

## Effect of Si/Al ratio of Mordenite and ZSM-5 type Zeolite Catalysts on Hydrothermal Stability for NO Reduction by Hydrocarbons

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### 1. INTRODUCTION

One of the most urgent and demanding challenges in environmental catalysis is to abate NO produced on a massive scale from lean-burn gasoline and diesel engines. The discovery by Iwamoto et al. that copper-ion-exchanged ZSM-5 (CuZSM-5) zeolite is much more active than earlier catalysts for selective catalytic reduction of NO in an oxidizing atmosphere by hydrocarbon has led to a tremendous interest in the use of a wide variety of transition-metal ions exchanged into zeolites with different framework structures and compositions as a catalyst for this reaction system [1]. However, there is a serious drawback in the practical application of transition-metal-ion-exchanged zeolites including CuZSM-5 to lean-burn engines, due to poor stability under hydrothermal conditions [1,2]. Thus, considerable effort has been made to elucidate the origin of the deactivation of the catalyst by H<sub>2</sub>O [2,3].

Recently, it has been shown that mordenite (MOR) zeolites in both synthetic (HM and CuHM) and natural (CuNZA) forms are highly active for the reduction of NO by hydrocarbons [4]. It was also observed that in the presence of H<sub>2</sub>O, the CuHM catalyst loses significantly its deNO<sub>x</sub> activity by the competitive adsorption of NO and H<sub>2</sub>O on the catalyst surface. Unlike CuHM, however, the CuNZA catalyst showed a peculiar water tolerance for NO removal reaction [4,5]. This result was rationalized by suggesting that the hydrothermal stability of CuNZA for NO reduction would be better than CuHM, because of its higher Si/Al ratio. In the present study, the hydrothermal stability of CuNZA, CuHM and CuZSM-5 with

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different Si/Al ratios for the NO reduction under a simulated lean NO<sub>x</sub> condition has been systematically reported. In addition, changes in the physicochemical properties of the catalysts induced by hydrothermal aging are also investigated to understand the catalyst deactivation behavior.

## 2. EXPERIMENTAL

A MOR type natural zeolite (NZ), mined from Youngil, Korea [6], and a synthetic MOR (Zeolon 900Na, PQ Corp.) were employed to obtain CuNZA and CuHM, respectively. Prior to Cu<sup>2+</sup> ion exchange, these two MOR materials were also dealuminated by acid treatment and steaming to increase Si/Al ratio in the zeolite. Five CuZSM-5 catalysts with Si/Al ratios ranging from 14 to 95 were prepared using the corresponding HZSM-5 purchased from Tosoh Corp. All Cu<sup>2+</sup>-exchanged zeolite catalysts were prepared by conventional liquid-phase and solid-state ion exchange methods that are described elsewhere [4,5]. Chemical analysis for Si, Al, Cu in catalysts was performed by AA. The degree of dealumination of the zeolites was confirmed by <sup>29</sup>Si and <sup>27</sup>Al MAS NMR. The physicochemical properties of zeolite catalysts employed in this study are listed in Table 1. A simulated lean-burn condition containing 1,200 ppm NO, 1,600 ppm C<sub>3</sub>H<sub>6</sub>, 3.2% O<sub>2</sub>, 3,000 ppm CO, 1,000 ppm H<sub>2</sub>, 10% CO<sub>2</sub>, 10% H<sub>2</sub>O and He (balance) was employed to examine the hydrothermal stability of the catalysts. The reaction products were analyzed by on-line gas chromatograph (Hewlett Packard 5890 Series II). The hydrothermally aged catalysts were characterized by XRD, ESR, XANES and BET measurements to investigate the cause of the catalyst deactivation.

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

Catalyst	Cu content (wt.%)	Si/Al	Cu/Al	Surface area (m <sup>2</sup> /g)
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-5-1	2.49	14	0.53	350
CuZSM-5-2	2.90	26	0.81	344
CuZSM-5-3	1.43	27	0.50	
CuZSM-5-4	1.20	34	0.53	400
CuZSM-5-5	0.44	95	0.52	330

### 3. RESULTS AND DISCUSSION

#### 3.1 Hydrothermal stability of MOR and MFI type zeolite catalysts

Figure 1 shows the hydrothermal stability of CuNZA2, CuHM1 and CuZSM-5-2 catalysts for NO reduction under the lean NO<sub>x</sub> condition. When the catalysts were aged at 800°C with 10% H<sub>2</sub>O for 6 h, the CuHM1 catalyst exhibited a deNO<sub>x</sub> efficiency of less than 5% at 450 °C, while 15 and 40% of NO conversion were still observed for CuNZA2 and CuZSM-5-2, respectively. Thus, the CuZSM-5-2 catalyst was found to exhibit the highest hydrothermal stability for NO reduction among these three types of zeolite catalysts. Another important observation is that the activity maintenance of the catalysts was proportional to the Si/Al ratio of the catalyst. This clearly shows that the hydrothermal stability of zeolite catalysts for NO reduction under the lean NO<sub>x</sub> condition primarily depends on the Si/Al ratio of the catalyst, despite the differences in the zeolite structure.

