CHAPTER VIII

THE EFFECT OF HYDROTHERMAL-TREATMENT ON NITRIC OXIDE CONVERSION OF CATALYSTS AND THE IMPROVEMENT IN STABILITY OF Cu/MFI CATALYST BY Pd MODIFICATION AGAINST HYDROTHERMAL-TREATMENT

8.1 Introduction

The environmental problems from stationary sources and transportation vehicles are still increasing irrespective of the recent advances in the catalytic technologies of NH_3-reduction and the use of three-way catalysts. Nitric oxide emitted from the combustion facilities and diesel engines is a special concern since it causes the acid rain and photochemical smog [1]. A number of studies concerning the elimination of NO have been made and many kinds of catalyst have been tried. Among those, copper ion-exchanged MFI (Cu/MFI) catalyst for NO removal is known as an effective one even under the condition of excess oxygen with coexistence of an appropriate reductant [9, 10]. It is accepted that Cu (II) state is predominant for NO removal in lean-burn condition [127, 128]. However, it is also known that Cu ion-exchanged zeolite is easily deactivated in high temperature conditions and/or the existence of steam which possibly occurs in practical use. In many researches it has been pointed out that the deterioration of Cu/H-ZSM-5 must be attributed to sintering of copper cluster [104], dealumination [46, 79], migration of copper species to inactive sites [45, 47, 74], and formation of copper oxides or copper aluminates [44, 45, 74]. However, it is generally recognized that the ion-exchanged Al-silicate catalysts have a disadvantage in thermal and hydrothermal stability, owing to both the sintering of exchanged metal components and the dislocation of the aluminium from the zeolite framework and there are the serious problems for the practical applications [94].

In order to overcome these difficulties, Inui et al. synthesized silicate crystals (metallosilicates) by isomorphous substitution of aluminium in MFI for other transition metal elements at the stage of gel formation before crystallization [95-97]. H-Co-silicate was active to combust hydrocarbons moderately enhancing more chance for hydrocarbons to be used for nitric oxide removal suitably as shown in Table.2.1 by Inui [103] This chapter concerns the activity for conversion of NO to N_2 of both 200%Cu/MFI

and H-Co-silicate under hydrothermal-treatment condition.

On the other hand, platinum-group metal catalysts have been also studied for nitric oxide conversion [14, 42], and it is known that platinum-group metal has the high resistance against a large amount of steam existed in the effluent [27]. For these reasons, in this chapter Cu ion-exchanged H-ZSM-5 was also modified with Pd (designated as Pd/Cu/H-ZSM-5) to improve the performance and stability for nitric oxide removal. In order to clarify the performance of the Pd/Cu/H-ZSM-5 for NO elimination, Cu ion-exchanged H-ZSM-5 (designated as Cu/H-ZSM-5) and Pd ion-exchanged H-ZSM-5 (designated as Pd/H-ZSM-5) were also employed, and the cause of difference in catalytic performance was discussed.

8.2 Experimental

8.2.1 Catalyst preparation

A MFI type zeolite having Si/Al atomic ratio of 50 was prepared by adopting the rapid crystallization method [97], and it was washed, dried, and calcined at 540°C for 3.5 h. This as-synthesized MFI was then ion-exchanged using ammonium nitrate solution to obtain NH_4/MFI. It was then washed, dried and calcined at 540°C for 3.5 h in air to convert into the protonated form (H/MFI). Amine complex salts of palladium (Mitsuwa Pure Chemical Industries Ltd.) and copper acetate (Wako Pure Chemical Industries Ltd.) were used as the source of metal for ion exchange of protonated sites in H/MFI. Cu/MFI and Pd/MFI were prepared by ion-exchange procedure at 80°C Cu and at 90°C Pd, respectively. They were washed, dried and calcined at 540°C for 3.5 h in air. As for Pd/Cu/MFI, successive ion exchange of MFI with palladium first and then copper was made adopting the same method as mentioned above. As for H-Co-silicate, Co-silicate MFI type zeolite supported by Prof. Inui's laboratory was also prepared by the rapid crystallization method. The charged Si/Co atomic ratio of Co silicate was set at 20. In order to investigate the effect of hydrothermal-treatment on the activity of catalyst, the catalyst was heated in a He stream while elevating temperature from room temperature to 600°C and 600 to 1,000°C with constant heating rates of 10 and 1.67°C/min, respectively. The catalyst sample was then kept at the desired temperature for 30 min while adding 10mol% of steam. Subsequently, the catalyst was cooled down to room temperature in He stream. Thus obtained catalyst in powder form was tabletted, crushed, and sieved to

12-22 mesh to provide the reaction.

8.2.2 Characterization

The bulk composition and BET surface area of sample were measured by Inductively Coupled Plasma analysis (ICP SHIMADZU ICPS-1000 II) and Shimadzu Flow Sorb II 2300 using liquid nitrogen as a probe molecule, respectively. Crystallinity of ZSM-5 was estimated by using SIEMENS D5000 diffractometer with CuKα radiation. IR spectra of self-supporting wafer made of mixture of KBr and sample were recorded by Nicolet model Impact 400 to evaluate MFI crystallinity. The IR absorption band at 550 cm^{-1} is indicative of the vibration of 5-mebered oxygen rings and that at 450 cm^{-1} of the internal vibration of TO$_4$ unit. Morphology of catalyst was observed by Scanning Electron Microscope Model JSM-6400. Acidity of the sample was measured by in situ-FTIR spectra. Pyridine was used as a probe molecule. The X-band spectra characteristics 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.

8.2.3 Reaction test

The catalytic reaction test was studied using an ordinary flow microreactor under atmospheric pressure. A 0.28 g portion of the catalyst was packed in a tubular reactor of 10 mm in inner diameter. The packed space of the reactor was 0.40 ml. It was heated up to 600°C in a He flow with a constant heating rate of 10°C/min, and maintained at that temperature for 30 min. A feed gas composed of 1,000 ppm NO, 1,000 ppm n-octane, 2 mol% O$_2$ and 10mol% H$_2$O balanced with He was then introduced into the reactor with a GHSV of 30,000 h^{-1}. Every 5 min after purging reaction gas to ensure the steady state of catalytic activity, the effluent gas composition was analyzed by gas chromatographs (Chrompack, Micro GC CP 2002with MS-5A and porapak Q column) equipped with integrators. The reactor temperature was then cooled down from 600 to 200°C with a constant cooling rate of 10°C/min. Every 50°C, the effluent gas was analyzed as the same method. The amount of N$_2$ and N$_2$O formed stands for the performance of the catalyst for nitric oxide conversion.

8.4 Results and discussion

8.4.1 Influence of hydrothermal-treatment on nitric oxide conversion of 200%Cu/MFI and H-Co-silicate catalysts

Figures 8.1 and 8.2 represent NO and n-octane conversions of 200%Cu/MFI. It is remarkable that hydrothermal-treatment affects the activity of 200%Cu/MFI more severely than only either thermal-treatment or the hydro-treatment. The activity of 200%Cu/MFI for conversion of NO is loss deeply when 200%Cu/MFI was pretreated at 800°C with 10mol% H_2O and at 1,000°C with 10mol% H_2O. Similarly, conversion of n-octane of 200%Cu/MFI is decreased with hydrothermal-treatment condition. Conversions of NO and n-octane of H-Co-silicate with hydrothermal-treatment were also studied and illustrated in Figures 8.3 and 8.4, respectively. H-Co-silicate pretreated at 800°C with 10mol% H_2O shows a dramatic increasing of conversion of NO higher than H-Co-silicate without pretreatment. This appearance is similar to H-Co-silicate pretreated by thermal-treatment. As compared with conversion of NO of H-Co-silicate pretreated by thermal-treatment at the same temperature condition, however, conversion of NO by H-Co-silicate pretreated by hydrothermal-treatment is much lower due to the more severe condition by hydrothermal-treatment. In additions, the activity for NO conversion by H-Co-silicate pretreated at 1,000°C with 10mol% H_2O is diminished comparing with that of H-Co-silicate without pretreatment. However, the hydro-thermal treatment impacts more severely on NO removal than the thermal treatment at the same level of temperature applied.

