Korean J. Chem. Eng., 17(3), 318-324 (2000)

Activity and Durability of Iron-exchanged Mordenite-type Zeolite Catalyst for the Reduction of NO by NH_3

Sung-Won Ham*, In-Sik Nam† and Young Gul Kim

Research Center for Catalytic Technology, Department of Chemical Engineering,
School of Environmental Engineering, Pohang University of Science &
Technology (POSTECH)/Research Institute of Industrial Science &
Technology (RIST), Pohang 790-330, Korea

(Received 9 November 1999 • accepted 11 February 2000)

Abstract−NO removal activity and the durability of iron-exchanged mordenite type zeolite catalyst (FeHM) have been examined in a continuous fixed bed flow reactor. The catalytic activity for NO reduction by NH_3 in the presence of oxygen was much higher than that in the absence of oxygen, and it was fully reversible with respect to the presence of oxygen in the feed gas stream. The oxidation ability of SCR catalysts including FeHM was critical for both reactions of NH_3 and SO_2 oxidation, thus for the NO removal activity and its sulfur tolerance. The maximum conversion of NO for FeHM catalyst with respect to the reaction temperature shifted to the higher temperature due to its mild oxidation ability. The deactivation behaviors such as the changes of the physicochemical properties of the catalyst and the loss of NO removal activity induced by SO_2 could not be distinguished, regardless of the metals exchanged in zeolite. However, the amount of deactivating agents deposited on the catalyst surface depended on the species of metals exchanged on the mordenite type zeolite, which was mainly attributed to the oxidation ability of metals for SO_2 conversion to SO_3.

Key words: Selective Catalytic Reduction, Nitric Oxide, Iron-exchanged Mordenite, Deactivation

INTRODUCTION

A catalyst employed in a commercial SCR process must possess high NO removal activity and selectivity, since the volume of the flue gas containing NO_x is extraordinarily large. Besides these requirements for a SCR catalyst, it should also exhibit the durability to the poisoning by SO_x commonly contained in the flue gas stream. Vanadia-titania-based catalysts have been most widely employed as a commercial SCR catalyst, since they reveal high NO removal activity and durability to the poisoning by sulfur compounds. However, the efforts still continue to develop "better" SCR catalyst, since there is a strong economic incentive for the development of highly active and durable catalyst.

The transition metal-exchanged zeolites have been investigated as a SCR catalyst due to the unique properties of zeolite such as metals exchanging and framework [Seiyama et al., 1977; Iizuka and Lunsford 1978; Kiovsky et al., 1980; Amiridis et al., 1993]. The NO removal activity and the sulfur poisoning of copper exchanged mordenite (CuHM) have been systematically studied in previous work [Ham et al., 1995; Chung et al., 1996]. CuHM catalyst showed high NO removal activity and sulfur tolerance depending on the reaction temperatures. However, the oxidation capability of CuHM catalyst for both NH_3 and SO_2 oxidation reactions was also enhanced by the increase of catalyst copper contents and thus narrowed the operating temperature window of SCR process including maximum NO conversion. This might cause severe catalyst deactivation and operational problems. It indicates that NO removal activity and the deactivation of mordenite zeolite by SO_2 are strongly influenced by the exchanged metals having the variety of oxidizing ability for both reactions of NH_3 and SO_2 oxidation. Therefore, the aim of the present study is to improve the sulfur poisoning of copper-exchanged mordenite by the substitution of metals on the catalyst surface for NO removal by NH_3 and thus to obtain better understanding of the effect of metals exchanged in zeolite on NO removal activity and the sulfur poisoning of transition metal exchanged zeolites. Among the other transition metals, iron was chosen in the present study, since iron-based catalysts already proved its high NO removal activity [Wong and Nobe, 1986; Amiridis et al., 1993].

The alteration of the physicochemical properties of iron-exchanged mordenite catalyst such as the sulfur contents deposited on the catalyst and BET surface area was examined to understand the deactivation behaviors of the catalysts by SO_2 contained in the feed gas stream. The deactivating agents deposited on the catalyst were identified by thermal analyses. The activity for SO_2 oxidation to SO_3 was also investigated for the elucidation of the formation of deactivating agents on the catalyst surface as well as of the importance of the reaction itself for the commercial application of the SCR process employing FeHM catalyst developed in the present study. The NO removal activity and the deactivation behaviors of FeHM were compared with those of CuHM containing the similar metal content to clarify the role of metals exchanged in mordenite for the NO removal activity and the sulfur poisoning of the catalysts.

