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Hydrothermal stability of dealuminated mordenite type zeolite catalysts for the reduction of NO by C_3H_6 under lean-burn condition

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Abstract

Hydrothermal stability of mordenite type catalysts including synthetic (CuHM) and natural (CuNZA) zeolites has been examined under a simulated lean NO_x wet condition. When the catalysts were hydrothermally aged at 800°C with 10% H_2O for 6 h, the NO removal activity at the reaction temperature of 450°C was higher for natural zeolite than for synthetic one. It was mainly due to the Si/Al ratio of the catalyst. CuHM and CuNZA catalysts were dealuminated to investigate the effect of Si content of the zeolites on the hydrothermal stability. After the aging at 800°C for 24 h in the presence of 10% H_2O, NO removal activity of the dealuminated CuHM catalysts at the reaction temperature of 500°C was in the order of the Si/Al ratio of the catalysts. Such a significant improvement of the deNO_x performance was also observed for the dealuminated CuNZA catalysts. It reveals that the Si/Al ratio of zeolite catalysts is one of the crucial characteristics enhancing the water tolerance and hydrothermal stability of the catalysts for NO reduction under the lean NO_x wet condition. In addition, the loss of NO removal activity of the catalysts upon the hydrothermal aging is mainly attributed to the chemical alteration of Cu^{2+} ions on the catalyst surface through the structural collapse of the zeolite catalysts.

Keywords: Hydrothermal stability; SCR by hydrocarbons; Mordenite; Natural zeolite; Si/Al and Cu/Al ratio of zeolite; Lean burn catalyst

1. Introduction

Current three-way catalyst could not be employed for the removal of NO_x from lean-burn gasoline and diesel engines, since the high level of O_2 is contained in the exhaust of the engine [1]. Selective reduction of NO_x by hydrocarbons over various types of catalyst has been investigated to reduce NO_x from the engine [1]. Transition metal ion-exchanged zeolite catalysts such as MOR and MFI types exhibit high deNO_x activity for NO reduction by hydrocarbons. However, the notable decrease of NO removal activity of MFI type zeolite catalyst, CuZSM-5 by H_2O was observed for the reduction [1,2]. Recently, several works were made to elucidate the cause of the deactivation of the catalyst by H_2O [2,3]. In addition, the improvement of the hydrothermal stability of zeolite catalysts is one of the most important challenges upon the commercial application of the catalyst to reduce NO_x from the engine [4].

High deNO_x performance of synthetic MORs (HM and CuHM) and MOR type natural zeolite (CuNZA) was observed for the reduction of NO by hydrocarbons [5]. When H_2O is existing in the feed gas stream, NO removal activity of the catalysts reduced by the competitive adsorption of NO and H_2O on the catalyst surface [5]. CuNZA catalyst showed a peculiar water tolerance for the removal reaction, which might be

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due to the high Si/Al ratio of the catalyst [5–7]. It is expected that CuNZA catalyst probably will also exhibit stronger hydrothermal stability for NO reduction than CuHM catalyst.

In the present study, the hydrothermal stability of CuNZA and CuHM catalysts for the reduction of NO was examined under a simulated lean NO_x wet condition. These two catalysts were dealuminated to elucidate the role of Si/Al ratio of the zeolite catalysts for their hydrothermal stability. The physicochemical properties of the catalysts after hydrothermal aging were also investigated to understand the aging mechanism of the catalyst.

2. Experimental

2.1. Catalyst preparation

A MOR type natural zeolite (NZ) mined from Youngil, Korea and synthetic MOR (Zeolon 900Na, PQ Corp.) were employed to obtain CuNZA and CuHM catalysts, respectively by ion-exchanging method. The natural zeolite was treated with a 1.0 N HCl solution at 93°C for 20 h in order to remove impurities contained in the ore and to stabilize the structure of the zeolite. Then, CuNZA catalyst was prepared by the further treatment of NZA (natural zeolite treated with the HCl solution) with a 1.5 N NH_4NO_3 solution followed by drying at 110°C for 10 h, calcining at 500°C for 10 h under air atmosphere and repeatedly soaking in a 1.0 N $Cu(NO_3)_2$ solution at 93°C for 40 h. CuHM catalyst was also obtained by the method described above. CuZSM-5 as a reference catalyst was prepared from a MFI type zeolite, HZSM-5 (Tosoh) by similar ion-exchanging method. Details for preparing the catalysts have been described elsewhere [5,6,7]. The content of Cu ions and the Si/Al ratio of the catalysts were determined by atomic absorption spectroscopy (Perkin–Elmer AAS 5100PC). The physicochemical properties of the catalysts prepared in the present study were listed in Table 1.

