Selective Catalytic Reduction of NO with Ammonia over Fe³⁺-Exchanged Mordenite (Fe–MOR): Catalytic Performance, Characterization, and Mechanistic Study

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Fe-exchanged zeolites, i.e., mordenite (MOR), clinoptilolite (HEU), beta, ferrierite (FER), and chabazite (CHA), are studied as catalysts for selective catalytic reduction (SCR) of NO with NH₃. It is found that SCR activity decreases in the following order: Fe-MOR > Fe-HEU > Fe-FER > Fe-beta > Fe-CHA. Fe-MOR and Fe-HEU are much more active than the commercial vanadia catalyst. For Fe-MOR, SCR activity increases with a decreasing Si/Al ratio. Moreover, SO₂ and SO₂ + H₂O improve SCR activity. On Fe-MOR, nearly 100% NO conversion is obtained at a high space velocity (GHSV = $4.6 \times 10^5 \text{ h}^{-1}$) in the presence of SO₂. The Fe-MOR catalysts are also characterized by H₂-TPR (temperature-programmed reduction) and Fourier transform infrared (FT-IR) spectroscopy. TPR profiles indicate that iron cations in the catalysts are present as approximately 73% Fe³⁺ and 27% Fe^{2+} . FT-IR spectra show that NO can be oxidized by O₂ to N₂O₃, NO₂, and nitrate adsorbed species, and that they are bonded to the iron cations. NH₃ molecules adsorb on Brønsted acid sites of the zeolite to form NH_4^+ ions. $NO + O_2$ is very active in reacting with NH_4^+ ions on Fe–MOR at 300°C, but it is less active with those on H-MOR. This is in good agreement with their SCR activities and is probably related to the fast formation of NO₂ on Fe-MOR. A possible reaction scheme for SCR reduction is proposed. NO reduction involves the reaction between NO₂ and a pair of NH⁺₄ ions to generate an active intermediate, which then reacts with NO to produce N₂ and H₂O. NO oxidation to NO₂ is the rate-determining step. © 2002 Elsevier Science (USA)

Key Words: selective catalytic reduction; SCR of NO with NH_3 ; Fe^{3+} -exchanged zeolites; Fe-MOR: Fe-HEU; Fe-beta; Fe-FER; Fe-CHA.

INTRODUCTION

Selective catalytic reduction (SCR) of NO_x (x = 1 and 2) with NH₃ is the most efficient technology for NO_x abatement from power plant exhaust gases. Many catalysts have been reported to be active for this reaction. They include

mixed oxides and ion-exchanged molecular sieves (1-3). The commercial catalysts are vanadia supported on titania with WO₃ and/or MoO₃ as promoters. Ion-exchanged molecular sieves have received much attention for the SCR reaction recently because they function in a broad temperature window and do not have the disposal problem that is associated with vanadia.

Various transition metal ion-exchanged molecular sieves, such as Ce-mordenite (MOR) (4, 5), Ce-ZSM-5 (6), VO-ZSM-5 (7), Cu-MOR (8, 9), Cu-ZSM-5 (10), Cu-Y (11), Fe-Y (12, 13), Fe-MOR (8), Fe-ZSM-5 (14-18), and pillared clays (PILC) (19–24), have been investigated for SCR reaction. They were reported to have various activities. Among them, Fe-exchanged molecular sieves (PILC and ZSM-5) were of special interest because their SCR activities were improved by the presence of H_2O and SO_2 and also they showed much higher SCR activities than the commercial vanadia catalysts (15, 16, 22, 23). The improvement of SCR activity by SO₂ at high temperatures was attributed to an increase in surface acidity due to sulfation of the iron sites (16, 22, 23, 25). Sulfated Fe_2O_3 has been known as a superacid (26). This would also increase NO reduction by NH₃ at high temperatures. In addition, the sulfation of the catalysts decreased NH₃ oxidation by O₂, a competitive reaction of the SCR reaction (25). Therefore, it is of interest to extend the SCR investigation to other iron ion-exchanged zeolites, such as mordenite, cliniptilolite (HEU), ferrierite (FER), beta-zeolite, and chabazite (CHA).