---

†To whom correspondence should be addressed.
E-mail: isnam@postech.ac.kr
*Present address: Department of Chemical Engineering, Kyungil University, Kyungsan 712-701, Korea

EXPERIMENTAL

1. Catalyst Preparation

The iron-exchanged hydrogen mordenite catalyst was prepared by ion-exchanging sodium type mordenite (NaM) obtained from P. Q. Corp. At first, 50 g of sodium mordenite (NaM) was exchanged with 1 L of NH_4Cl solution (1 M) at 90 °C for 24 h. The remained chloride ions were washed with deionized water until no formation of white AgCl precipitate by adding $AgNO_3$ to the solution. The obtained NH_4M was mixed with 1.5 L deionized water and then continuously bubbled with O_2-free He to remove the oxygen dissolved in water overnight at room temperature. After this procedure, the $FeSO_4{\cdot}7H_2O$ and 1 M H_2SO_4 were added to the solution to adjust the $FeSO_4$ concentration and pH of the solution near 3.5. Prior to ferrous cation exchange, the removal of oxygen dissolved in the solution and the control of pH of the solution should be cautiously conducted to prevent the hydrolysis at low pH and the formation of iron hydroxide at high pH [Petunchi and Hall, 1982]. The ferrous ions were exchanged at room temperature for 24 h and followed by washing, drying and then calcining in muffle furnace at 500 °C for 8 h.

The iron content of FeHM catalyst employed in this study was 1.9 wt% and designated as FeHM43. The number in the name of catalyst indicates the exchange ratio of ferric ions (Fe^{3+}) in percentage to the total exchangeable cations based on the chemical formula of mordenite. The FeHM43 catalyst contained 1.1 ferric ions per unit cell of the zeolite.

The copper-exchanged hydrogen mordenite (CuHM) catalyst was also prepared by ion-exchanging the same parent material of sodium type mordenite (NaM). The details of preparing the CuHM catalyst was already described in the previous study [Ham et al., 1995a]. The copper contents of CuHM catalyst employed in this study was 2.3 wt% and designated as CuHM31. It contained 1.2 cupric ions per unit cell of the zeolite.

2. Characterization of the Catalyst

To examine the alteration of the physicochemical properties of the catalyst due to the deactivation by SO_2, the samples of the finely ground catalyst after SCR reaction with SO_2 were employed for the catalyst characterization. The total sulfur contents of the deactivated catalysts was measured by conventional oxidation method using a LECO sulfur analyzer (SC32). BET surface area of the catalysts before and after the reaction was examined by Micromeritics Accusorb 2100E using N_2 at 77 K. For the measurement of BET surface area, the catalyst was pretreated in vacuo at 150 °C for 12 h.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the deactivated catalyst were performed by a Perkin-Elmer 1700 thermal system. The heating rate was 10 °C/min in flowing N_2. Temperature-programmed desorption (TPD) of the deactivated catalysts was carried out with the heating rate of 10 °C/min under the flow of He of 40 cc/min. The composition of the evolving gases during the TPD experiments were identified with a quadrupole-mass spectrometer (VG Instrument Ltd. MMPC-300D).

3. Reaction Apparatus and Procedures

Parametric and durability studies of the catalysts in the presence and the absence of SO_2 were conducted with a tubular downflow reactor operating under isothermal and slightly above atmospheric pressure. The details of reaction apparatus was described in previous studies [Nam et al., 1990; Ham et al., 1992]. The typical composition of the feed gas stream for the activity test is 500 ppm NO, 500 ppm NH_3, 5% O_2 and balance N_2. The reactor space velocity based on the ratio of the toal gas flowrate to the volume of the catalyst bed was 100,000 h^{-1}, otherwise specified.

The apparatus for SO_2 oxidation experiment was identical to that employed for the parametric and durability studies except the SO_3 absorption train. The reactant gases consisted of SO_2 2,000 ppm, O_2 5% and N_2 balance. Since only a small percent of SO_2 is converted to SO_3, it is extremely difficult to analyze SO_3 by GC and/or IR detector for SO_2. Therefore, SO_3 in the downstream of the reactor was absorbed into the solution of 80% isopropyl alcohol in deionized water. For the measurement of SO_3 concentration, an aliquot of the absorbing solution was titrated with 0.01 N barium perchlorate ($Ba(ClO_4)_2{\cdot}3H_2O$) using a thorin indicator [Bauerle et al., 1978].