MOR type zeolite was dealuminated in HCl solution to increase the Si/Al ratio of the catalyst. NZA catalyst was further treated with 1.0 N HCl solution at 93°C to prepare the natural zeolite with high Si content. Then, the dealuminated CuNZA catalyst was prepared by repeatedly soaking the NZA in a 1.0 N $Cu(NO_3)_2$ solution at 93°C for 40 h. The dealuminated CuHM catalyst was similarly prepared after the dealumination of HM as described above. The degree of dealumination of HM and NZA zeolites was confirmed by a solid state ^{29}Si and ^{27}Al MAS NMR spectroscopy (Bruker DPX 300). The physicochemical properties of the dealuminated CuNZA and CuHM catalysts were also listed in Table 1.

Table 1
Physicochemical properties of MOR type zeolite catalysts employed in the present study

Catalyst	Cu content (wt%)	Si/Al	Cu/Al	Surface (m^2/g)
HM1		5		449
HM2		10		
HM3		20		449
CuHM1	2.02	6	0.16	368
CuHM2	4.20	5	0.30	
CuHM3	2.55	12	0.34	434
CuHM4	1.03	12	0.14	
CuHM5	1.73	22	0.45	450
CuNZA1	4.37	4	0.25	179
CuNZA2	1.84	10	0.24	232
CuNZA3	1.75	14	0.28	
CuNZA4	1.64	19	0.31	128
CuZSM-5	2.90	26	0.81	344

2.2. DeNO$_x$ activity of MOR type zeolite catalysts

A simulated lean-burn engine exhaust containing 1200 ppm NO, 1600 ppm C_3H_6, 3.2% O_2, 3000 ppm CO, 1000 ppm H_2, 10% CO_2, 10% H_2O and He (balance) was employed to examine NO removal activity of the fresh and dealuminated MOR type zeolite catalysts for NO reduction in a fixed-bed flow reactor system. The deNO_x activity of the catalyst was observed before and after the hydrothermal aging at 800°C for 4–24 h in the presence of 10% H_2O. It should be noted that the deNO_x activity maintenance of the aged catalyst might simply reveal the hydrothermal stability of the catalyst for NO reduction under the lean-burn wet condition. Total gas flow rate was 300 cm^3/min, which corresponds to the reactor space velocity of 14 000/h. Reactants and products were analyzed by an on-line gas chromatograph (Hewlett–Packard 5890 Series II) equipped with TCD for N_2, O_2 and CO by 13X molecular-sieve column and with FID for hydrocarbons, CO_2 and N_2O by Porapak Q column.

NO removal activity of the catalysts was evaluated in terms of the conversion of NO into N_2 as $2[N_2]_{out}/[NO]_{in}$.

2.3. Catalyst characterization

Solid state ^{29}Si and ^{27}Al MAS NMR analysis for HM and NZA zeolites with respect to the degree of the catalyst dealumination were carried out [6]. At the magnetic field of 7.05 T, the frequencies of ^{29}Si and ^{27}Al are 59.6 and 78.2 MHz, respectively. A spectral width of 23.8 kHz, an acquisition time of 0.086 s, and a delay time between pulses of 2 s were used for the recording of both ^{29}Si and ^{27}Al NMR spectra. Pulse lengths of 0.01 and 0.003 ms for ^{29}Si and ^{27}Al NMR spectra, respectively, were also selected to ensure the uniform excitation of low and high electric field gradients.

X-ray powder diffraction of the catalyst was examined by a M18XHF diffractometer (MAC Science) with Ni-filtered Cu Kα radiation. ESR measurements were carried out with a Bruker ER 200D-SCR spectrometer operated in the X-band microwave frequency of 9.45 GHZ. ESR spectra were recorded at room temperature. Prior to each measurement, the catalyst was dehydrated at 500°C for 2 h under the flow of 5% oxygen in He balance, followed by evacuation at room temperature.

3. Results and discussion

3.1. Hydrothermal stability of MOR type zeolite catalysts

CuNZA catalyst prepared from a MOR type natural zeolite has shown strong water tolerance for the reduction of NO by hydrocarbons such as C_3H_6 and C_2H_4 [5,6]. When 7.3% H_2O exists in the feed gas stream, CuNZA exhibited the loss of deNO$_x$ activity <5% for NO reduction by C_3H_6, while the significant decrease of NO removal activity has been observed for CuHM catalyst under the similar reaction condition [5,6]. Therefore, it is expected that CuNZA catalyst may reveal better hydrothermal stability for NO reduction than CuHM.