8.4.2 Characterization of 200%Cu/MFI and H-Co-silicate with hydrothermal-treatment
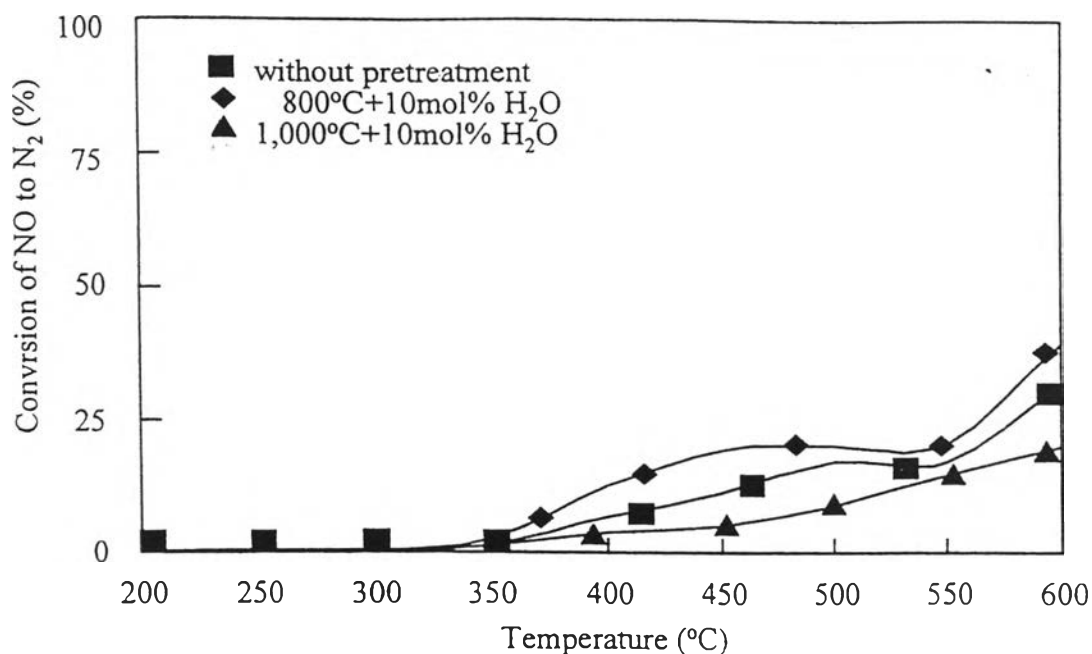
8.4.2.1 BET surface area and bulk compositions

Table 8.1 shows the BET surface area, bulk composition of catalysts with hydrothermal-treatment. As shown in Table 8.1, 200%Cu/MFI loses BET surface area with hydrothermal-treatment condition especially at the hydrothermal-treatment condition of 1,000°C with 10mol% H_2O. As for H-Co-silicate, the decreasing trend of BET surface area with hydrothermal-treatment also occurred but gradually. Additionally, the amount of metal on the catalysts is not changed relative to that on the catalysts without pretreatment. It can be implied that there is no evaporation of metal by
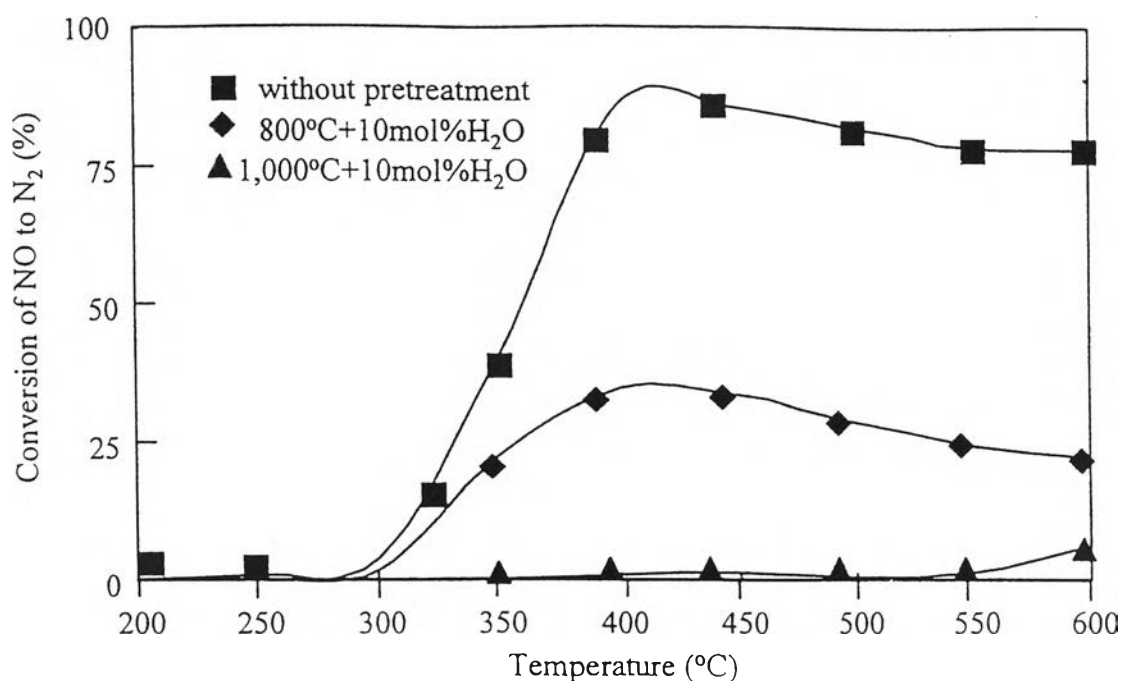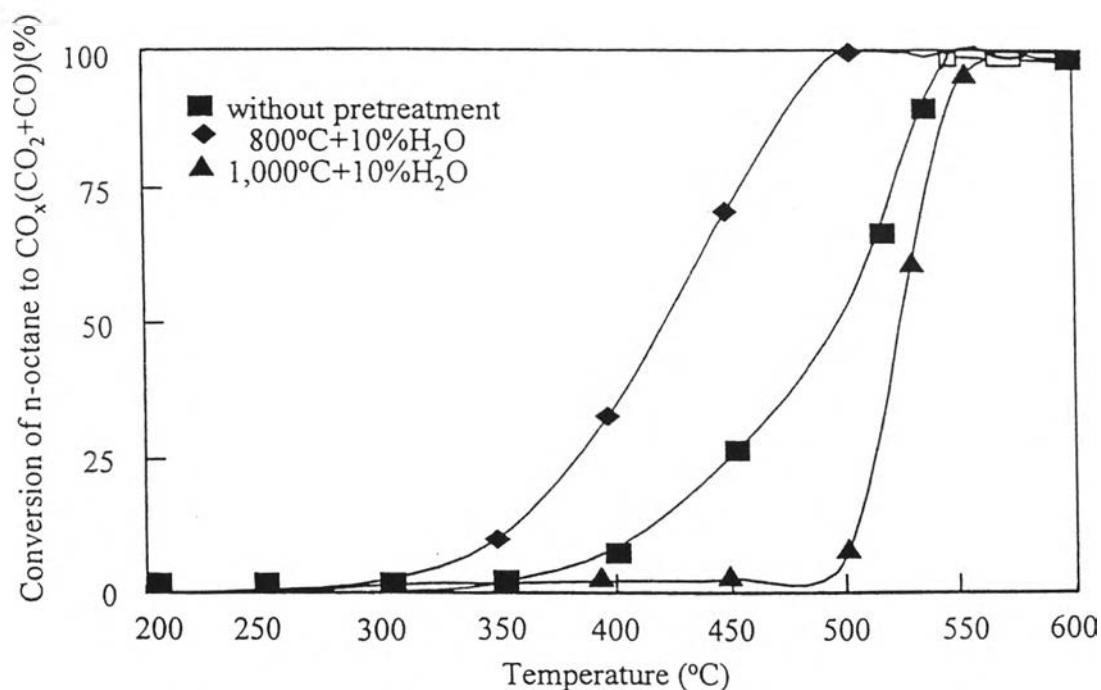
Figure 8.1 The effect of hydrothermal-treatment on the activity of NO conversion of 200%Cu/MFI. Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, O_2 2mol%, H_2O 10mol%, He balance, GHSV 30,000 h^{-1}.
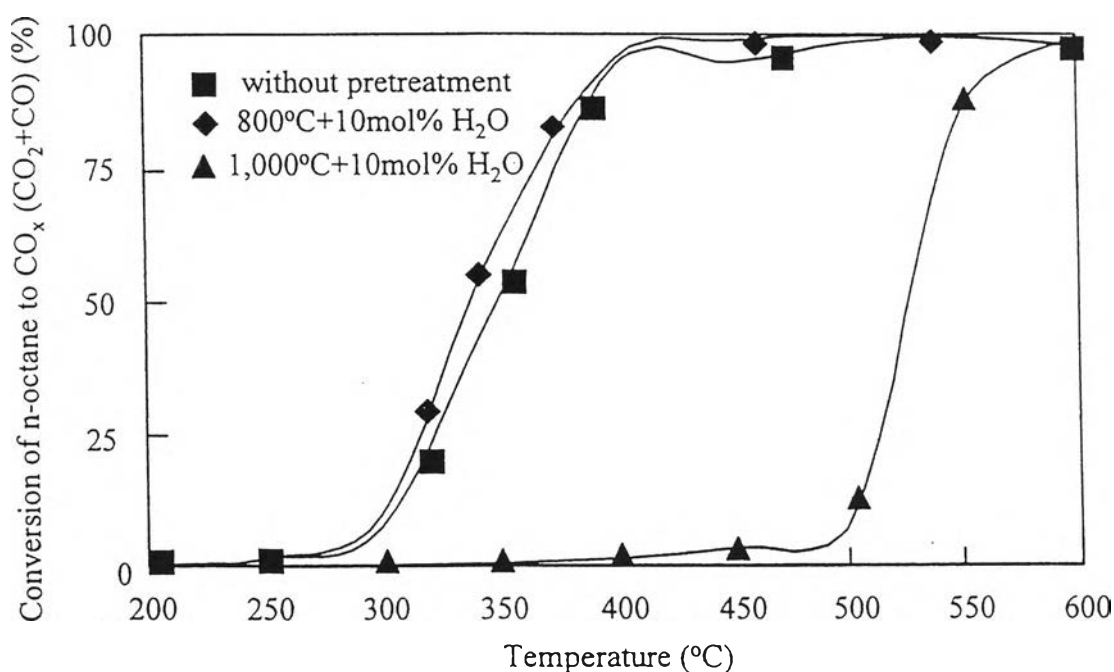
Figure 8.2 The effect of hydrothermal-treatment on the activity for n-octane conversion of 200%Cu/MFI. Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, O_2 2mol%, H_2O 10mol%, He balance, GHSV 30,000 h^{-1}