Great effort has been put into understanding the kinetics and mechanism of the SCR reaction. The mechanism has been intensively studied for vanadia catalysts and several different mechanisms were proposed (1-3, 27-39). Most researchers agree that the SCR reaction on vanadia catalysts follows an Eley–Rideal-type mechanism, i.e., a strongly adsorbed ammonia species reacting with a gaseous or weakly adsorbed NO molecule to form molecular N₂, although which ammonia adspecies (Brønsted or Lewis) is involved in the reaction is still under debate (2). Temperatureprogrammed desorption and Fourier transform infrared (FT-IR) experiments showed that NO does not adsorb on



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the surface of oxidized vanadia under reaction conditions (2). Despite interest in the ammonia SCR over zeolite-type catalysts, there have been few studies of the mechanism over this type of catalyst. It was reported that both NH₃ and NO_r could adsorb on molecular sieves (5, 13, 23–25, 40–47). In the presence of NO + O₂, adsorbed NO₂/NO₃⁻ species were observed by FT-IR on Fe-exchanged TiO₂-PILC (45) and ZSM-5 (40-43, 46). On Cu-ZSM-5, Kamatsu et al. (10) reported that the reaction order was first-order with respect to NO, half-order for O₂, and zero-order for NH₃. They proposed a mechanism for NO reduction involving the reactions among NO, NO₂, and NH₃ (that was adsorbed on copper dimer). Over H-ZSM-5, Eng and Bartholomew (48, 49) detected NO₂ formation and concluded that it was an intermediate for the ammonia SCR reaction. In our previous work on the Fe-TiO₂-PILC and Fe-ZSM-5 catalysts (45-47), we also proposed a mechanism for NO reduction in which a pair of NH_3 adsorbed species (NH_4^+ or coordinated NH₃) react with NO₂ + NO to generate N₂ and H_2O . Therefore, NO_x species (NO + NO₂) may also play an important role in the reduction of NO by ammonia on molecular sieve catalysts.

In this work, we investigated Fe-exchanged zeolites (mordenite, cliniptilolite, ferrierite, beta-zeolite, and chabazite) for the SCR of NO by ammonia. Effects of iron content, Si/Al ratio, H₂O, and SO₂ on SCR activity were studied. The Fe–MOR catalysts were also characterized by H₂-TPR (temperature-programmed reduction) and FT-IR spectroscopy. The adsorption of NO + O₂ and NH₃ on the catalysts and the reactions among them were studied. The reaction mechanism for NO reduction is discussed.

EXPERIMENTAL

Preparation of Catalyst

The starting materials used for preparation of the catalysts are as follows. Mordenites (MOR, Si/Al = 6.4, 10, and 45), NH₄-beta (Si/Al = 12.5), and NH₄-ferrierite (FER, Si/Al = 10) were obtained from Zeolyst International Co. Clinoptilolite (HEU, Si/Al = 5) and chabazite (CHA, Si/Al = 2) were provided by Steelhead Minerals and GSA Resources, respectively. The non-NH₄-form zeolites were first transformed to NH₄-zeolites by exchanging with 0.5 M NH₄Cl solution (four times) at room temperature.