RESULTS

1. NO Removal Activity of the Catalysts

Fig. 1 shows the activity of the catalysts employed in this study for NO reduction by NH_3 in the presence of oxygen at the reaction temperatures up to 500 °C. HM catalyst itself shows considerable activity for NO reduction and the activity is improved by the increase of the reaction temperatures. The activity of HM catalyst for NO reduction is mainly attributed to Brønsted acid sites where NH_3 can be easily adsorbed [Ramis et al., 1992; Chen and Yang, 1993; Choi et al., 1996]. The addition of iron or copper ions to HM significantly enhances NO removal activity at the relatively lower reaction temperatures compared with that of HM. The dramatic increase of the catalytic activity for NO removal of FeHM43 and CuHM31 compared with that of HM at the lower reaction temperature can be considered to be due to the iron and copper ions offering new

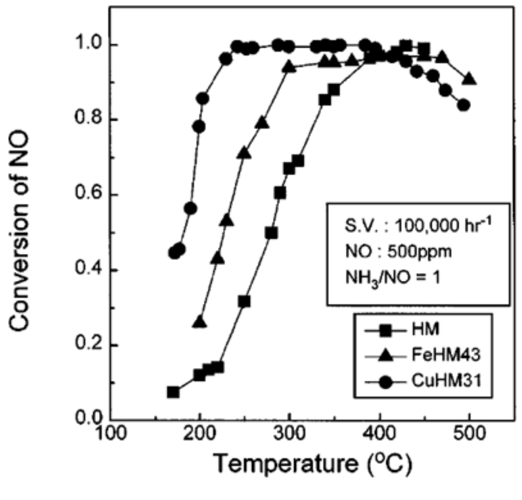

Fig. 1. NO removal activity of HM, FeHM43 and CuHM31 catalysts (Space velocity: 100,000 hr^{-1}, [O_2]=5%, [NO]=[NH_3]=500 ppm).

reaction sites on the catalyst surface [Williamson and Lunsford, 1976; Choi et al., 1991, 1996].

One of the features of the metal-exchanged mordenite catalysts for NO reduction is the exhibition of a maximum NO removal activity with respect to the reaction temperatures as observed in many other SCR catalysts [Nam et al., 1986a; Medros et al., 1989]. Comparing the NO removal activity of FeHM43 and CuHM31, it was observed that the apparent NO removal activity of FeHM43 began to decline at 470 °C much higher than that of CuHM31 at 400 °C. Since the decline of the activity at higher reaction temperatures is attributed to the onset of NH_3 oxidation reaction, it indicates FeHM43 catalyst has less activity for NH_3 oxidation reaction than CuHM31. Although FeHM43 catalyst exhibits less NO removal activity at the relatively lower reaction temperatures, the reaction temperature where the activity begins to decline is higher than that of CuHM catalyst. Consequently, the maximum conversion of NO for FeHM43 catalyst shifts to the higher reaction temperatures than that for CuHM31 catalyst. It indicates that the oxidation capability of the metals exchanged on the catalyst surface is crucial for the range of the operating temperature window for SCR process.

Fig. 2 shows the transient behavior for NO removal activity of FeHM43 catalyst with respect to the existence of oxygen in the feed gas stream at two different reaction temperatures. After the shutoff of oxygen supply to the reactor system, NO removal activity gradually decreases and reaches its steady-state conversion after an hour of the operation at 400 °C and 0.5 hour at 250 °C. The rate of the activity loss was slower at 400 °C than that at 250 °C. However, upon the addition of oxygen in the feed gas stream, the initial activity was rapidly restored within several minutes. The change of the NO removal activity was fully reversible with respect to the existence of oxygen in the feed gas stream.

Many investigators have observed that oxygen in the feed gas stream considerably increased the rate of NO reduction by NH_3 [Markvart and Pour, 1967; Takagi et al., 1976; Kiovsky et al., 1980]. Especially, for metal exchanged zeolites, the increase of NO removal activity by oxygen has been well known to be closely related to the redox couple of the exchanged metals on the catalyst surfaces [Amiridis et al., 1993; Ito et al., 1994]. It has been also observed that oxygen in the feed gas stream significantly accelerated the rate of NO reduction by NH_3 and its effect on NO removal activity was fully reversible [Ham et al., 1996]. Based upon ESR study, the redox behavior of copper ions was closely related to NO removal activity by the introduction of oxygen to the feed gas stream. The trend of the activity change of FeHM43 catalyst with respect to the existence of oxygen is quite similar to that of CuHM31 catalyst. Therefore, the effect of oxygen on NO removal activity of FeHM43 catalyst also seems to be closely related to the oxidation state of iron ions. For FeHM43 catalyst, most of iron species on the catalyst surface may be in the form of ferric ions (Fe^{3+}) under the presence of oxygen and can be easily reduced to ferrous ions (Fe^{2+}) during SCR reaction without the feed of oxygen to the reactor. This redox behavior of iron ions on zeolite leads to the fully reversible transient behavior by oxygen for this reaction stream. The NO removal reaction rate for iron-exchanged Y zeolite was also increased by the two orders of magnitude in the presence of oxygen [Amiridis et al., 1993]. It has been also observed that the loss of the catalytic activity in the absence of oxygen was related to the reduction of ferric to ferrous ions by Mössbauer spectroscopy [Schmidt et al., 1992].