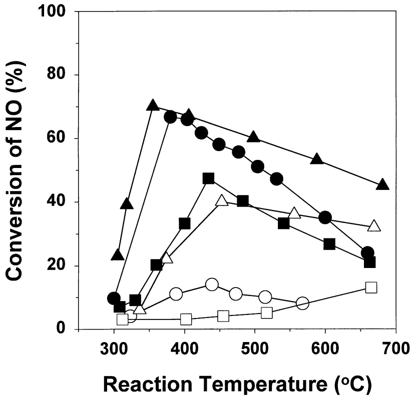

Fig. 1. Hydrothermal stability of CuNZA2 (●, ○), CuHM1 (■, □) and CuZSM-5 (▲, △) catalysts. Closed and open symbols indicated fresh catalysts and hydrothermally aged ones at 800°C for 6 h in the presence of 10% H_2O, respectively.

Fig. 1 presents the hydrothermal stability of CuNZA2 and CuHM1 catalysts for NO reduction under the lean NO$_x$ wet condition. When the catalysts were aged at 800°C with 10% H_2O for 6 h, CuHM1 catalyst exhibited the deNO$_x$ efficiency <5% at 450°C, while 15% of NO conversion remained at the reaction temperature for CuNZA2. It reveals that CuNZA2 catalyst contains stronger hydrothermal stability for NO reduction than CuHM1. It may be due to the higher Si/Al ratio of CuNZA2 catalyst than that of CuHM1, as listed in Table 1. Such a speculation may be supported by the highest hydrothermal stability of CuZSM-5 employed as a reference catalyst in the present study. The catalyst after the aging still exhibited 40% of NO conversion at 450°C.

When CuNZA2 and CuHM1 catalysts were aged at 800°C for 24 h in the presence of 10% H_2O, the deNO$_x$ performance at the reaction temperatures covered in the present work was hardly observed, while CuZSM-5 catalyst still revealed ca. 40% of NO removal activity at 450°C. However, no activity was found for the CuZSM-5 catalyst when aged at 900°C with 10% H_2O for 24 h. The activity maintenance of CuHM1, CuNZA2 and CuZSM-5 catalysts was proportional to the Si/Al ratio of the catalyst [8]. It suggests that the hydrothermal stability of zeolite catalyst for NO reduction reaction under the lean NO$_x$ wet condition primarily depends on the Si content of the catalysts. When H_2O was eliminated from the feed gas stream, 10–15% of NO conversion for the catalysts was restored. Note that the effect of H_2O on the catalytic performance of the zeolite catalyst was fully reversible for this catalytic system as observed in the previous studies [1,2,5,6].

3.2. $DeNO_x$ activity of dealuminated MOR type zeolite catalysts

As discussed in Fig. 1, the higher the Si/Al ratio of CuHM1, CuNZA2 and CuZSM-5 catalysts as listed in Table 1, the stronger the hydrothermal stability of the catalyst was obtained for NO removal reaction. It suggests that the Si content of the catalyst plays an important role for the maintenance of the hydrothermal stability of zeolite catalysts for NO reduction. However, the zeolite structure of the catalysts examined is not identical to each other. Therefore, the identical MOR type zeolite catalysts containing the variety of Si contents were prepared by the dealumination to clearly elucidate the role of Si/Al ratio of the zeolite catalyst for the present catalytic system.

Fig. 2 shows the solid state ^{29}Si MAS NMR spectra of synthetic MOR (HM1) catalyst upon the dealumination. The ^{29}Si NMR spectrum of HM1 catalyst without dealumination exhibits two intense broad peaks at −107.5 and −111.6 ppm for Si(1Al) and Si(0Al), respectively and a very weak low-field shoulder at ca. −98.7 ppm for Si(2Al). It well agrees with the ^{29}Si NMR spectra of synthetic mordenite examined by the previous studies [9,10]. When the HM1 catalyst was progressively dealuminated, the intensity of the NMR peaks at −107.5 and −98.7 ppm gradually decreased as observed for HM2 and HM3 catalysts. Similar NMR peaks at ca. −107.7 and −111.4 ppm were also observed for NZA with the weak shoulder at −98.3 ppm, and the intensity of the peaks was significantly reduced with respect to the degree of the dealumination of the catalyst. It indicates that the framework aluminum contained in HM and NZA catalysts were successfully removed from the structure of the zeolites.