Fe-exchanged zeolites were prepared by using the conventional ion-exchange procedure. $FeCl_2 \cdot 4H_2O$ (99%) was obtained from Aldrich. Typically, 2 g of NH₄-form zeolite was added to 200 ml of a 0.05 M FeCl₂ solution with constant stirring. After 24 h, the mixture was filtered and washed five times with deionized water. The obtained catalysts were first dried at 120°C in air for 12 h, then calcined at 500°C for 6 h. Most Fe²⁺ in the catalysts was oxidized to Fe^{3+} (46). Finally, the obtained samples were pressed and ground to 60-100 mesh. The Fe and Al contents in the samples were measured by neutron activation analysis. The iron-exchange extent was calculated using $3 \times$ (number of iron ions)/(number of aluminum atoms). Preparation of the catalysts and the resulting Fe contents are summarized in Table 1. For catalyst designation, the number in parentheses after Fe indicates the Fe-exchange level and the other number in parentheses shows the ratio of Si to Al; e.g., Fe(56)–MOR(6.4) indicates the Fe-exchange level is 56% and the Si/Al ratio is 6.4.

Preparation Conditions and Iron Contents of Fe-Exchanged Mordenites				
Sample ^a	Si/Al	Fe content (wt%)	Preparation condition	
Fe(56)-MOR(6.4)	6.4/1	2.1	Exchanging NH ₄ -mordenite with FeCl ₂ solution for 2 h at room temperature (once)	
Fe(59)-MOR(6.4)	6.4/1	2.4	Exchanging NH ₄ -mordenite with FeCl ₂ solution for 24 h at room temperature (once)	
Fe(84)-MOR(6.4)	6.4/1	3.1	Exchanging NH ₄ -mordenite with FeCl ₂ solution for 24 h at room temperature (3 times)	
Fe(73)-MOR(10)	10/1	1.8	Exchanging NH ₄ -mordenite with FeCl ₂ solution for 24 h at room temperature (once)	
Fe(94)-MOR(45)	45/1	0.68	Exchanging NH ₄ -mordenite with FeCl ₂ solution for 24 h at room temperature (once)	
Fe(81)-HEU(5)	5/1	3.5	Exchanging NH ₄ -clinoptilolite with FeCl ₂ solution for 24 h at room temperature (once)	
Fe(72)-beta(12.5)	12.5/1	1.6	Exchanging NH ₄ -beta with FeCl ₂ solution for 24 h at room temperature (once)	
Fe(21)-FER(10)	10/1	0.56	Exchanging NH ₄ -ferrierite with FeCl ₂ solution for 24 h at room temperature (once)	
Fe(56)-CHA(2)	2/1	6.0	Exchanging NH ₄ -chabazite with FeCl ₂ solution for 24 h at room temperature (once)	

TABLE 1

^a For example, F	e(56) - MOR(6.4)	indicates the	Fe-exchange	level is 56%	and Si/Al	ratio is 6.4

Catalytic Activity Measurement

The SCR activity measurement was carried out in a fixed-bed quartz reactor, and 50 mg (0.065 ml) of catalyst was used. The flue gas was simulated by blending different gaseous reactants. The typical reactant gas composition was as follows: 1000 ppm NO, 1000 ppm NH_3 , 2% O_2 , 500 ppm SO_2 (when used), 2.5% water vapor (when used), and balance He. The total flow rate was 500 ml/min (ambient conditions) and thus a very high GHSV (gas hourly space velocity) was obtained $(4.6 \times 10^5 \text{ h}^{-1})$. The premixed gases (1.01% NO in He, 1.00% NH₃ in He, and 0.99% SO₂ in He) were supplied by Matheson. Water vapor was generated by passing He through a gas-wash bottle containing deionized water. The tubings of the reactor system were heat traced to prevent formation and deposition of ammonium sulfite/bisulfite and ammonium nitrate. The NO and NO₂ concentrations were continually monitored by a chemiluminescent NO/NO_x analyzer (Model 42C, Thermo Environmental Instruments Inc.). To avoid errors caused by the oxidation of ammonia in the converter of the NO/NO_x analyzer, an ammonia trap containing phosphoric acid solution was installed before the sample inlet to the chemiluminescent analyzer. Since N₂O formation was not detected with Fe-exchanged molecular sieves in our previous work (15, 16, 22, 23), N₂O or N₂ was not analyzed in this work. NO conversions were obtained using the difference of NO_x concentrations before and after reactions. All of the data were obtained after 20 min when the SCR reaction reached steady state.

