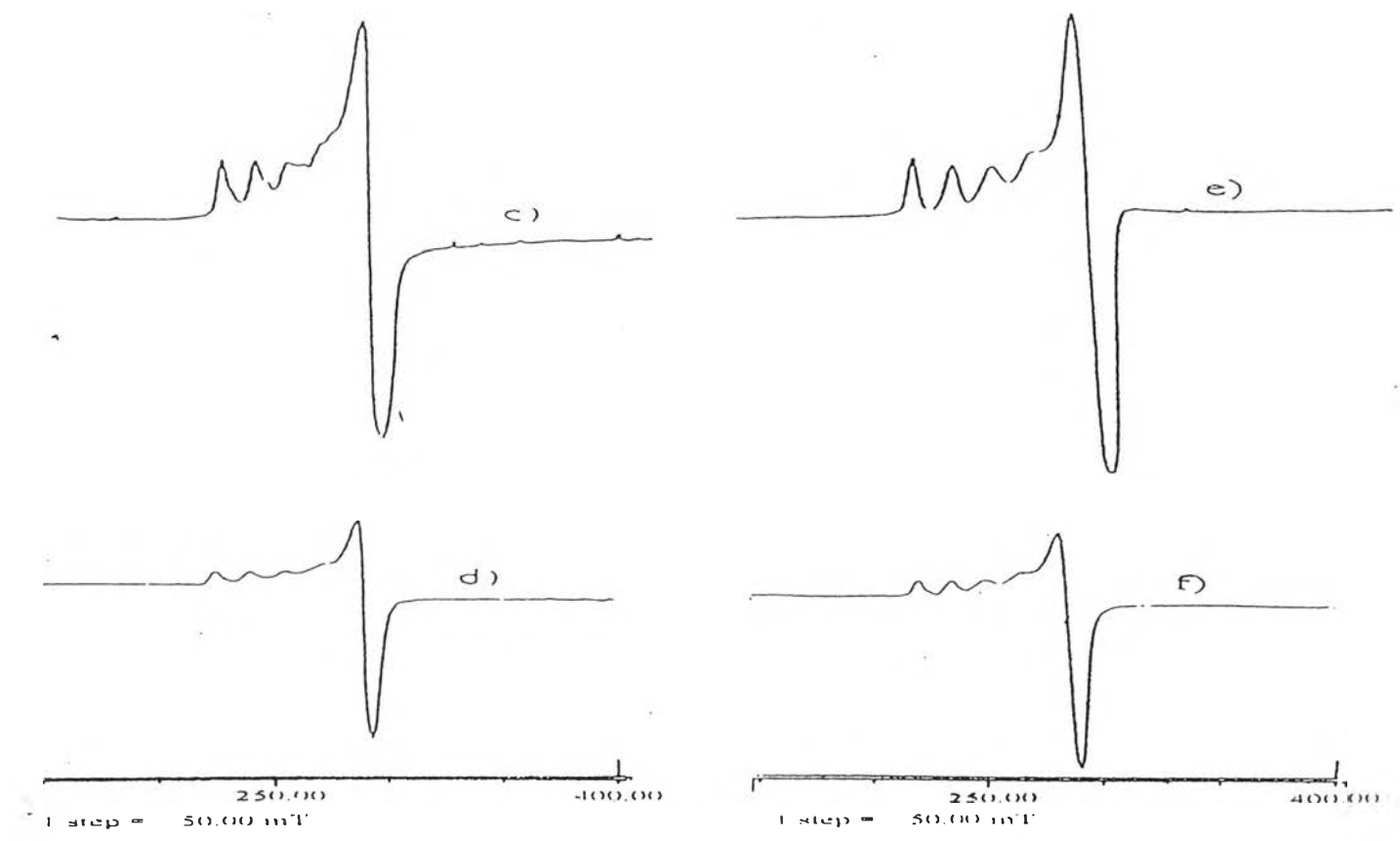


Figure 9.6 ESR spectra of high spin Cu^{2+} of Cu/Co-silicate and 200%Cu/MFI with and without pretreatment at 1,000°C. c) Cu/Co-silicate without pretreatment, d) Cu/Co-silicate pretreated at 1,000°C e) 200%Cu/MFI without pretreatment, f) 200%Cu/MFI pretreated at 1,000°C