2. Sulfur Poisoning of FeHM Catalyst

The effect of reaction temperature on NO removal activity of FeHM43 catalyst in the presence of 2,000 ppm SO_2 was examined in Fig. 3. The activity for NO reduction in the presence of SO_2 notably depends on the reaction temperatures. No deactivation was observed up to 12 h of the operation time at higher reaction temperatures above 350 °C. However, at the reaction temperatures below 300 °C, the activity gradually decreased with respect to the reactor on-stream time. Particularly, the activity loss was severe at 250 °C. The reaction temperature appears to be an important parameter for the catalyst deactivation. It may

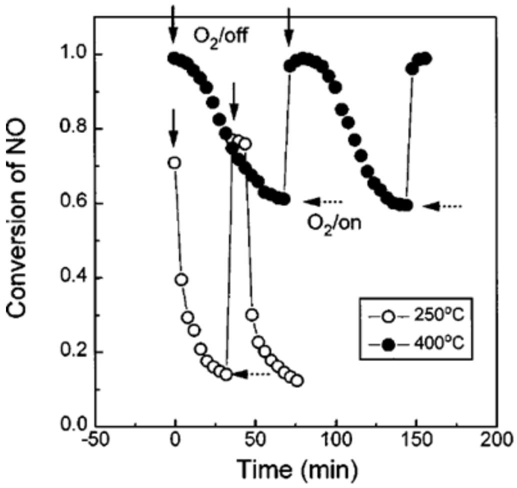

Fig. 2. Transient behavior of NO removal activity in the presence and the absence of oxygen over FeHM43 catalyst (Space velocity: 100,000 hr^{-1}, $[O_2]$=5%, [NO]=$[NH_3]$=500 ppm).

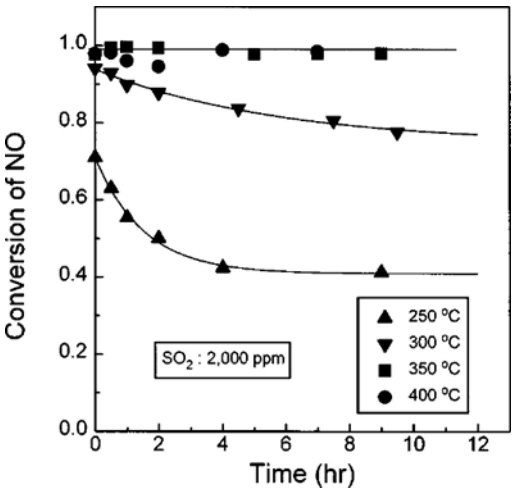

Fig. 3. Effect of reaction temperature on the deactivation of FeHM43 catalyst by SO_2 (Space velocity: 100,000 hr^{-1}, $[O_2]$=5%, [NO]=$[NH_3]$=500 ppm, $[SO_2]$=2,000 ppm).

Table 1. Physicochemical properties of FeHM43 and CuHM31 catalysts deactivated by SO_2

Catalyst	Temperature (°C)	Operating hours (h)	S content (wt. %)	Surface area (m^2/g)
FeHM43	fresh	0	0	378
	250	1.0	0.93	151
	250	12.0	1.72	51
	250	24.0	2.18	18
	400	1.0	0.52	295
	400	12.0	0.96	261
	400	24.0	1.40	203
CuHM31	fresh	0	0	467
	250	0.1	0.85	261
	250	12.0	1.98	36
	250	50.0	2.88	13
	400	0.2	0.72	402
	400	12.0	1.13	332
	400	48.0	1.78	261

also imply that the intrinsic reaction rate at the high reaction temperature can partly compensate the activity loss due to the deactivation by SO_2.

To understand the deactivation characteristics of FeHM43 catalyst by SO_2 during SCR reaction, the physicochemical properties of the deactivated catalyst such as BET surface area and the sulfur contents deposited on the catalyst were determined as listed in Table 1. The changes of physicochemical properties of FeHM43 were also compared with those of CuHM31. The BET surface area and the sulfur contents of the catalyst reveal two distinctive characteristics with respect to the reaction temperatures. Under the identical operating conditions such as the reactor on-stream time and the feed concentration of SO_2, more sulfur deposited on the catalyst surface at 250 °C than at 400 °C. It indicates that the lower the reaction temperature, the easier the sulfur compounds as a deactivating agent form on the catalyst surface. It was also observed that the amount of sulfur deposited on FeHM43 catalyst was less than that on CuHM31 catalyst under the identical operating conditions. The BET surface area gradually decreased with the increase of the reaction time and thus with the increase of sulfur contents deposited on the catalyst surface.