Fig. 3 presents the activity of the dealuminated CuHM catalysts for NO reduction under the simulated lean NO_x wet condition. About 45% of NO conversion at the reaction temperature of 450°C were observed for CuHM1 catalyst. When the Si/Al ratio of the CuHM1 catalyst increased by the dealumination, NO removal activity in the range of the reaction temperatures covered in the present study was significantly improved as observed for CuHM3 and CuHM5 catalysts in Fig. 3. Such an improvement of the catalytic activity upon the dealumination may be primarily due to the increase of Si/Al ratio of the catalyst. However, the contribution of Cu/Al ratio of the catalysts to the improvement of NO removal activity can not be excluded, since Cu/Al ratio of CuHM3 and CuHM5 catalysts is higher than that of CuHM1 catalyst.

To clearly elucidate the cause of the significant enhancement of the $deNO_x$ activity over the dealuminated CuHM catalysts, the activity of the catalysts containing the variety of Si/Al and Cu/Al ratios was examined in Fig. 4. The Si/Al ratio of CuHM1 catalyst is quite similar to that of CuHM2 catalyst, while these

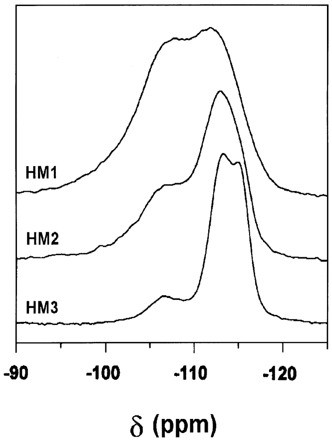

Fig. 2. Solid state ^{29}Si MAS NMR spectra of the dealuminated HM catalysts.

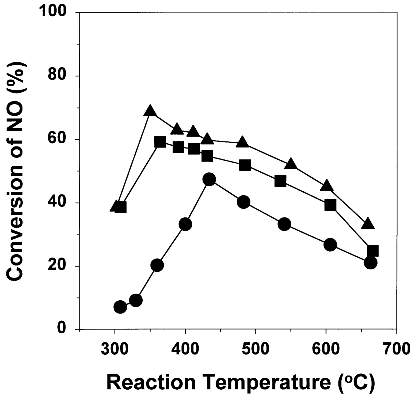

Fig. 3. NO removal activity of the dealuminated CuHM catalysts: (●) CuHM1; (■) CuHM3; (▲) CuHM5.

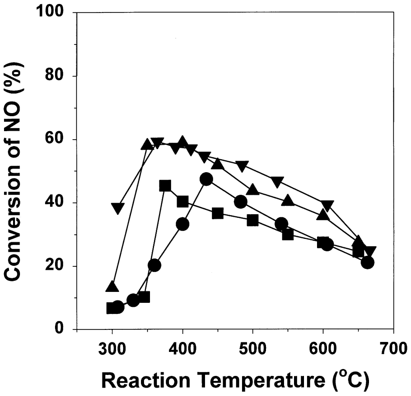

Fig. 4. Effect of Si/Al and Cu/Al ratios of the dealuminated CuHM catalysts on their NO removal activity: (●) CuHM1; (■) CuHM2; (▼) CuHM3; (▲) CuHM4.

two catalysts contain Cu/Al ratios of 0.16 and 0.30, respectively. However, the conversion of NO was not distinctive for the catalysts, even though the reaction temperature exhibiting the maximum NO removal activity of the catalysts is slightly shifted. For CuHM1 and CuHM4 catalysts containing similar Cu/Al ratios, the significant improvement of the deNO$_x$ activity at the reaction temperatures covered in the present work was observed by the dealumination of the catalysts. It primarily indicates that the enhancement of NO removal activity of CuHM catalyst upon the dealumination was not due to the Cu/Al ratio of the catalyst. It could be also supported not only from the distinctive deNO$_x$ activity of CuHM2 and CuHM3, but also from the similar performance of CuHM3 and CuHM4 catalysts. Therefore, the improvement of NO removal activity of CuHM catalyst by the dealumination under the lean NO$_x$ wet condition was mainly attributed to the increase of the Si/Al ratio of the catalyst.