Figure 8.3 The effect of hydrothermal-treatment on the activity for NO conversion of H-Co-silicate. Feed gas: NO 1,000 ppm , n-octane 1,000 ppm, O_2 2mol%, H_2O 10mol%, He balance, GHSV 30,000 h^{-1}

Figure 8.4 The effect of hydrothermal-treatment on the activity for n-octane conversion of H-Co-silicate. Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, O_2 2mol%, H_2O 10mol%, He balance, GHSV 30,000 h^{-1}

hydrothermal-treatment. It is necessary to apply XRD method for the investigation of crystallinity of sample.

Table 8.1 BET surface area, bulk composition of catalysts with hydrothermal-treatment.

Sample	Pretreatment condition	BET surface area $(m^2/g.cat)$	Si/Me atomic ratio
200%Cu/MFI	without pretreatment	360	51
	800°C+10 mol% H_2O	300	54
	1,000°C+10 mol% H_2O	97	58
H-Co-silicate	without pretreatment	350	257
	800°C+10 mol%H_2O	352	258
	1,000°C+10 mol%H_2O	284	258

8.4.2.2 Crystallinity by XRD characterization

X-ray diffraction lines of 200%Cu/MFIs and H-Co-silicates with and without hydrothermal-treatment are depicted sequentially in Figures 8.5 and 8.6. The intensity of X-ray diffraction lines of 200%Cu/MFI pretreated at 1,000°C with 10 mol% H_2O diminishes enormously comparing with that of 200%Cu/MFI without pretreatment. The change of crystallinity pattern from MFI structure to crystobalite form occurs for 200%Cu/MFI pretreated at 1,000°C with 10mol% H_2O as similar as 200%Cu/MFI pretreated by high thermal-treatment condition. As for H-Co-silicate, the intensity of X - ray diffraction lines of H-Co-silicate pretreated at 1,000°C with 10 mol% H_2O is lowered relative to that of H-Co-silicate without pretreatment. However, there is no identification of the change of MFI structure of H-Co-silicate. This is a more advantage of H-Co-silicate to maintain MFI structure more effectively than 200%Cu/MFI.

From many characterizations cited above, it can be concluded that the loss of crystallinity of the framework brings about the unstability of catalyst structure to maintain the activity for NO conversion in severe condition as same as its activity without pretreatment. This is an another reason causing the decrement of the activity for

NO conversion of both 200%Cu/MFI and H-Co-silicate pretreated by hydrothermal treatment.

Although 200%Cu/MFI loss the activity for conversion of NO to N_2 more steeply than H-Co-silicate, 200%Cu/MFI pretreated at 800°C with 10 mol% H_2O exhibits higher conversion of NO to N_2 than H-Co-silicate pretreated at 800°C with 10mol% H_2O. It is well known that copper-based catalyst promotes high activity for both decomposition and SCR of nitric oxide [9, 10, 128, 129]. It is accepted that Cu^{2+} state is predominant for NO removal in lean-burn condition [46, 47]. Nevertheless, Cu-ion-exchanged zeolite is easily deactivated in high temperature condition and/or the existence of steam that possibly occurs in practical use. It can be implied that the transformation of copper species to be inactive species is a limitation of this catalyst for NO removal in severe condition. This reason can be supported by many researches [45, 47, 78]. Pd modification of copper ion-exchanged MFI zeolite (Pd/Cu/MFI) was also paid attention in this study to improve the performance for NO elimination under severe condition. In order to distinguish easily, 200%Cu/MFI and Pd/MFI were compared for this purpose as well. The effect of hydrothermal-treatment at 800°C with 10 mol% H_2O on nitric oxide conversion of catalysts was investigated since the high crystallinity of 200%Cu/MFI catalyst still exist.

8.4.3 Change in physical properties of catalysts by the hydrothermal-treatment at 800°C with 10 mol% H_2O

Table 8.2 shows physical properties of catalysts before and after use for the reaction. Crystallinity determined by XRD profiles was calculated using the intensity of diffraction line at 23.5° 2θ, which was compared with that of MFI material as the reference. The relative intensity ratio of 550 to 450 cm^{-1} bands (I_{550}/I_{450}), expresses a quantitative index of crystallinity around the oxygen rings of MFI zeolite. The data of XRD and IR spectra of used catalysts differ in minor degree from those of fresh ones. Therefore, it is concluded that the slight collapse of MFI framework does not affect on the deactivation as supported by Yan et al [46] and Martinez et al [47], although BET surface area of used catalysts showed some decrease relative to that of fresh ones.