TPR Experiment

H₂-TPR was performed in a fixed-bed quartz reactor with an inner diameter of 10 mm. In the experiment, 0.1 g of catalyst was pretreated in a flow of He (50 ml/min, purity 99.9998%) at 400°C for 30 min to remove adsorbed species (e.g., H₂O). After the sample was cooled to room temperature in He, the reduction of the Fe–MOR was carried out from 20 to 600°C in a flow of 5.34% H₂/N₂ (27 ml/min) at 10°C/min. The consumption of H₂ was monitored continuously with a thermal conductivity detector. The water produced during reduction was trapped in a 5A molecular sieve column.

FT-IR Study

Infrared spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer with a TGS detector. Self-supporting wafers of 1.3 cm in diameter were prepared by pressing 20-mg samples and were loaded into a high-temperature IR cell with BaF₂ windows. The wafers could be pretreated *in situ* in the IR cell. Unless otherwise indicated, the wafers were first treated at 450°C in a flow of He for 15 min, and then cooled to desired temperatures, i.e., 400, 350, 300, 200, 100, and 30°C. At each temperature, the background spec-

trum was recorded in flowing He and was subtracted from the sample spectrum that was obtained at the same temperature. The IR spectra were recorded by accumulating 32 scans at a spectral resolution of 4 cm^{-1} .

During the FT-IR experiments, the gas mixtures had the same concentrations as that used in the activity measurements, i.e., 1000 ppm NO (when used), 1000 ppm NH₃ (when used), $2\% O_2$ (when used), and balance He. The total gas flow rate was 500 ml/min (ambient conditions).

NO Oxidation to NO₂

The experiment of NO oxidation to NO₂ was performed in a fixed-bed, quartz flow reactor. A 50-mg sample was used and the conversion at each temperature was obtained after 1 h of steady state reaction. The reactant gas composition was as follows: 1000 ppm NO, 2% O₂, and balance He. The total flow rate was 500 ml/min (ambient conditions). NO concentration was continually monitored by the chemiluminescent NO/NO_x analyzer. NO conversion to NO₂ was obtained by using the equation NO conversion to NO₂ = (([NO_x] – [NO])/[NO_x]) × 100%, where NO_x represents NO + NO₂.

RESULTS

SCR Activities on Fe-Exchanged Zeolites

The SCR activities on different Fe-exchanged zeolites (Fe-MOR, Fe-HEU, Fe-FER, Fe-beta, and Fe-CHA) are summarized in Table 2. Under the conditions with a high space velocity (GHSV = 4.6×10^5 h⁻¹), Fe-MOR and Fe-HEU showed high SCR activities. NO conversions (95-98%) were obtained at 400-450°C. By comparison, much lower NO conversions were observed on Fe-FER, Fe-beta, and Fe-CHA under the same reaction conditions. It is clear that the structure of molecular sieves has a strong effect on SCR activity. SCR activity can also be represented quantitatively by turnover frequency (TOF) and the first-order rate constant (k) (since the reaction is known to be first-order with respect to NO under stoichiometric NH₃ conditions on molecular sieves (45)). TOF is defined as the number of NO molecules converted per Fe per second. By assuming a plug flow reactor (in a fixed bed of catalyst) free of diffusion limitation, the rate constant (k) can be calculated from the NO conversion (X) using

$$k = -\frac{F_0}{[NO]_0 W} \ln(1 - X),$$
 [1]

where F_0 is the molar NO feed rate, $[NO]_0$ is the molar NO concentration at the inlet (at the reaction temperature), and W is the catalyst amount (g). From the NO conversions and Fe contents or catalyst amounts in the above catalysts, TOFs and first-order rate constants were calculated; they