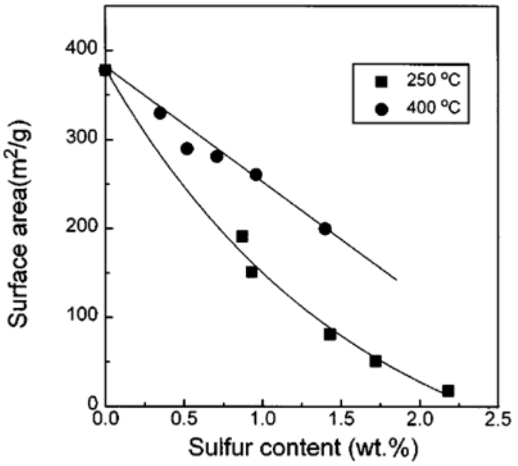

Fig. 4. Effect of sulfur contents on BET surface area of FeHM43 catalyst.

The BET surface area of the deactivated catalyst was correlated with the sulfur contents deposited on the catalyst surface to illustrate the deactivation characteristic by SO_2 as shown in Fig. 4. The change of BET surface area also shows two distinctive features depending on the reaction temperatures, i.e., a linear decrease at 400 °C of the reaction temperature and an exponential decrease at 250 °C. Therefore, the decrease of BET surface area was more pronounced at 250 °C than at 400 °C under the same level of the catalyst sulfur contents. It indicates that the deactivation modes in this reaction system vary with respect to the reaction temperatures. This type of deactivation behavior was already discussed as a proof of pore filling and blocking by a deactivating agent [Nam et al., 1986b]. At 250 °C, the deactivating agent forms near the entrance of catalyst pores causing pore blocking, while it forms in the deep inside pores creating pore filling by capillary condensations at 400 °C.

Thermal analyses such as thermogravimetric analysis (TGA), differential thermal analysis (DTA) and temperature programmed desorption (TPD) were carried out to identify the deactivating agent formed on the catalyst surface. Fig. 5 show the TGA, DTA and SO_2 TPD spectra of the deactivated FeHM43 catalyst at two distinctive reaction temperatures, i.e., 250 °C (Fig. 5A) and 400 °C (Fig. 5B), respectively. From the TGA spectra, apparent weight losses are observed at the two regions of temperatures. The first peak is believed to be mainly due to the de-

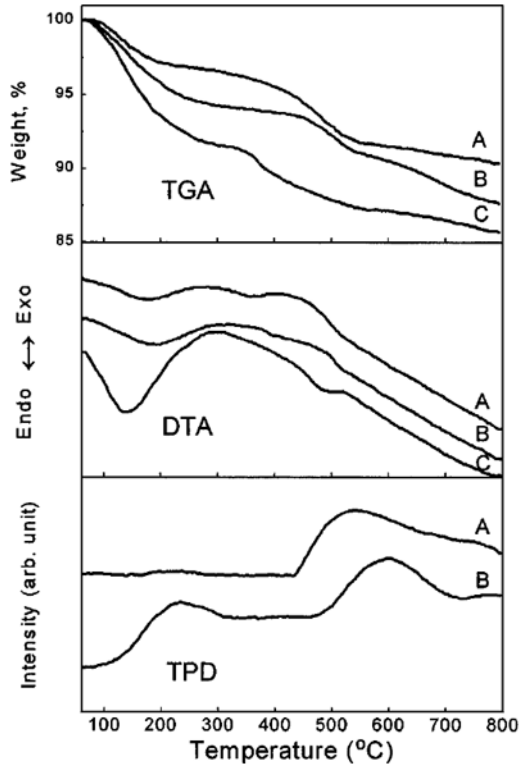

Fig. 5. TGA, DTA and SO_2 TPD spectra of the catalysts deactivated by SO_2 (A) FeHM43 at 250 °C; (B) FeHM43 at 400 °C; (C) $(NH_4)_2SO_4$-impregnated FeHM43.

hydration of the catalyst at 100 °C, while the second peak from 250 to 500 °C is attributed to the decomposition of sulfur compounds, which is identified by the SO_2 evolution from TPD spectra at 450 °C. The endothermic peaks are also observed at the temperatures corresponding to the dehydration and the decomposition of sulfur compounds from the DTA spectra. Among the possible sulfur compounds deposited on the catalyst, ammonium sulfate [$(NH_4)_2SO_4$] is most likely to be the sulfur compounds exhibiting the weight loss within the range of 250-500 °C. For the identification of the deactivating agent on the catalyst surface, the thermal analyses of ammonium sulfate-impregnated FeHM43 catalyst was examined and it shows similar weight loss and thermal behavior to that of the deactivated FeHM43 catalysts as shown in Fig. 5C. Another possible sulfur compound causing weight loss at 250 to 500 °C might be ammonium bisulfate (NH_4HSO_4) on the catalyst surface, since it also shows similar thermal behavior to that of ammonium sulfate.