The scanning electron micrographs (SEM) of fresh and used Cu/MFI and Pd/Cu/MFI after crashing to powder form in a mortar are shown in Figures 8.7 and 8.8,
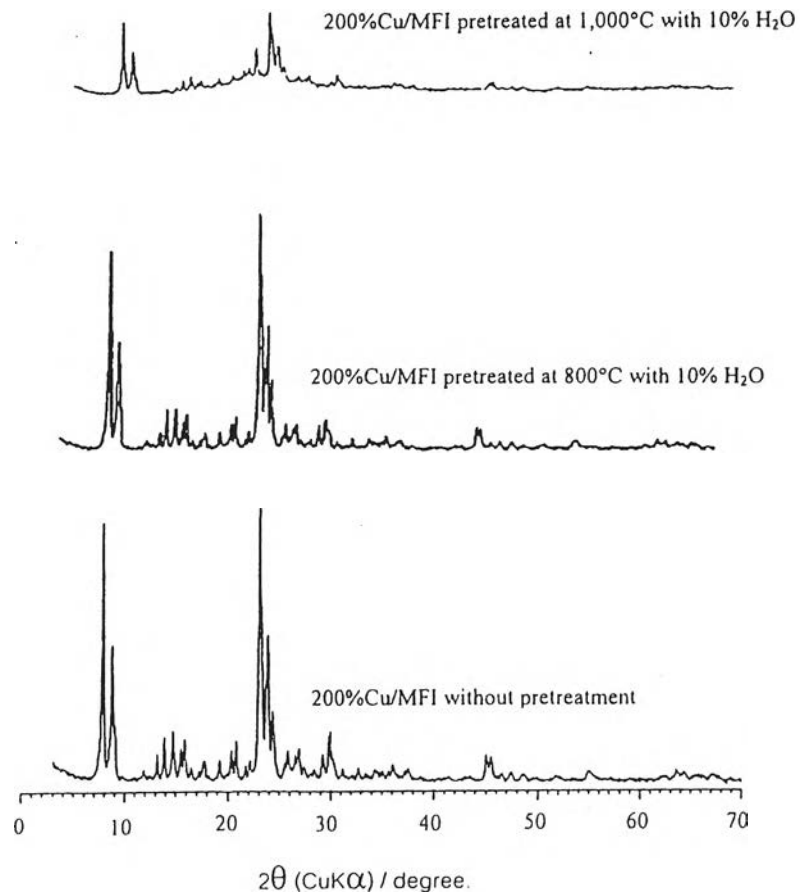
200%Cu/MFI pretreated at 1,000°C with 10% H_2O

200%Cu/MFI pretreated at 800°C with 10% H_2O

200%Cu/MFI without pretreatment

2θ (CuKα) / degree.

Figure 8.5 XRD patterns of 200%Cu/MFI with hydrothermal-treatment

H-Co-silicate pretreated at 1,000°C with 10% H_2O

H-Co-silicate pretreated at 800°C with 10% H_2O

H-Co-silicate without pretreatment

2θ (CuKα) / degree.
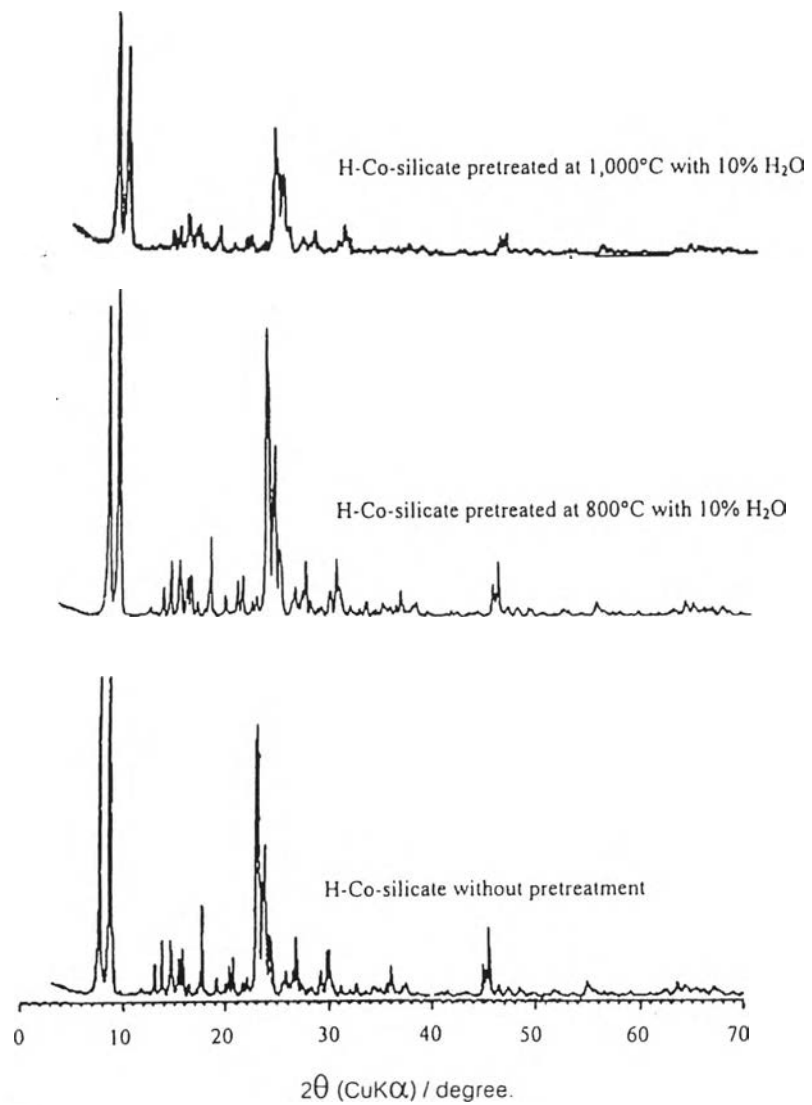
Figure 8.6 XRD patterns of H-Co-silicate with hydrothermal-treatment

Table 8.2 Data of catalysts in physical; bulk compositions, BET surface area and crystallinity of 200%Cu/MFI, Pd/Cu/MFI and Pd/MFI, respectively.

Sample	Pretreatment temperature (°C)	BET surface area (m²/g.cat)	Me/Al atomic ratio		crytallinity (%)	I_{550}/I_{450} ratio
			Cu/Al	Pd/Al		
200%Cu/MFI	without pretreatment	360	0.91	-	100	0.8
	800°C+10%H_2O	300	0.93	-	97	0.74
Pd/Cu/MFI	without pretreatment	334	0.80	0.027	101	0.72
	800°C+10%H_2O	303	0.81	0.026	100	0.72
Pd/MFI	without pretreatment	321	-	0.025	99	0.72
	800°C+10%H_2O	303	-	0.025	102	0.70

respectively . Unit particles of fresh Cu/MFI (Fig. 8.7 (a)) markedly agglomerated to considerably larger size, as high as 10 times diameter, by the use of the reaction (Fig. 8.7, (b)). It indicates that ion-exchanged copper easily makes its cluster and further growth by sintering accompanying with gathering unit particles of MFI material. On the other hand, in the case of Pd/Cu/MFI, no significant change of its morphology is observed by the use for the reaction. It means that the Pd part, which has a less tendency toward sintering than Cu has, would interfere the progress of Cu sintering, and consequently, the agglomeration of MFI particles is largely retarded.

Figures (A) and (B) in Figure 8.9 show in-situ FTIR spectra of pyridine adsorbed on fresh catalysts of Cu/MFI and Pd/Cu/MFI, respectively at different temperatures. Numbers of bands were appeared in the region of interest between 1,400 and 1,640 cm^{-1}. Brønsted acidity, representing pyridinium ion on protonate sites and Lewis acidity describing coordinately bonded pyridine on sites as electron pair acceptor give the band at around 1540 cm^{-1} and in the range of 1,440-1,465 cm^{-1}, respectively [122]. The amount of acid can be measured quantitatively by the intensity of the spectra. On the other hand, the strength of acidity can be evaluated by the presence of Brønsted and/or Lewis acidity with increasing temperature. It can be demonstrated that Pd/Cu/MFI expressed stronger Lewis acidity than Cu/MFI. Primet and Taarit [129] reported that the wave number of pyridine adsorbed on Pd^{2+} was approximately at 1,456 cm^{-1}, which is typical for Lewis acidity. Therefore, it is suggested that palladium species in Pd/Cu/MFI are highly dispersed. Existence of such isolated Pd^{2+} ions and/or fine particles of palladium oxides are supported by Misono and co-workers [130].