Fig. 5 shows the deNO$_x$ performance of CuNZA catalyst prepared from MOR type natural zeolite for NO reduction with respect to the Si contents of the catalyst. CuNZA1 catalyst exhibited 50% of NO removal activity at the reaction temperatures ranged from 400 to 450°C. When the catalyst is dealuminated, the activity of the catalyst is significantly improved at the reaction temperatures examined in the present study as observed for CuNZA2 and CuNZA3 catalysts. It should be noted that all three catalysts contain the similar Cu/Al ratio as listed in Table 1. It indicates that the Si/Al ratio of the catalyst again plays a critical role for the improvement of NO removal activity of the dealuminated CuNZA catalysts.

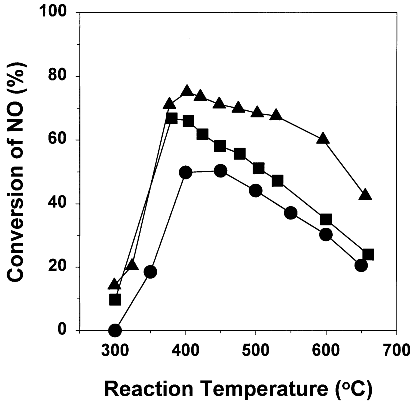

Fig. 5. NO removal activity of the dealuminated CuNZA catalysts: (●) CuNZA1; (■) CuNZA2; (▲) CuNZA3.

To understand the main reason for the high performance of the deNO$_x$ activity over MOR type zeolite catalysts as the Si contents of the catalysts increases by the dealumination, TPD experiments of H_2O were made for the catalysts as shown in Fig. 6. The primary desorption of H_2O from the surface of CuHM1 catalyst was observed at the temperature up to 450°C, and of CuHM5 catalyst up to 350°C. By the comparison of the amount and the temperature of H_2O desorption, CuHM1 catalyst contains larger H_2O adsorption capacity than CuHM5. The highest hydrophobicity of CuHM5 might be primarily due to the high Si/Al ratio of the catalyst. It is generally known that the surface

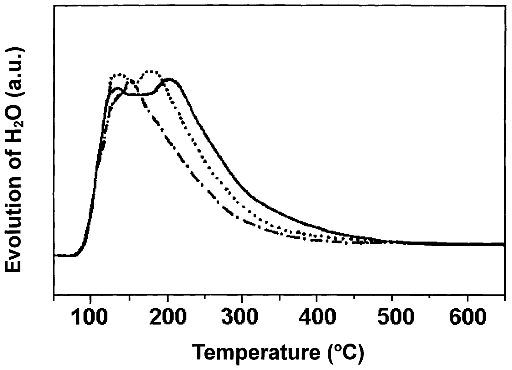

Fig. 6. H_2O TPD for dealuminated CuHM catalysts: (—) CuHM1; (. . .) CuHM3; (-·-) CuHM5. The temperature ramping rate was 10°C/min and the flow rate of He as a carrier gas was 40 cm^3/min.

of zeolite catalyst becomes hydrophobic as the Si/Al ratio of zeolite increases.

Recently, it was observed that CuNZA catalyst containing the Si/Al ratio of 9.2 was much more hydrophobic than HM and CuHM containing 5.2 of the ratio [6]. The hydrophobicity of ZSM-5 as a MFI type zeolite also becomes stronger when the Si/Al ratio of the zeolite increases [11]. The amount of H_2O adsorption on the surface of zeolite catalysts generally decreases as the ratio increases. Kim et al. [6] reported that the deNO$_x$ activity of a MOR type zeolite catalyst was mainly reduced by the competitive adsorption of NO and H_2O on the catalyst surface. Therefore, the significant increase of NO removal activity of the dealuminated CuHM catalysts such as CuHM3 and CuHM5 was mainly due to the increase of the Si/Al ratio of the catalysts. In addition, the adsorption of C_3H_6 on the zeolite is also improved by the dealumination. It well agreed with the increase of the surface organophilicity of zeolites upon the dealumination [11]. Such a modified surface characteristic of the dealuminated catalyst might be a source of the improvement of NO removal activity for this reaction system.