Based upon the thermal analyses, the deactivating agent deposited on FeHM43 catalyst is ammonium salts such as $(NH_4)_2SO_4$ and/or NH_4HSO_4 as also observed for CuHM31 catalyst [Ham et al., 1995a]. Although these ammonium salts are the primary deactivating agent deposited on the catalyst, some other ammonium salts may form at the high reaction temperature of 400 °C as observed in first SO_2 peak of TPD spectrum. Since the deactivation test was conducted at higher reaction temperature than the decomposition temperatures of ammonium salts, it may be the residuals existing on the catalyst surface by the decomposition of ammonium sulfate and ammonium bisulfate as extensively discussed in the previous study [Ham et al., 1995a].

DISCUSSION

Along with the catalytic performance for NO removal, the conversion of SO_2 to SO_3 is also a critical parameter determining the possibility of the use of catalyst for the SCR process, since SO_3 produced by SO_2 oxidation can reduce the catalytic performance and cause problems for reactor operation. Since the primary deactivating agents, ammonium salts are formed on the catalyst surface through the reaction of SO_3 with NH_3 and water, the oxidation capability of the catalyst for the conversion of SO_2 to SO_3 plays a crucial role for the formation of ammonium salts in this reaction system.

In order to examine the effect of the exchanged metals on the oxidation capability of the catalysts, the SO_2 oxidation activity of FeHM43 catalyst was compared with that of CuHM31 containing the similar metal loadings as shown in Table 2. Although the formation of SO_3 by the SO_2 oxidation is thermodynamically favored over the entire reaction temperature covered in the present study, both catalysts reveal very low conversion of SO_2 to SO_3 less than a few percent. The oxidation activity of FeHM43 catalyst was much less than that of CuHM31 at each reaction temperature examined in this work. CuHM31 catalyst shows the higher activity for SO_2 oxidation than FeHM43, which is probably attributed to the strong oxidizing capability of copper ions on mordenite catalyst than iron ions. It is also consistent with the result that the NH_3 oxidation reaction over CuHM31 is faster than that over FeHM43 by the comparison of the reaction temperature at the maximum NO conversion where NO conversion begins to decrease as shown in Fig. 1. In addition, the deactivating agents on the catalyst surface, ammonium salts can be easily formed when NH_3, SO_3 and H_2O concentrations are high enough at lower temperatures, since it is an exothermic reaction [Pins and Nuninga, 1993]. It may be a reason why the sulfur contents deposited on CuHM31 is higher than that on FeHM43 under the identical operating condition as shown in Table 1. Therefore, the distinction of the SO_2 oxidation activity between FeHM43 and CuHM31 catalysts causing the difference in SO_3 concentration during the course of the reaction seems to be a critical criterion for producing and depositing ammonium salts such as ammonium sulfate and ammonium bisulfate on the catalyst surface.

Table 2. Comparison of the activity of FeHM43 and CuHM31 catalysts for SO_2 oxidation

Catalyst	Reaction temp. (°C)	SO_3 conc. (ppm)	Conversion* (%)
FeHM43	250	11.2	0.56
	300	14.2	0.71
	350	16.0	0.80
	400	22.0	1.10
CuHM31	250	13.6	0.68
	300	19.4	0.97
	350	29.9	1.50
	400	66.7	3.34

*based on SO_2 feed concentration of 2,000 ppm
reactor space velocity: 50,000 hr^{-1}

Fig. 6 shows the activity change of FeHM43 catalyst for the reduction of NO with respect to the sulfur contents of the catalyst deposited on the catalyst surface. The catalytic activity was defined as the ratio of the reaction rate for deactivated catalysts to that for a fresh catalyst based on the first-order reaction kinetics. The reaction rate of SCR system over iron-exchanged mordenite type catalyst was well correlated by irreversible first-order kinetics with respect to NO [Ham, 1995b]. The catalytic activity exponentially decreases with the sulfur contents of the catalyst at 250 °C, while no deactivation is observed at 400 °C, despite the deposition of sulfur on the catalyst surface. As extensively discussed in the previous work for CuHM31 catalyst revealing similar trend of the catalyst deactivation, it is probably due to the difference in the location of the deactivating agents, which are mainly ammonium sulfate and/or ammonium bisulfate in the pores of the catalyst structure. At the low reaction temperature of 250 °C, the ammonium salts can deposit near the entrance of catalyst pores, causing severe pore blocking and thus reducing the catalytic performance. However, at higher reaction temperature of 400 °C above the decomposition temperatures of the ammonium salts formed on the catalyst surface, they can form at the deep inside pores by the capillary condensation, causing pore filling. The vapor pressure of a substance in micropores is much lower than that on free surfaces. Therefore, the ammonium sulfate and ammonium bisulfate can form and deposit on such a small pore of mordenite by the capillary condensation even at the temperature above their decomposition tem-