SCR Activities on Fe-Exchanged Zeolites

Catalyst ^a	Temperature (°C)	NO conversion (%)	$\begin{array}{c} k^b \times 10^{-2} \\ (\mathrm{cm}^3/\mathrm{g/s}) \end{array}$	$\begin{array}{c} \text{TOF}^c \\ (\times 10^3) \end{array}$
Fe(59)–MOR(6.4) (mordenite)	350 400 450	85 98 92	6.6 15 10	13 15 14
Fe(81)–HEU(5) (clinoptilolite)	350 400 450	89 94 95	7.7 11 12	9.6 10 10
Fe(21)–FER(10) (ferrierite)	350 400 450	48 47 44	2.4 2.4 2.3	16 16 15
Fe(72)-beta(12.5)	350 400 450	11 30 20	0.41 1.3 0.90	2.6 7.1 4.8
Fe(56)–CHA(2) (chabazite)	350 400 450	12 21 27	0.45 0.89 1.3	0.75 1.3 1.7

Note. Reaction conditions: 0.05 g of catalyst; $[NO] = [NH_3] = 1000$ ppm; $[O_2] = 2\%$; He = balance; total flow rate = 500 ml/min; and GHSV = 4.6 × 10⁵ h⁻¹.

^{*a*} For catalyst designation, the number in parentheses after Fe indicates the Fe-exchange level and the other number in parentheses shows the ratio of Si to Al.

^b First-order rate constant, as defined in the text, calculated using Eq. [1].

^c Overall TOF (turnover frequency) is defined as the number of NO molecules converted per Fe per second.

are compared in Table 2. Both NO conversion and the rate constant on Fe-exchanged zeolites decreased in the following order: Fe-MOR > Fe-HEU > Fe-FER > Fe-beta > Fe-CHA, whereas TOF was also affected by iron content (Table 2).

Effect of Fe Content on SCR Activity over Fe-MOR

The effect of Fe content on SCR activity is summarized in Table 3. H–MOR showed very low activity for the SCR reaction. After iron was exchanged to H–MOR, SCR activity was enhanced significantly (Table 3). NO conversion and the rate constant increased with increasing Fe content at low temperatures. TOF decreased with increasing Fe content in the Fe–MOR catalysts.

Effect of Si/Al Ratio on SCR Activity over Fe-MOR

It is known that the Si/Al ratio in zeolites affects their acidity–basicity and cation exchange capacity. The effect of Si/Al ratio on SCR activity over Fe–MOR was studied. As shown in Fig. 1, the ratio of Si/Al had a strong effect on NO conversion. With an increase in Si/Al ratio, NO conversion decreased rapidly at the temperature range of $300-500^{\circ}C$ (Fig. 1). High NO conversions were obtained over Fe–MOR (Si/Al = 6.4), but very low NO conversions were obtained

on Fe–MOR (Si/Al=45). This result indicates that the Fe–MOR with low Si/Al ratio is favorable to a high NO conversion.

Effects of H₂O and SO₂ on SCR Activity

Because resistance to H_2O and SO_2 is an important factor for SCR catalysts, we studied the effects of H_2O and SO_2 on catalytic performance over Fe–MOR (Fig. 2). When 2.5% H_2O was added to the reaction gases, NO conversions were decreased only slightly at 300–400°C and such decreases diminished at higher temperatures. However, the presence of SO_2 and $SO_2 + H_2O$ increased NO conversion significantly and also widened the temperature window, suggesting a promoting role by SO_2 on Fe–MOR. Near 100% NO conversions were obtained at 350–450°C in the presence of SO_2 and $SO_2 + H_2O$ (Fig. 2). This observation is similar to that on Fe-exchanged pillared clay (22, 23) and ZSM-5 (15, 16).