3.3. Hydrothermal stability of dealuminated MOR type zeolite catalysts

When CuNZA2, CuHM1 and CuZSM-5 catalysts were aged at 800°C for 6 h in the presence of 10% H_2O, the maintenance of the deNO$_x$ activity of the catalysts for NO mainly depends on the Si/Al ratio of the catalysts shown in Fig. 1. As the ratio of the catalyst increases, the hydrothermal stability of the catalyst significantly improves. The dealuminated CuHM and CuNZA catalysts also exhibited higher NO removal activity than the fresh catalysts before dealumination as revealed in Figs. 3 and 5. It was simply due to the increase of the Si contents of the catalysts as discussed. Such an increase of the ratio could provide the hydrophobic surface of the catalyst, which may compensate the degree of the loss of the deNO$_x$ activity of the catalysts under the lean NO$_x$ wet condition. Therefore, it is easily expected that the dealuminated MOR type zeolite reveals the strong hydrothermal stability of the catalysts for NO reduction under the lean NO$_x$ wet condition.

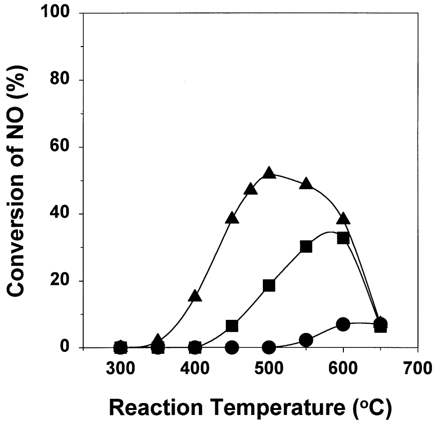

Fig. 7. Hydrothermal stability of dealuminated CuHM catalysts: (●) CuHM1; (■) CuHM3; (▲) CuHM5. The catalysts were aged at 800°C for 24 h in the presence of 10% H_2O.

Fig. 7 exhibits the hydrothermal stability of the dealuminated CuHM catalysts for this catalytic system. CuHM1 catalyst revealed ca. 50% of NO conversion at 450°C as depicted in Fig. 3. No performance at the reaction temperatures below 550°C was, however observed for the catalyst aged at 800°C with 10% H_2O for 24 h. 20% of NO conversion at the reaction temperature of 500°C was attained for CuHM3 catalyst containing the Si/Al ratio of 12. Especially, CuHM5 catalyst exhibited >50% of NO conversion at the reaction temperature even after the hydrothermal aging. Note that the fresh CuHM3 and CuHM5 catalysts revealed NO removal activity of ca. 50 and 60%, respectively as shown in Fig. 3.

As observed in Figs. 3 and 7, the loss of NO conversion for CuHM1, CuHM3 and CuHM5 catalysts at the reaction temperature of 500°C was ca. 40, 30 and 10%, respectively. The activity maintenance of the catalyst after the aging was also in the order of CuHM1 (0%) < CuHM3 (20%) < CuHM5 (50%) at 500°C. It clearly presents that the hydrothermal stability of CuHM catalysts was significantly improved by the increase of the Si content of the catalyst. It also illustrates that the Si content of CuHM catalysts is one of the crucial characteristics of the catalyst determining the hydrothermal stability for this catalytic system. In addition, CuHM5 catalyst exhibits stronger hydrothermal stability than CuZSM-5 containing the highest Si contents among the catalysts examined in the present study. It should be noted that the notable

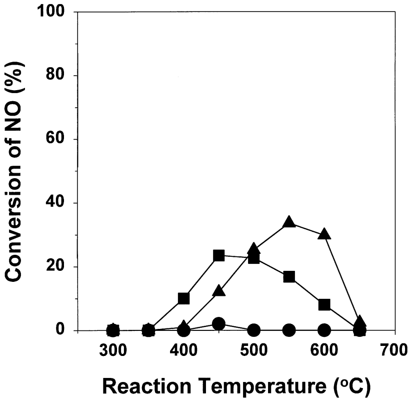

Fig. 8. Hydrothermal stability of dealuminated CuNZA catalysts: (●) CuNZA2; (■) CuNZA3; (▲) CuNZA4. The catalysts were aged at 800°C for 24 h in the presence of 10% H_2O.

improvement of the hydrothermal stability of the dealuminated catalysts was not simply due to the distinctive Cu/Al ratios of the catalyst as discussed.

The role of the Si/Al ratio of MOR type natural zeolite for the hydrothermal stability of the catalyst was also examined. Fig. 8 shows the activity maintenance of the dealuminated CuNZA catalysts for NO removal reaction after the hydrothermal aging at 800°C for 24 h in the presence of 10% H_2O. No catalytic activity was observed for CuNZA2 catalyst, while CuNZA3 catalyst exhibited NO removal activity higher than 20% at 450°C. For CuNZA4 catalyst, the maximum NO conversion of 35% appeared at 550°C where which is higher than the temperature for CuNZA2 and CuNZA3 catalysts.