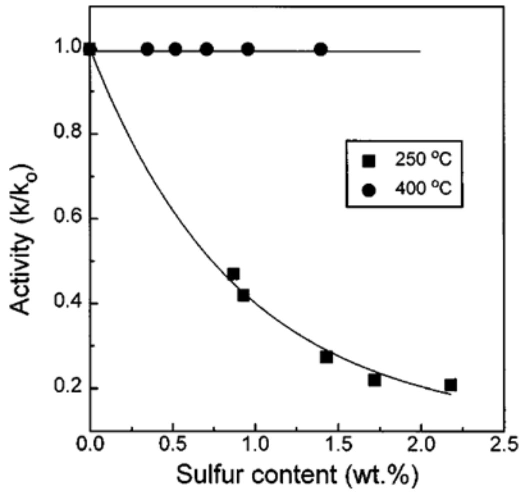

Fig. 6. Effect of sulfur contents on NO removal activity of FeHM43 catalyst.

peratures. It is believed to be one of the reasons why the catalytic activity varies with respect to the reaction temperatures. It may also be a reason why the BET surface area varies with the reaction temperatures at the identical level of the sulfur contents of the catalysts as shown in Fig. 3.

CONCLUSIONS

Iron-exchanged mordenite type zeolite is an active catalyst for the reduction of NO by NH_3 in the presence of oxygen. The redox behavior of Fe ions on the catalyst surface seems to be closely related to the enhancement of NO removal activity in the presence of oxygen as observed in many other transition metal-exchanged mordenite zeolite. The oxidation capability of the metals exchanged on the catalyst is critical for both reactions of NH_3 and SO_2 oxidation, and thus for the NO removal activity and the deactivation behavior of the catalyst. At the nearly identical levels of metal loadings of the catalysts, FeHM reveals less oxidizing capability for NH_3 oxidation reaction than CuHM. It can be easily understood by the comparison of the reaction temperature at the maximum conversion of NO over the catalysts. The deactivating agents deposited on the catalyst were identified as $(NH_4)_2SO_4$ and/or NH_4HSO_4 by the thermal analyses. The deactivation behaviors of both catalysts such as the changes of the physicochemical properties and NO removal activity by the deposition of deactivating agents on the catalyst surface were quite similar. However, the amount of deactivating agents deposited on the catalyst surface was higher on the catalyst with the higher oxidizing capability. This was mainly due to the difference in the activity of SO_2 oxidation to SO_3. It can be concluded that the NO removal activity and sulfur poisoning of metal exchanged mordenite zeolite were significantly influenced by the undesirable side reactions such as NH_3 and SO_2 oxidation reactions for SCR process. The oxidation capability of the catalyst for both reactions totally depends on the characteristic of the metals exchanged on the surface of mordenite type zeolite catalyst.

REFERENCES

Amiridis, M. D., Puglisi, F., Dumesic, J. A., Millman, W. S. and Topsøe, N.-Y., "Kinetic and Infrared Spectroscopic Studies of Fe-Y Zeolites for the Selective Catalytic Reduction of Nitric Oxide by Ammonia," *J. Catal.*, **142**, 572 (1993).

Bauerle, G. L., Wu, S. C. and Nobe, K., "Parametric and Durability Studies of NO_x Reduction with NH_3 on Fe-Cr Oxide Catalysts," *Ind. Eng. Chem. Prod. Res. Dev.*, **17**(2), 123 (1978).

Chen, J. P. and Yang, R. T., "Selective Catalytic Reduction of NO_x with NH_3 on SO_4^{2-}/TiO_2 Superacid Catalyst," *J. Catal.*, **139**, 277 (1993).

Choi, E. Y., Nam, I. S., Kim, Y. G., Chung, J. S., Lee, J. S. and Nomura, M., "An X-ray Absorption Study of Copper Ion Exchanged H-mordenite for Selective Catalytic Reduction of NO by NH_3," *J. Mol. Catal.*, **69**, 247 (1991).

Choi, E. Y., Nam, I. S. and Kim, Y. G., "TPD Study of Mordenite-type Zeolites for Selective Catalytic Reduction of NO by NH_3," *J. Catal.*, **161**(2), 597 (1996).

Chung, C. M., Choi, H., Choo, S. T., Nam, I. S. and Kim, Y. G., "A Kinetic Study for Selective Catalytic Reduction of NO by NH_3 over Cu-exchanged Mordenite Type Zeolite Catalyst," *HWAHAK KONGHAK*, **34**, 790 (1996).

Ham, S. W., "Activity and Durability of Copper Ion-exchanged Mordenite for NO Reduction by NH_3," Ph. D. Thesis, Dept. of Chem. Eng., Pohang Univ. of Sci. & Tech. (1995b).

Ham, S. W., Choi, H., Nam, I. S. and Kim, Y. G., "Deactivation of Copper-Ion-Exchanged Hydrogen-Mordenite-Type Zeolite Catalyst by SO_2 for NO Reduction by NH_3," *Catal. Today*, **11**, 611 (1992).