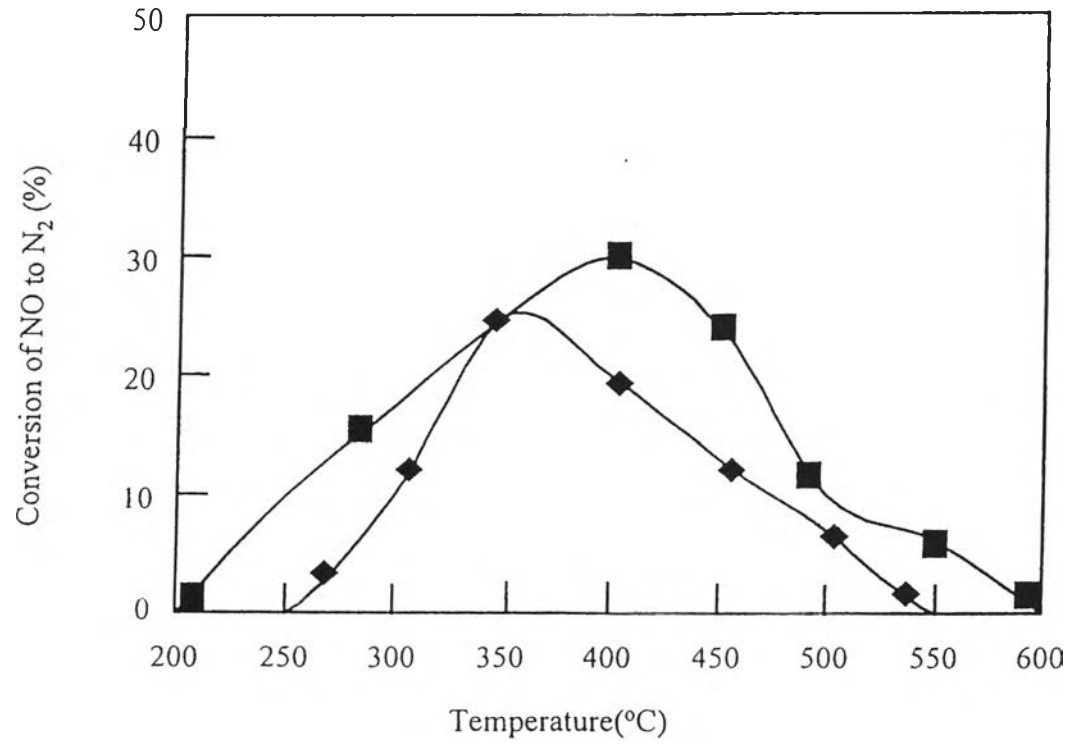


Figure 9.7 NO decomposition of Cu/Co-silicate with and without pretreatment at 1,000°C
Symbol: ◆ Cu/Co-silicate without pretreatment, ■ Cu/Co-silicate pretreated at 1,000°C
Feed gas: NO 1,000 ppm, He balance, GHSV 30,000 h⁻¹