To further elucidate the role of Si/Al ratio of the catalysts for the hydrothermal stability, MOR type zeolite catalysts with different Si/Al ratio were examined. Figure 2 shows that deNO<sub>x</sub> activity of CuNZA catalyst was significantly improved by dealumination. Especially, the CuNZA4 catalyst with a Si/Al ratio of 19 still showed more than 35% of NO conversion at 550°C even after the aging at 800°C with 10% H<sub>2</sub>O for 24 h.

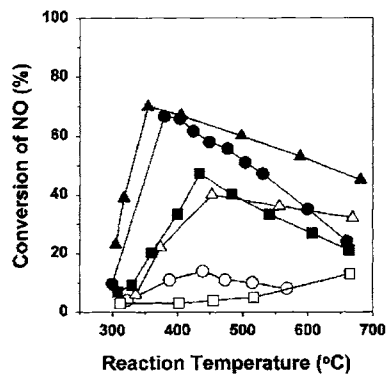


Figure 1. Hydrothermal stability of CuNZA2 (●,○), CuHM1 (■,□) and CuZSM-5-2 (▲,△) catalysts. Closed and open symbols indicate fresh catalysts and hydrothermally aged ones at 800°C for 6 h with 10% H<sub>2</sub>O, respectively.

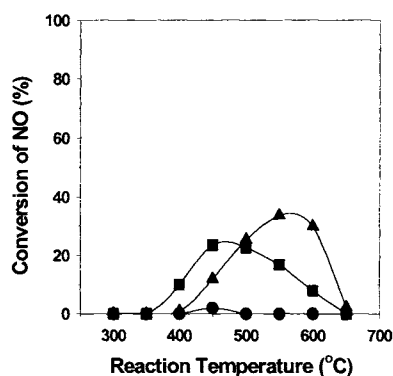


Figure 2. Hydrothermal stability of the dealuminated CuNZA catalysts: CuNZA2 (●), CuNZA3 (■) and CuNZA4 (▲). These catalysts were hydrothermally aged at 800°C for 24 h with 10% H<sub>2</sub>O.

#### 3.2 Effect of Si/Al ratio of MOR and MFI type zeolite catalysts

To understand the origin of the significant enhancement of the deNO<sub>x</sub> activity over the dealuminated CuHM catalysts, the activities of CuHM catalysts with different Si/Al and Cu/Al ratios have been examined and are given in Figure 3. Note that the Si/Al ratio of

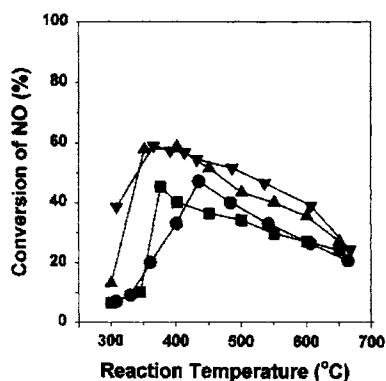


Figure 3. Effect of Si/Al and Cu/Al ratios of the dealuminated CuHM catalysts on their NO removal activity : CuHM1 (●), CuHM2 (■), CuHM3 (▼) and CuHM4 (▲).

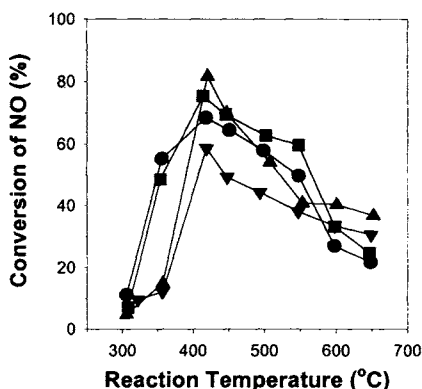


Figure 4. Effect of Si/Al ratio of the CuZSM-5 catalysts on their NO removal activity : CuZSM-5-1 (●), CuZSM-5-3 (■), CuZSM-5-4 (▲) and CuZSM-5-5 (▼).

CuHM1 is quite similar to that of CuHM2, while these two catalysts contain Cu/Al ratios of 0.16 and 0.30, respectively. However, the conversion of NO was found to be 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 with similar Cu/Al ratios, on the contrary, a significant improvement in the deNO<sub>x</sub> activity was observed after dealumination. A similar result was also observed from the distinctive deNO<sub>x</sub> activities of CuHM2 and CuHM3. Therefore, the improvement in the NO removal activity of CuHM catalysts upon dealumination cannot be attributed to the difference in Cu/Al ratio of the catalyst but the increase in Si/Al ratio. This speculation can be further supported by the catalytic results obtained from CuNZA and CuZSM-5 with different Si/Al ratios. Figure 4 shows NO removal activity of CuZSM-5 with similar Cu/Al ratios. There may be an optimal Si/Al ratio for CuZSM-5 catalyst to remove NO by hydrocarbons. Therefore, it is most likely that the Si/Al ratio of the zeolite catalyst is still one of the most critical properties determining NO removal activity of the catalyst for this reaction system.