Figures 8.10 and 8.11 depict ESR spectra of Cu/MFI and Pd/Cu/MFI, respectively. The spectra of fresh Cu/MFI and Pd/Cu/MFI are similar. These indicate that two Cu^{2+} species located in two different coordinations (a square pyramidal environment with $g_{\parallel}$=2.31-2.33, $A_{\parallel}$=142.5G and a square planar one with $g_{\parallel}$= 2.27-2.29, $A_{\parallel}$ ~ 155G). These are typically found in many literatures [47, 78, 127, 131]. Shelef [128] proposed that Cu^{2+} in a square planar configuration is very active for NO removal. As compared with fresh catalysts, Pd/Cu/MFI after pretreatment exhibits the same features. As for Cu/MFI, however, the pretreated Cu/MFI not only loses the intensity of ESR spectra, but it also has a change in the shape of the signal. This means

that the amount of two Cu^{2+} species in both square pyramidal and square planar coordinations were diminished due to pretreatment. Additionally, a new spectrum with $g_{\parallel}$=2.30, $A_{\parallel}$=156G appears although part of two Cu^{2+} species remained. The new ESR signal indicates the change in the coordination of Cu^{2+}. From ESR results as mentioned above, it is suggested that modified Pd can preserve most parts of active Cu^{2+} species even after pretreatment at 800°C and 10 mol% H_2O addition.

8.4.4 Change in catalytic performance by the hydrothermal-treatment at 800°C and 10 mol% H_2O.

In order to compare the catalytic performance of the three kinds of catalyst, NO conversion reaction was carried out. In both the pretreatment and the catalytic reaction test, enough partial pressure of steam, i.e. 10 mol%, was added in each feed gas. By the addition of such a considerably high partial pressure of steam, n-octane combustion was fairly retarded and N_2O was observed in the effluent gas, whereas in the reaction gas without H_2O, N_2O was not detected on Cu/MFI.

The effects of the reaction temperature on the conversion of n-octane to CO_x and conversion of NO to N_2 and N_2O on the three catalysts are shown in Figures 8.12 and 8.13. On Pd/MFI, n-octane combusts most easily from a lowest temperature range, but major product of conversion of NO is N_2O and N_2 formed in minor extent. On the other hand, on other two kinds of catalysts, a considerable amount of NO converts to N_2, and N_2O forms only a lower temperature range. At above 400°C, NO to N_2 conversion on Cu/MFI decreases with an increase of temperature, while that on Pd/Cu/MFI increased.

It is interesting that the activity for conversion of n-octane on Pd/Cu/MFI is rather lower than those of other catalysts, resulting the effective use of n-octane reaction upon the NO conversion on Pd/Cu/MFI at the high temperature range. The reason for the decrease in conversion of n-octane on Pd/Cu/MFI would be attributed to some change of Pd and Cu on the MFI catalyst such as alloying due to the pretreatment at a high temperature range. This would bring about the decrease in the catalytic activity for conversion of n-octane.

Stability of the catalytic activity for conversion of NO to N_2 against the hydrothermal-treatment condition was compared between Cu/MFI and Pd/Cu/MFI, and is shown in Figure 8.14. Without the pretreatment, both catalysts exhibit very similar
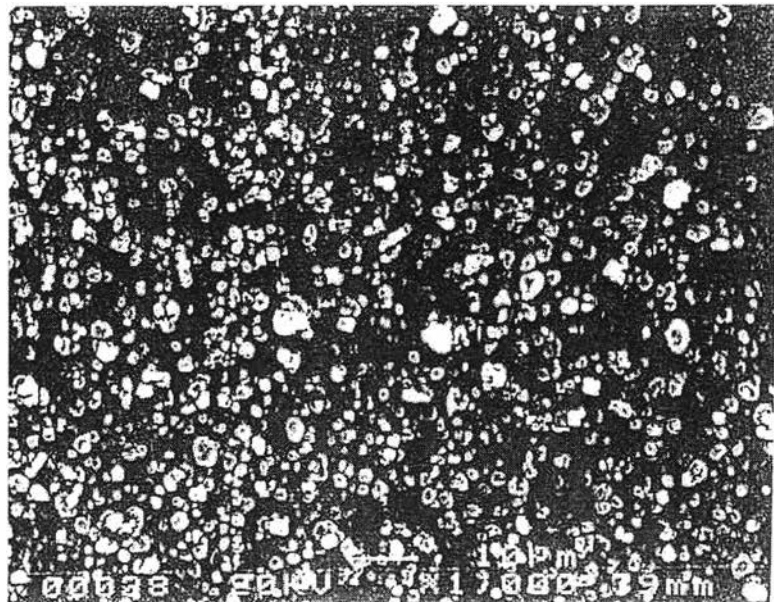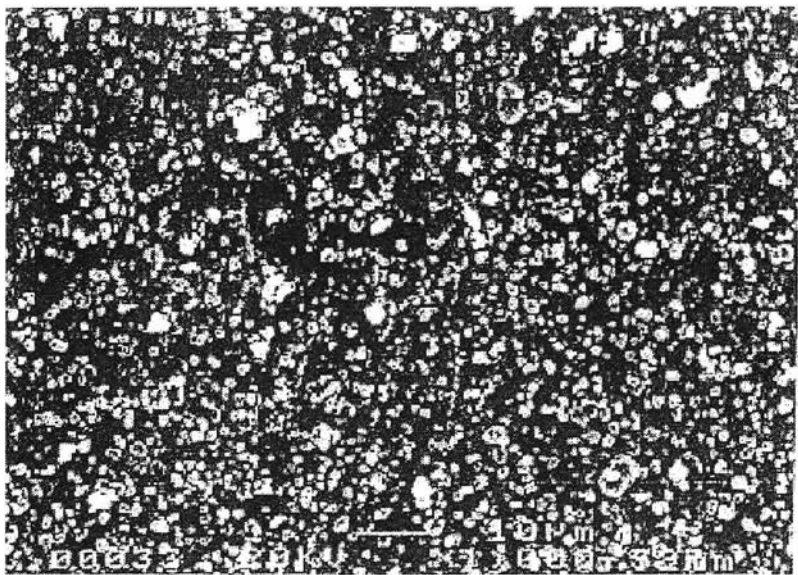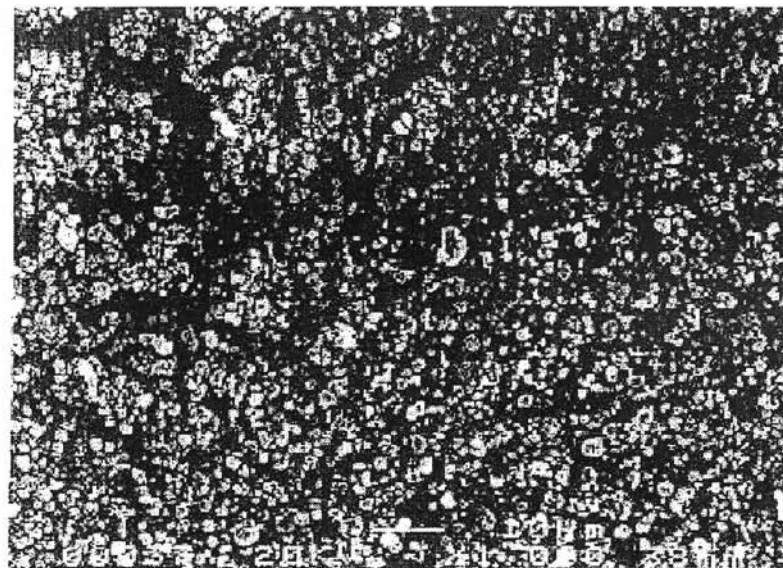
(a)
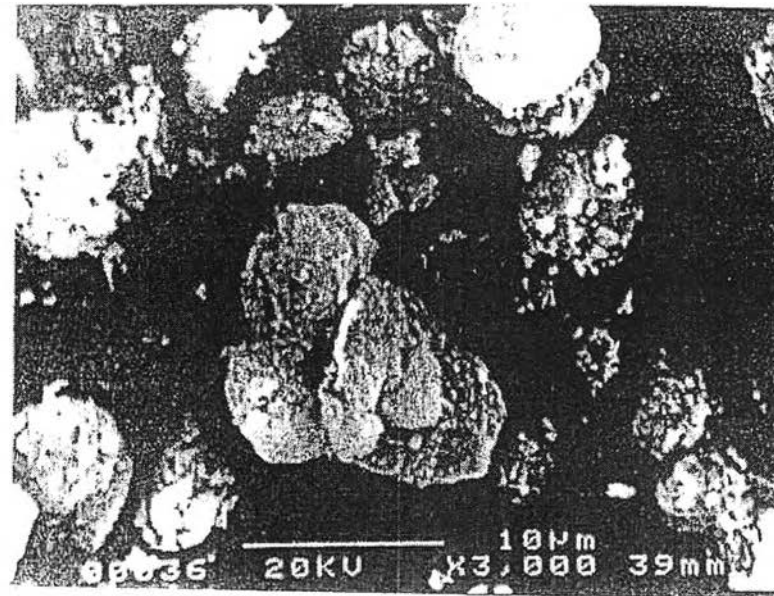
(b)