Fresh CuNZA2, CuNZA3 and CuNZA4 catalysts showed NO conversion of 58% at 450°C, 72% at the 450°C and 57% at 550°C, respectively. However, the catalysts after the aging exhibited 0, 25 and 35% of NO conversion as shown in Fig. 8. It presents that the degree of the activity loss of the three catalysts by the hydrothermal aging was in the order of CuNZA2 > CuNZA3 > CuNZA4. It also reveals that the hydrothermal stability of CuNZA catalyst prepared from MOR type natural zeolite is again significantly improved by the increase of the Si/Al ratio of the catalyst as the dealumination proceeds. It evidently supports that the Si content of MOR type zeolites may be the most important characteristics of the catalyst determining the hydrothermal stability of the catalyst.

3.4. Characteristics of MOR type zeolite catalysts by hydrothermal aging

3.4.1. BET surface area

The hydrothermally aged catalysts were characterized to elucidate the cause of the activity loss upon the inactivation of the catalysts. Table 2 shows the change of the surface area of the catalysts employed in the present study, when they were aged at 800°C in the presence of 10% H_2O. The surface area of fresh CuNZA2 catalyst revealing the deNO$_x$ activity of 55% at 450°C is 232 m^2/g. When the catalyst was hydrothermally aged at 800°C, the gradual loss of the surface area was observed with respect to the inactivation time. The catalyst aged at 800°C with 10% H_2O for 6 h only retained 64 m^2/g of the surface area. About 15% of NO conversion at the reaction temperature of 450°C still remained for CuNZA2 catalyst aged for 6 h. For 24 h of the aging duration, no NO removal activity of the catalyst was attained, and the surface area of the catalyst notably decreased down to 26 m^2/g. Such a decreasing trend in the surface area of the catalyst well agreed with the degree of the catalytic activity loss for NO removal reaction upon the hydrothermal aging. It presents that the cause of the reduction of NO removal activity for CuNZA2 catalyst under the lean NO$_x$wet condition was primarily

Table 2
Surface area of MOR type zeolite catalysts aged in the presence of 10% H_2O

Catalyst	Hydrothermal aging condition		Surface area (m^2/g)
	Temperature (°C)	Duration (h)	
CuHM1	Fresh		368
	800	24	22
CuHM3	Fresh		434
	800	24	154
CuHM5	Fresh		450
	800	24	330
CuNZA2	Fresh		232
	800	4	129
	800	6	64
	800	10	47
	800	24	26
CuZSM-5	Fresh		344
	800	24	249
	900	24	27

due to the loss of the catalyst surface area by the hydrothermal aging. Such a loss of the catalyst surface area also suggests the collapse of the catalyst structure upon the inactivation.

CuHM1 hydrothermally aged at 800°C for 24 h lost the surface area of the catalyst from 368 to 22 m^2/g as listed in Table 2and exhibited no deNO$_x$ activity at all. CuZSM-5 employed as a reference catalyst maintained 70% of the initial surface area of the catalyst even after the hydrothermal aging. The catalyst still exhibited 40% of NO conversion at 450°C. However, the significant loss of the surface area was observed for the catalyst when it was aged at 900°C for 24 h. It should be noted that CuZSM-5 aged at 900°C revealed no NO removal activity at all. It presents that the reduction of the surface area of the catalysts mainly depends on both the aging temperature and duration.

Based upon the degree of the loss of the catalyst surface area by the hydrothermal aging, CuZSM-5 showed stronger stability than CuNZA2 and CuHM1 catalysts. It also supported that CuZSM-5 catalyst exhibited the best maintenance of NO removal activity as observed in Fig. 1. It is again attributed to the high Si/Al ratio of the catalyst. It could be also deduced from the reduction of the surface area of the dealuminated CuHM catalysts listed in Table 2. The degree of the surface area loss for CuHM3 and CuHM5 catalysts was notably improved by the increase of the Si/Al ratio of the catalyst upon the dealumination. It well agreed with the maintenance of the deNO$_x$ activity of the catalysts as shown in Fig. 7.

3.4.2. X-ray diffraction (XRD)

When CuHM1 catalyst was hydrothermally aged at 800°C, the structural collapse of the catalyst was clearly observed by the comparison of the intensity of the XRD peak of the catalyst with respect to the aging duration as shown in Fig. 9. As the aging time increases, the structure of the catalyst was progressively destroyed. The intensity of the characteristic diffraction peaks of the catalyst aged at 800°C for 24 h was significantly reduced as depicted in Fig. 9(e). It might well reflect not only the loss of the deNO$_x$ activity of the catalyst for NO reduction under the simulated lean-burn condition but the reduction of the catalyst surface area by the hydrothermal aging.