### 3.3 Characterization of the zeolite catalysts

When CuZSM-5-2 catalyst was hydrothermally aged at 900°C, structural collapse of the catalyst was clearly observed by a comparison of the intensity of the XRD peak of the catalyst with respect to the aging duration shown in Figure 5. As the aging time and temperature increase, the structure of the catalyst was progressively destroyed. Thus, the intensity of the characteristic diffraction peaks of the catalyst aged at 900°C for 24 h was significantly reduced as depicted in Figure 5(f). This might well reflect not only the loss of the deNO<sub>x</sub> activity of the catalyst but also the reduction of the catalyst surface area by hydrothermal aging. A remarkable decrease of XRD peak intensity by hydrothermal aging

was also observed for CuHM1 and CuNZA2 catalysts. For the dealuminated catalysts, the degree of structural destruction of the catalysts examined by XRD well agreed with the rate of the activity maintenance of the catalyst. This again supports the speculation that the Si/Al ratio of the catalyst plays an important role for the destruction of zeolite structure by hydrothermal aging as expected.

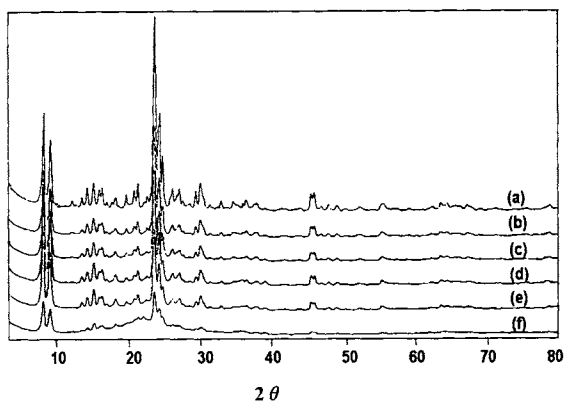


Figure 5. X-ray powder diffraction pattern of CuZSM-5-2 catalysts : (a) fresh, (b) aged at 700°C without H<sub>2</sub>O for 2 h, (c) aged at 800°C with 10% H<sub>2</sub>O for 4 h, (d) aged at 800°C with 10% H<sub>2</sub>O for 6 h, (e) aged at 800°C with 10% H<sub>2</sub>O for 24 h and (f) aged at 900°C with 10% H<sub>2</sub>O for 24 h.

The destruction of the catalyst structure upon the hydrothermal aging may alter the ionic state of Cu<sup>2+</sup> ions on the catalyst surface. An alteration of the chemical environment of Cu<sup>2+</sup> ions on the hydrothermally aged catalyst surface was examined by ESR as shown in Figure 6. The low field hyperfine structure of CuZSM-5-2 catalyst was notably reduced when aged at 900°C with 10% H<sub>2</sub>O for 24 h. This suggests that Cu<sup>2+</sup> 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 Cu<sup>2+</sup> ions was also observed for CuHM1 and CuNZA2 catalysts after hydrothermal aging. Therefore, it is clear that the loss of Cu<sup>2+</sup> ions on the catalyst surface occurred upon hydrothermal aging and thereby caused a significant loss of NO removal activity of the catalysts.

Additionally, the alteration of Cu<sup>2+</sup> ions to the copper oxides has been confirmed by X-ray absorption near edge structure (XANES). As shown in Figures 7 and 8, isolated Cu<sup>2+</sup> ions were transformed to Cu<sub>2</sub>O after hydrothermal aging, as already examined by XRD and ESR studies. Therefore, hydrothermal aging caused the structural destruction of zeolite and the decrease of surface area, and then Cu<sup>2+</sup> ions transformed to copper oxides that may not be active reaction sites for the present reaction system. Based upon the peak intensity of Cu<sub>2</sub>O, the zeolite with a higher Si/Al ratio results in less formation of Cu<sub>2</sub>O on the catalyst surface.

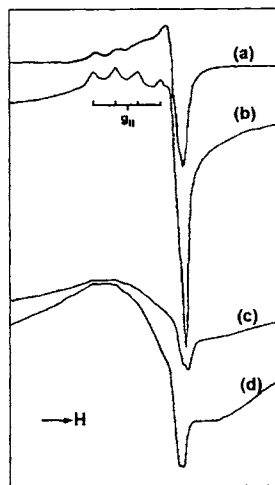


Figure 6. Cu<sup>2+</sup> ESR spectra of CuZSM-5-2 catalysts : (a) fresh, (b) aged at 800°C with 10% H<sub>2</sub>O for 4 h, (c) aged at 800°C with 10% H<sub>2</sub>O for 24 h and (d) aged at 900°C with H<sub>2</sub>O for 24 h.

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