Figures8.7. Scanning electron micrographs of 200%Cu/MFI
a) 200% Cu/H- ZSM-5 without pretreatment ,b)200% Cu/H-ZSM-5 pretreated 800°C with 10%H2O

Figures8.8. Scanning electron micrographs of Pd/Cu/MFI
c) Pd/Cu/MFI without pretreatment ,b)Pd/Cu/MFI pretreated 800°C with 10%H2O

performance for NO to N_2 conversion, however, the big difference brings about by the pretreatment. The degree of the decrease in the activity is much larger on Cu/MFI. On the other hand, on Pd/Cu/MFI, as the activity rather increases with an increase of the reaction temperature, at higher temperature range around 600°C, the activity is nearly comparable to those of non-treated catalysts.

The reason for this apparently unique phenomenon is because as the combustion activity was moderated in Pd/Cu/MFI by the treatment, the role of reduction of catalyst surface could be extended up to higher temperature range than that of Cu/MFI. Because intermediate combustion products are apt to keep catalyst surface reductive until more higher temperature range than that of Cu/MFI, and NO could be converted maintaining a high level. These phenomena consistently coincide and are understandable with the Microscopic Sequential Reaction Mechanism [48, 50, 58, 132, 133].

This phenomenon is caused by the ability of Pd to preserve some parts of Cu^{2+} species active for conversion of NO supported by ESR data in figures 8.10 and 8.11. However, the activity of pretreated Pd/Cu/MFI for nitric oxide removal is