H₂-TPR Profiles of Fe–MOR

 H_2 -TPR profiles of Fe–MOR are shown in Fig. 3. Three reduction peaks were seen, at 56, 304, and 377°C, on the

TABLE 3

SCR Activities on Fe-MOR(6.4) Catalysts

Catalyst ^a	Temperature (°C)	NO conversion (%)	$k^b \times 10^{-2}$ (cm ³ /g/s)	TOF^{c} (×10 ³)
H-MOR(6.4)	300	4	0.13	_
	350	5	0.18	_
	400	5	0.19	_
	450	3	0.12	_
	500	2	0.087	
Fe(56)-MOR(6.4)	300	34	1.3	5.9
	350	85	6.6	15
	400	97	13	17
	450	92	10	16
	500	88	9.2	15
Fe(59)-MOR(6.4)	300	35	1.4	5.3
	350	85	6.6	13
	400	98	15	15
	450	92	10	14
	500	86	8.5	13
Fe(84)-MOR(6.4)	300	49	2.2	5.8
	350	95	10	11
	400	98	15	12
	450	93	11	11
	500	89	9.5	11

Note. Reaction conditions are the same as those in Table 2.

^{*a*} For catalyst designation, the number in parentheses after Fe indicates the Fe-exchange level and the other number in parentheses shows the ratio of Si to Al.

 b First-order rate constant, as defined in the text, calculated using Eq. [1].

^c Overall TOF (turnover frequency) is defined as the number of NO molecules converted per Fe per second.



FIG. 1. Effect of Si/Al ratio on NO conversion over Fe (59% exchange)–MOR (Si/Al = 6.4), Fe (73% exchange)–MOR (Si/Al = 10), and Fe (94% exchange)–MOR (Si/Al = 45). Reaction conditions: 50 mg of catalyst, 1000 ppm NO, 1000 ppm NH₃, 2% O₂, balance He, and GHSV = $4.6 \times 10^5 \text{ h}^{-1}$.



FIG. 2. Effects of H₂O and SO₂ on NO conversion over Fe (59% exchange)–MOR (Si/Al = 6.4). Reaction conditions: 50 mg of catalyst, 1000 ppm NO, 1000 ppm NH₃, 2% O₂, 500 ppm SO₂ (when used), 2.5% H₂O (when used), balance He, and GHSV = $4.6 \times 10^5 \text{ h}^{-1}$.



FIG. 3. H₂-TPR profiles of (a) Fe (84% exchange)–MOR (Si/Al = 6.4), (b) Fe (59% exchange)–MOR (Si/Al = 6.4), and (c) Fe (56% exchange)–MOR (Si/Al = 6.4).

three Fe–MOR samples. The peak at 56°C is very weak, which is probably due to reduction of adsorbed species on the surface (e.g., O₂ adsorbed species). The strong peak at 304°C and its shoulder at 377°C can be attributed to the reduction of iron species at two different sites. The intensity of the shoulder increased significantly with iron content in the catalysts. The TPR profiles are similar to that of Fe-ZSM-5 (46). On the Fe–ZSM-5, we found that, when Fe^{2+} ions were exchanged to ZSM-5 and calcined at 500°C in air, most Fe²⁺ ions were oxidized to Fe³⁺ ions in the zeolite, which was proved by an electron spin resonance signal at g = 4.29 and a X-ray photoelectron spectroscopy band at 711.7 eV for Fe^{3+} (46). The Fe^{3+} in the Fe–ZSM-5 could be partially reduced to Fe^{2+} by H_2/N_2 at 300-600°C, but the Fe^{2+} could not be further reduced to Fe metal below 700°C. Hence it is reasonable to deduce that most iron in Fe-MOR was in the ferric form. Integration of the area of the TPR peaks for Fe-MOR yielded H₂/Fe molar ratios of 0.36–0.37. These are close to the value of 0.5 required for the reduction of Fe^{3+} to Fe^{2+} . The lower ratio of H_2 consumption to Fe suggests that some Fe²⁺ ions (\approx 26–28%) also existed in the Fe-MOR that was pretreated at 400°C in He.