Ham, S. W., Choi, H., Nam, I. S. and Kim, Y. G., "Effect of Copper Contents on Sulfur Poisoning of Copper Ion-Exchanged Mordenite for NO Reduction by NH_3," *Ind. & Eng. Chem. Res.*, **34**, 1616 (1995a).

Ham, S. W., Choi, H., Nam, I. S. and Kim, Y. G., "Effect of Oxygen on Selective Catalytic Reduction of NO by NH_3 over Copper Ion Exchanged Mordenite-Type Zeolite Catalyst," *Catal. Lett.*, **42**, 35 (1996).

Iizuka, T. and Lunsford, J. H., "Active Intermediates in the Reduction of Nitric Oxide by Ammonia over a CoY Zeolite," *J. Am. Chem. Soc.*, **100**, 6106 (1978).

Ito, E., Hultermans, R. J., Lugt, P. M., Burgers, M. H. W., Rigutto, M. S., van Bekkum, H. and van den Bleek, C. M., "Selective Catalytic Reduction of NO_x with Ammonia over Cerium-Exchanged Mordenite," *Appl. Catal. B:Environmental*, **4**, 95 (1994).

Kiovsky, J. R., Kotadia, P. B. and Lim, C. T., "Evaluation of a New Zeolitic Catalyst for NO Reduction with NH_3," *Ind. Eng. Chem. Prod. Res. Dev.*, **19**, 218 (1980).

Markvart, M. and Pour, V., "The Influence of Oxygen on the Catalytic Reduction of Nitric Oxide by Ammonia," *J. Catal.*, **7**, 279 (1967).

Medros, F. G., Eldridge, J. W. and Kittrell, J. R., "Dual-catalytic System to Broaden the Window of Operability in the Reduction of NO_x with Ammonia," *Ind. Eng. Chem. Res.*, **28**, 1171 (1989).

Nam, I. S., Eldridge, J. W. and Kittrell, J. R., "Model of Temperature Dependence of a Vanadia-Alumina Catalyst for NO Reduction by NH_3: Fresh Catalyst," *Ind. Eng. Chem. Prod. Res. Dev.*, **25**, 186 (1986a).

Nam, I. S., Eldridge, J. W. and Kittrell, J. R., "Deactivation of a Vanadia-Alumina Catalyst for NO Reduction by NH_3," *Ind. Eng. Chem. Prod. Res. Dev.*, **25**, 192 (1986b).

Nam, I. S., Hwang, W. C., Ham, S. W. and Kim, Y. G., "Activity and Durability of Natural Zeolite Containing Cupric Ions for NO Reduction by NH_3," *Catalytic Science and Technology*, **1**, 165 (1990).

Petunchi, J. O. and Hall, W. K., "Redox Catalysis over Iron Zeolites: Kinetics and Mechanism," *J. Catal.*, **78**, 327 (1982).

Pins, W. L. and Nuninga, Z. L., "Design and Experience with Catalytic Reactors for SCR-DENOX," *Catalysis Today*, **16**, 187 (1993).

Ramis, G., Busca, G., Bregani, F. and Forzatti, P., "Fourier Transform-Infrared Study of the Adsorption and Coadsorption of Nitric Oxide, Nitrogen Dioxide and Ammonia on Vanadia-Titania and Mechanism of Selective Catalytic Reduction," *Appl. Catal.*, **64**, 243 (1992).

Schmidt, R., Amiridis, M. D., Dumesic, J. A., Zelewski, L. M. and Millman, W. S., "In Situ Mössbauer Spectroscopy Studies of Fe-Y Zeolites for the Selective Catalytic Reduction of Nitric Oxide by Ammonia," *J. Phys. Chem.*, **96**, 8142 (1992).

Seiyama, T., Arakawa, T., Matsuda, T., Takita, Y. and Yamazoe, N., "Catalytic Activity of Transition Metal Ion Exchanged Y Zeolites in the Reduction of Nitric Oxide with Ammonia," *J. Catal.*, **48**, 1 (1977).

Takagi, M., Kawai, T., Soma, M., Onishi, T. and Tamaru, K., "Mechanism of Catalytic Reaction between NO and NH_3 on V_2O_5 in the Presence of Oxygen," *J. Phys. Chem.*, **80**(4), 430 (1976).

Williamson, W. B. and Lunsford, J. H., "Nitric Oxide Reduction with Ammonia over Cu(II)Y Zeolites," *J. Phys. Chem.*, **80**(24), 2664 (1976).

Wong, W. C. and Nobe, K., "Reduction of NO with NH_3 on Al_2O_3- and TiO_2-Supported Metal Oxide Catalysts," *Ind. Eng. Chem. Prod. Res. Dev.*, **25**, 179(1986).