lower than that of fresh one. This may be due to the low amount of Pd that is unable to preserve all active copper species and/or dealumination. Rokosz et al. [134] reported that the addition of Pd could stabilize the tetrahedral Al of the zeolite structure. Therefore, dealumination was not significant to lower the activity for nitric oxide conversion but the instability of copper species active for nitric oxide removal.

8.5 Conclusion

Hydrothermal-treatment affect on the activity of both 200%Cu/MFI and H-Co-silicate. It showed more severe deactivation than thermal-treatment and hydro-treatment. The stability of the Cu/H-ZSM-5 for NO removal against a hydrothermal-treatment condition could be improved by modification with Pd. The collapse of ZSM-5 framework in minor extent gave no significant effect on deactivation even after the pretreatment at 800°C in N_2 stream involving 10 mol% H_2O. The crucial effect of Pd modification on NO conversion is due to preservation of active Cu^{2+} species from the sintering.
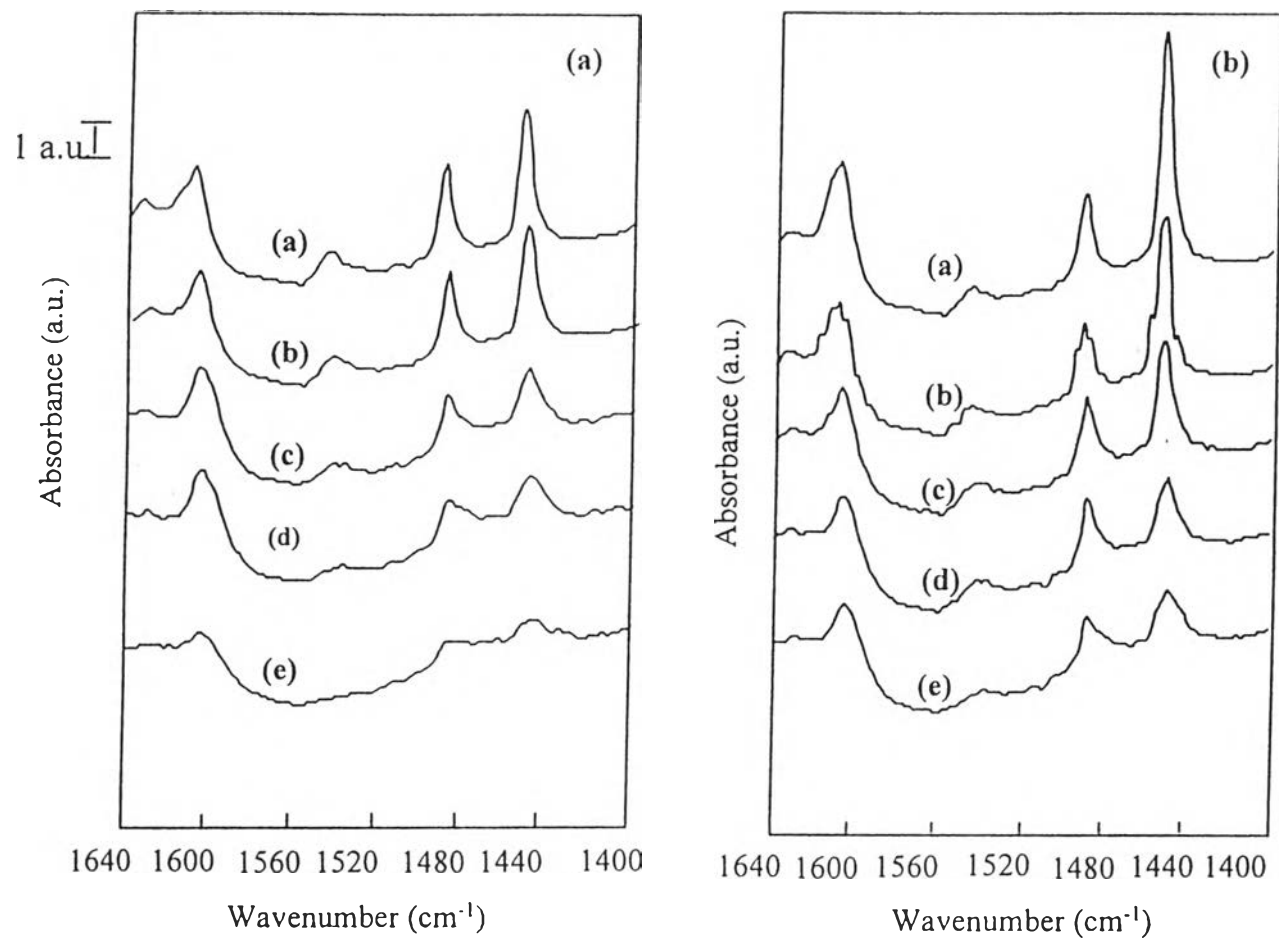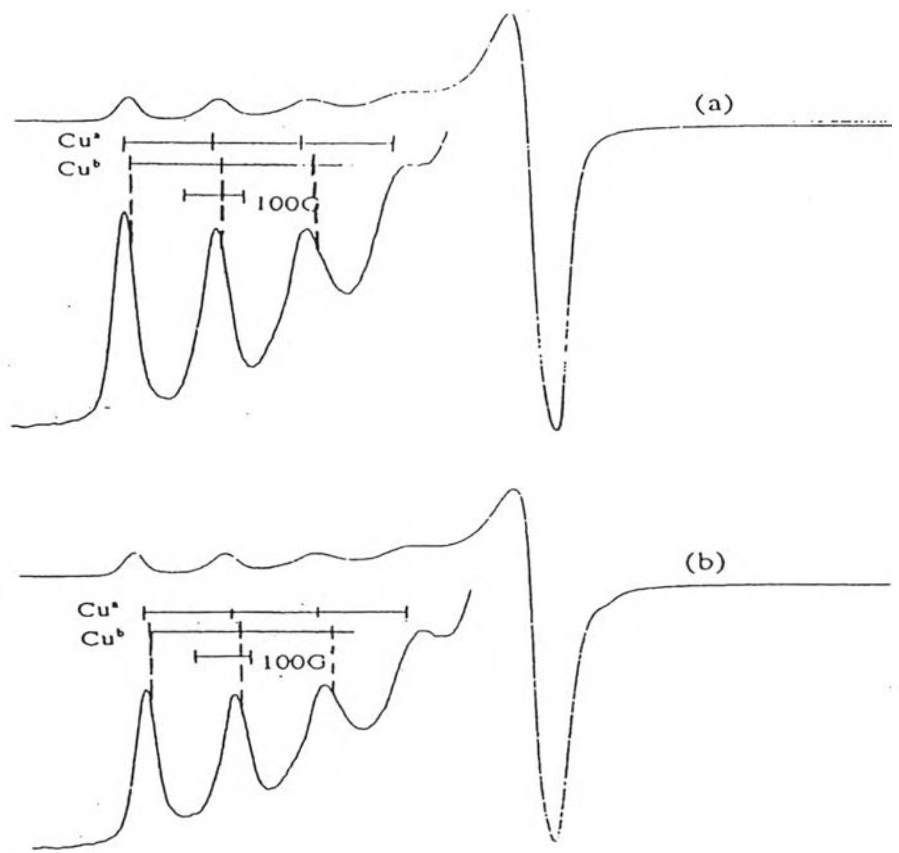
Figure 8.9. In situ FT-IR spectra of pyridine adsorbed on catalysts without pretreatment :
(a) 200%Cu/MFI; (b) Pd/Cu/MFI: (a) at 150°C; (b) at 200°C; (c) at 250°C; (d) at 300°C; (e) at 350°C
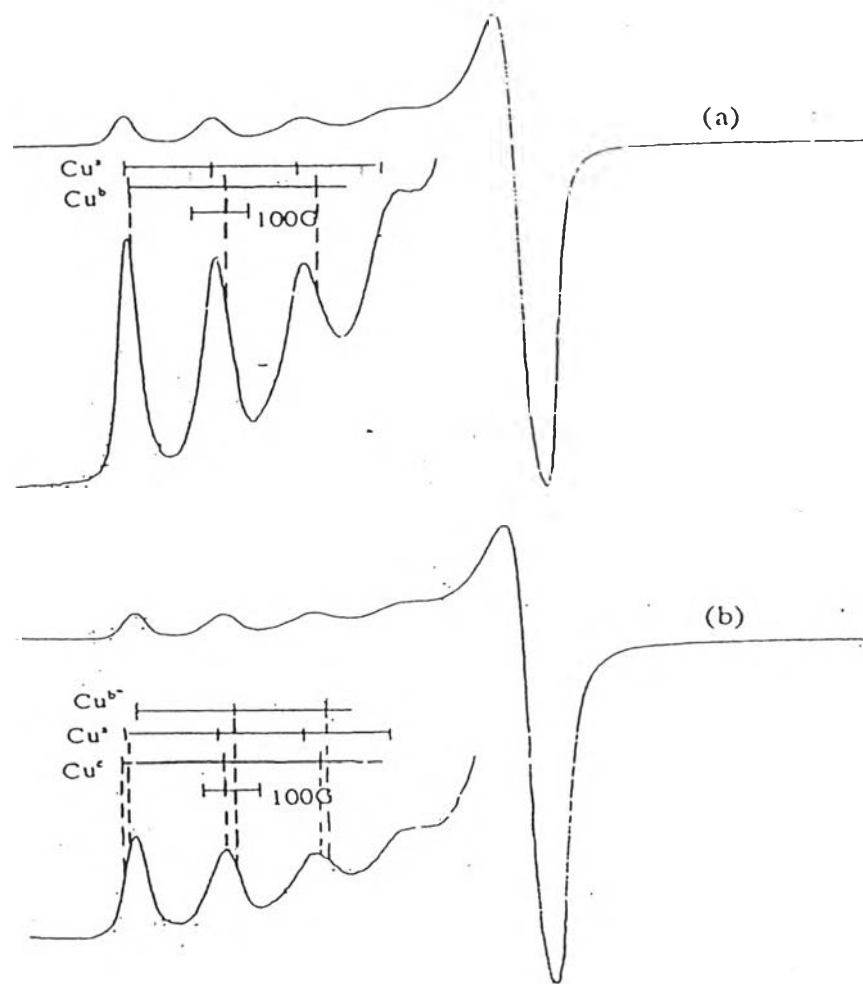
Figure 8.10 ESR spectra of high spin Cu^{2+} of 200%Cu/MFIs
a) 200%Cu/MFI without pretreatment, b) 200%Cu/MFI pretreated at 800°C with 10mol% H_2O