FIG. 4. IR spectra of Fe (59% exchange)–MOR (Si/Al = 6.4) treated in flowing 1000 ppm NH₃/He at 30°C for 30 min and then purged by He at (a) 30, (b) 100, (c) 200, (d) 300, and (e) 400°C.

FT-IR Studies

The IR spectra of ammonia adsorbed on Fe(59)-MOR(6.4) at different temperatures are shown in Fig. 4. After the sample was treated in flowing 1000 ppm NH₃/He for 30 min and then purged with He for 15 min at 30°C, a strong band at 1463 cm^{-1} and weaker bands at 3360, 3267, 2950, 2741, 1696, 1602, 1293, and 2600–2900 cm⁻¹ were observed (Fig. 4a). The broad band between 2600 and 2900 cm^{-1} is attributed to physisorbed ammonia. The bands at 1696 and 1463 cm⁻¹ are due to the symmetric and asymmetric bending vibrations, respectively, of NH₄⁺ ions that were chemisorbed on the Brønsted acid sites, while the bands at 1602 and 1293 cm⁻¹ can be assigned to asymmetric and symmetric bending vibrations, respectively, of the N-H bonds in NH₃ coordinately linked to Lewis acid sites (45, 50). The bands at higher wavenumbers are attributed to the N-H stretching vibration of NH⁺₄ ions located at the AlO₄ tetrahedra of the mordenite framework. The bands at 3360 and 3267 cm^{-1} can be assigned to NH_4^+ ions with three hydrogen atoms bonded to three oxygen ions of AlO₄ tetrahedra (3H structure), while the bands at 2950 and 2741 cm⁻¹ were due to the NH₄⁺ ions with two hydrogen atoms bonded to AlO₄ tetrahedra (2H structure) (46, 49, 51). The above results indicate that there are more Brønsted acid sites than Lewis acid sites on Fe–MOR at room temperature. With increasing temperature, the intensities of the 3360- and 3267-cm⁻¹ bands increased first (at the expense of the 2950- and 2741cm⁻¹ bands), passing through a maximum at 200–300°C, and then decreased at higher temperatures (Figs. 4b–4e). This suggests a NH₄⁺ transformation from a 2H structure to a 3H structure with increasing temperature. The intensities of all other bands decreased as temperature was increased (Figs. 4b–4e), indicating desorption of NH₃. The IR bands due to NH₄⁺ ions with the 3H structure (at 3360, 3267, and 1463 cm⁻¹) were still detected at 400°C in He (Fig. 4e). This result indicates that NH₄⁺ ions with 3H structures are more stable at high temperatures than the other ammonia adsorbed species.

 NH_3 adsorption was also studied on H–MOR and other Fe–MOR at 300°C. As shown in Fig. 5, the IR bands due to NH_4^+ were observed. The intensities of the NH_4^+ bands decreased with an increase in iron content in the catalysts, suggesting the same sites for NH_4^+ and iron ions. A similar observation was also reported on Fe–ZSM-5 by Lobree *et al.* (42).



FIG. 5. IR spectra (at 300°C) of (a) H–MOR (Si/Al = 6.4), (b) Fe (59% exchange)–MOR (Si/Al = 6.4), and (c) Fe (84% exchange)–MOR (Si/Al = 6.4) which were treated in flowing 1000 ppm NH₃/He at 300°C for 30 min.



FIG. 6. IR spectra of Fe (59% exchange)–MOR (Si/Al = 6.4) treated in flowing 1000 ppm NO + 2% O₂/He at 30°C for 30 min and then purged by He at (a) 30, (b) 100, (c) 200, (d) 300, and (e) 400°C.