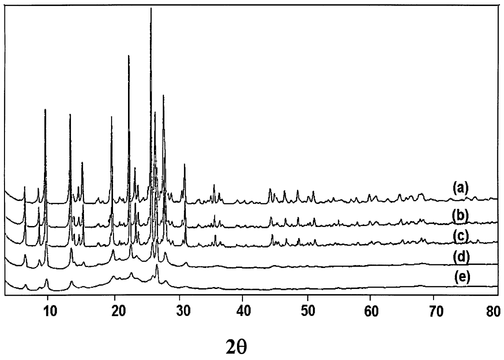

Fig. 9. X-ray powder diffraction pattern of CuHM1 catalyst. Hydrothermal aging condition: (a) fresh; (b) at 700°C without H_2O for 2 h; (c) at 700°C with 10% H_2O for 24 h; (d) at 800°C with 10% H_2O for 6 h; (e) at 800°C with 10% H_2O for 24 h.

Although the remarkable decrease of XRD peak intensity by the hydrothermal aging was also observed for CuNZA2 and CuZSM-5 catalysts, the degree of the reduction of the peak intensity was much weaker than CuHM1 catalyst. For the dealuminated catalysts, the structural destruction of the catalysts examined by XRD well agreed with the activity maintenance of the catalyst. Again the Si/Al ratio of the catalyst plays an important role for the destruction of zeolite structure by aging as expected.

3.4.3. Electron spin resonance (ESR)

The destruction of the catalyst structure upon the hydrothermal aging may alter the ionic state of Cu^{2+} ions on the catalyst surface. It is well known that the copper ions contained in the zeolite catalyst play a major role for the reduction of NO by NH_3 as well as by hydrocarbons [12–15]. An alteration of the chemical environment of Cu^{2+} ions on the catalyst surface was examined by ESR spectra for the hydrothermally aged catalysts.

As shown in Fig. 10, the low field hyperfine structure of CuHM1 catalyst was notably reduced when it is aged at 800°C with 10% H_2O for 24 h. It suggests that Cu^{2+} ions on the catalyst surface were probably transferred to copper oxide species by the sintering of the metal ions through the structural collapse of the catalyst. Such an alteration of the copper ions was similarly observed for CuNZA2 and CuZSM-5 catalysts after the hydrothermal aging. It reveals that the loss of Cu^{2+} ions on the catalyst surface occurred upon

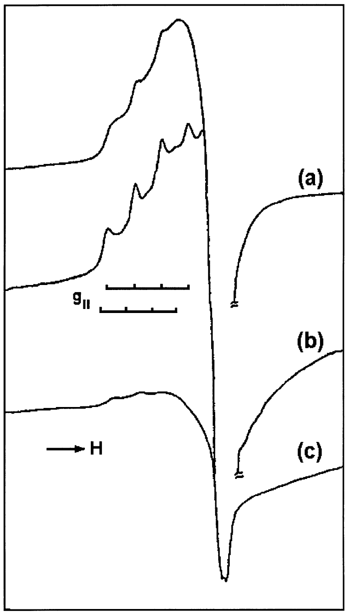

Fig. 10. Cu^{2+} ESR spectra of CuHM1 catalyst. Hydrothermal aging condition: (a) fresh; (b) at 700°C without H_2O for 2 h; (c) at 800°C with 10% H_2O for 24 h.

the hydrothermal aging and thereby created the significant loss of NO removal activity of the catalysts. Cu K-edge absorption for the aged catalysts examined in this study is under investigation to further identify the final form of copper compounds on the catalyst surface.

4. Conclusions

The hydrothermal stability of the zeolite catalysts for NO reduction by hydrocarbons becomes stronger as the Si/Al ratio increases, regardless of the types of zeolite employed in the present study. It is evident that the Si/Al ratio of the zeolite catalyst is one of the most critical properties determining the hydrothermal stability of the catalyst for this catalytic system. The loss of NO removal activity of the zeolite catalysts was mainly due to the chemical alteration of Cu^{2+} ions on the catalyst surface by the sintering of the metal ions through the collapse of the zeolite structure resulting the significant reduction of the catalyst surface area.

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