Figure 8.11 ESR spectra of high spin Cu^{2+} of Pd/Cu/MFIs
a) Pd/Cu/MFI without pretreatment, b) Pd/Cu/MFI pretreated at 800°C with 10mol% H_2O
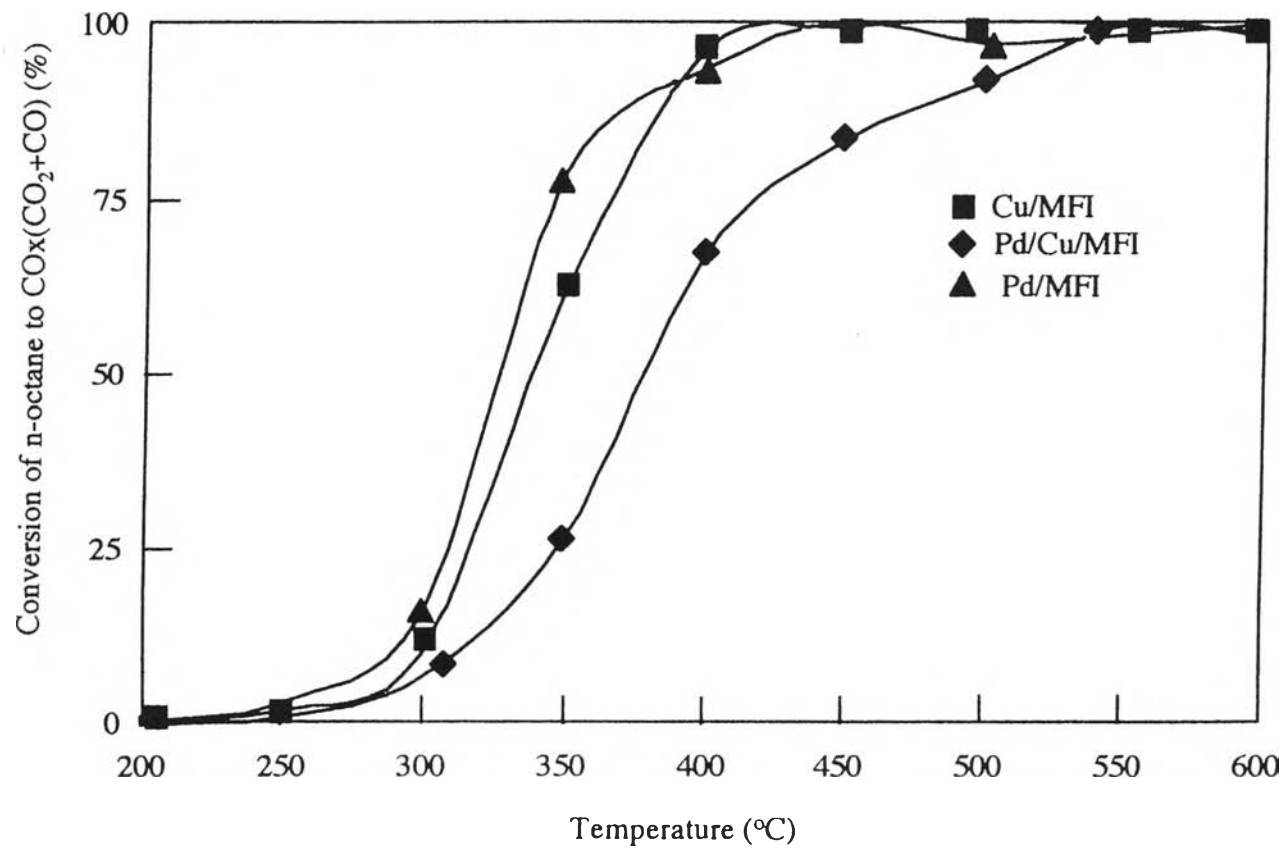
Figure 8.12 n-Octane conversion on catalysts pretreated at 800°C with H_2O 10mol%. Reaction gas: NO 1,000 ppm, n-C_8H_{18} 1,000 ppm, O_2 2%, H_2O 10%, He balance, GHSV 30,000 h^{-1}
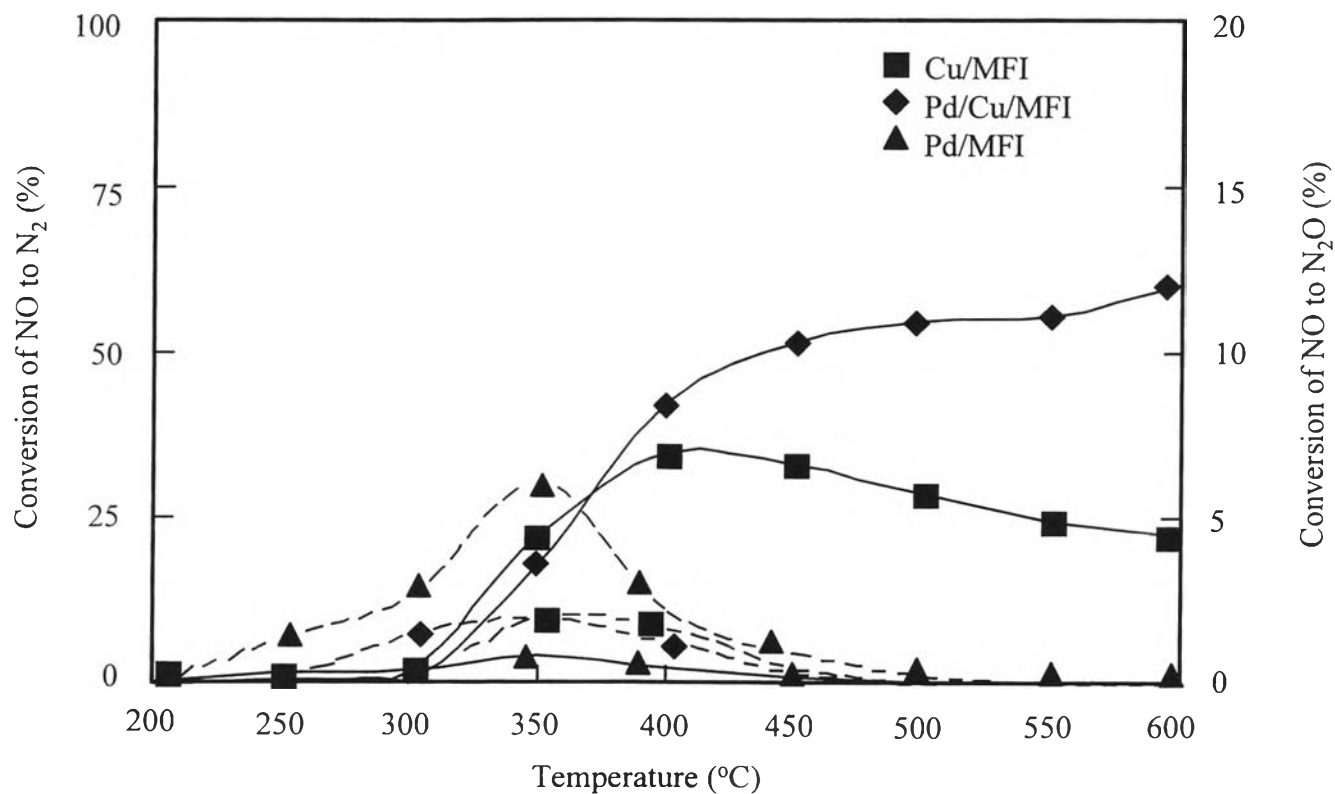
Figure 8.13 Conversion of NO of catalysts pretreated at 800°C with H_2O 10mol% for 30 min
Solid line: Conversion of NO to N_2; Broken line: Conversion of NO to N_2O Reaction gas: NO 1,000 ppm, n-octane 1,000 ppm, O_2 2mol%, H_2O 10mol%, He balance, GHSV 30,000 h^{-1}
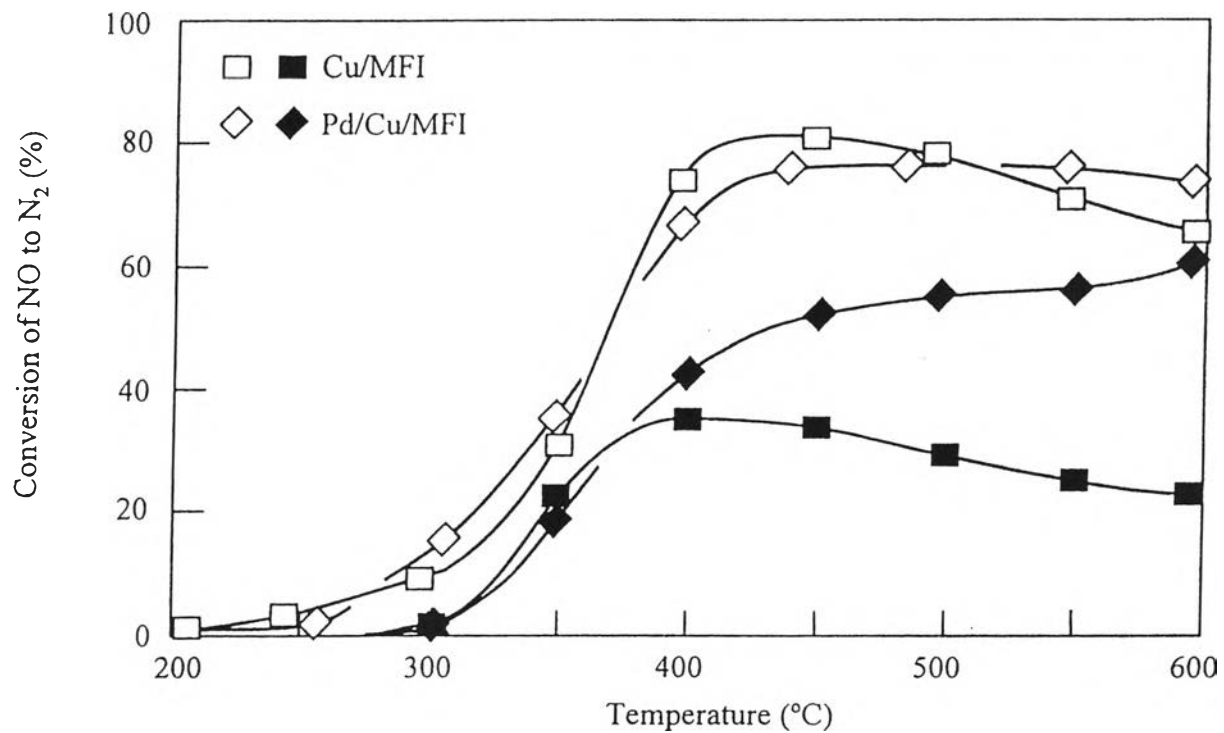
Figure 8.14 Effect of hydrothermal-treatment on conversion of NO to N_2 of catalysts.
Open symbol: without pretreatment; Closed symbol: with hydrothermal-treatment at 800°C with H_2O
10mol% for 30 min; Reaction gas: NO 1,000 ppm,n-C_8H_{18} 1,000 ppm, O_2 2%, H_2O 10%, He balance,
GHSV 30,000 h^{-1}