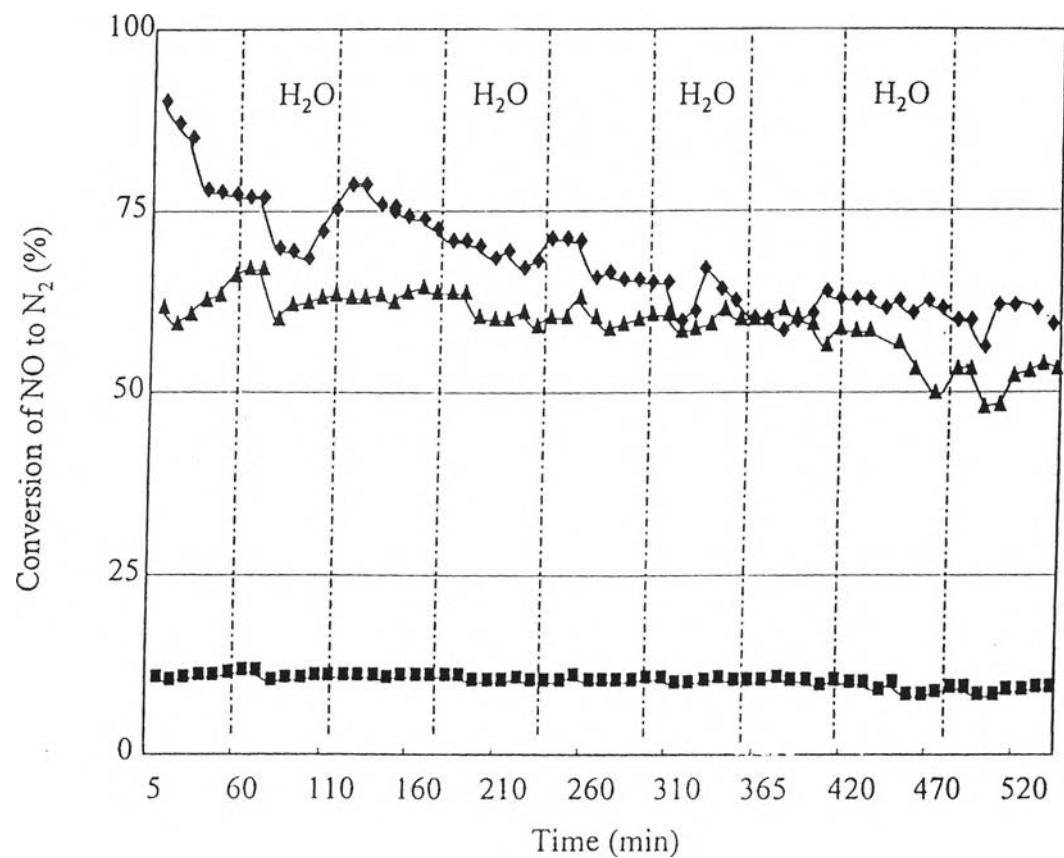


Figure 9.8 The stability of catalysts for conversion of NO to N₂ against 10mol% H₂O at reaction temperature of 400°C;◆ 200%Cu/MFI, ▲ Cu/Co-silicate, ■ H-Co-silicate. Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, O₂ 2mol%, He balance with a GHSV 30,000 h⁻¹

N₂ of 200%Cu/MFI, during nitric oxide conversion. At first, the reaction test is operated in a dry condition for 1 h and then 10 mol% H₂O is introduced in the inlet reaction gas mixture for 1 h. Every 1 h, the reaction test was changed into dry and wet conditions as a cycle. As demonstrated in Figure 9.8, it shows that 200%Cu/MFI loses the activity for conversion of NO to N₂. The activity of 200%Cu/MFI seems to be irreversibly changed while stop introducing 10 mol% H₂O. The activity of 200%Cu/MFI decreases by around 27% after stability test for 9 h. In contrast, H-Co-silicate exhibits the stable activity for conversion of NO to N₂ along 9 h of stability test although it has low activity for conversion of NO to N₂ in this reaction condition. As for Cu/Co-silicate, it shows higher conversion of NO to N₂ than H-Co-silicate. The reasonable explanation is the addition of Cu in H-Co-silicate promoting high conversion of NO to N₂. Furthermore, conversion of NO to N₂ of Cu/Co-silicate is relatively constant comparing with that of 200%Cu/MFI. However, the activity for conversion of NO to N₂ of Cu/Co-silicate is gradually diminished after 7 h. This appearance may be caused by the loss of some part of Cu exhibiting high NO conversion.

9.4 Conclusion

Cu/Co-MFI and H/Co-MFI which are metallosilicates are stable against high thermal-treatment at 1,000°C in contrast with Cu/MFI. Interestingly, comparing with conversion of NO of both Cu/Co-MFI and H/Co-MFI without pretreatment, the activity for nitric oxide removal of both pretreated catalysts can be enhanced using high temperature pretreatment. Furthermore, Cu/Co-MFI without pretreatment promoted higher activity for conversion of NO than H/Co-MFI without pretreatment. Nevertheless, pretreated Cu/Co-MFI did not exhibit higher activity than pretreated H/Co-MFI. The thermal-treatment at 1,000°C affected the state of copper ion-exchanged. Relating to Cu²⁺ ion exchanged on H/Co-MFI without pretreatment, the amount of Cu²⁺ species were decreased when were ion-exchanged on pretreated H/Co-MFI. The similar trend appeared on Cu/MFI with and without pretreatment.