Figure 6 shows the IR spectra of Fe(59)-MOR(6.4) after it was treated with $NO + O_2$ for 30 min followed by purging with He for 15 min at room temperature. When 1000 ppm NO + 2% O_2 was introduced to the sample, a strong peak was observed at 1878 cm⁻¹. This band is close to the vibration frequency of gaseous NO (1880 cm^{-1}) and has been assigned to Fe^{2+} mononitrosyls $[Fe^{2+}(NO)]$ (41– 43, 46). After the NO_x -treated sample was purged with He, the band at 1878 cm⁻¹ disappeared and four bands were observed at 1684, 1623, 1570, and 1371 cm⁻¹ (Fig. 6a). The band at 1684 cm⁻¹ is probably due to adsorbed N₂O₃ species because it is close to the IR band at 1690 cm^{-1} for gaseous N_2O_3 (52). The band at 1623 cm⁻¹ and those at 1570 and 1371 cm⁻¹ can be assigned to adsorbed NO₂ and nitrate species, respectively (41-43, 45, 46, 53, 54). The above observation suggests that some NO molecules were oxidized to NO_{x} by O_{2} . When increasing temperature, the bands at 1684 and 1570 cm⁻¹ decreased significantly, whereas those at 1623 and 1371 cm⁻¹ increased first, and then decreased at above 100°C. The N₂O₃ band at 1684 cm⁻¹ and the nitrate band at 1371 cm⁻¹ disappeared at 200°C (Fig. 6c). All of the other bands vanished at 400°C (Fig. 6e).

The IR spectra of H–MOR and Fe–MOR in flowing $NO + O_2$ at 200°C are shown in Fig. 7. Three bands, due

to adsorbed NO (1878 cm⁻¹), NO₂ (1617 cm⁻¹), and nitrate (1570 cm⁻¹) species, were detected on the Fe–MOR. Their intensities increased with iron content. By comparison, these bands were not observed on the H–MOR. This result indicates clearly that the NO_x species were adsorbed on the iron sites of the Fe–MOR.

The IR spectra of the reaction between NH₄⁺ and $NO + O_2$ on Fe(59)-MOR(6.4) are shown in Fig. 8. The fresh Fe-MOR was first treated with 1000 ppm NH₃/He for 30 min followed by a He purge at 300° C. NO + O₂ was then introduced into the sample and IR spectra were recorded as a function of time. As noted above, NH_4^+ ions with the 3H structure (3354, 3260, and 1435 cm^{-1}) were generated after Fe-MOR was treated with NH₃/He and their IR bands did not decrease in flowing He for 30 min. After 1000 ppm NO + 2% O_2 /He was passed over the sample for 1–3 min, the bands attributed to NH_4^+ ions decreased. At the same time, two new bands were observed, at 1875 and 1622 cm⁻¹ (Fig. 8c). As mentioned above, they are due to NO and NO₂ adsorbed species, respectively. The 1622 cm⁻¹ band may also come from adsorbed H₂O generated during the reaction. These results indicate that the reaction between NH_4^+ ions and $NO + O_2$ occurred. With increasing time,



FIG. 7. IR spectra of (a) H–MOR (Si/Al=6.4), (b) Fe (59% exchange)–MOR (Si/Al=6.4), and (c) Fe (84% exchange)–MOR (Si/Al=6.4) which were treated in flowing 1000 ppm NO + 2% O_2 /He at 200°C for 30 min.



FIG. 8. IR spectra taken at 300° C on passing 1000 ppm NO + 2% O₂/He over NH₃ presorbed on Fe (59% exchange)–MOR (Si/Al = 6.4) for (a) 0, (b) 1, (c) 3, and (d) 5 min.

the NH₄⁺ bands were further decreased and vanished at 5 min, while only NO and NO₂ adsorbed species were detected (Fig. 8d). In contrast, the NH₄⁺ ions on H–MOR was much less active in reacting with NO + O₂ than those on Fe–MOR. When 1000 ppm NO + 2% O₂ was passed over the H–MOR that was treated with NH₃ at 300°C, the intensities of the NH₄⁺ bands decreased and vanished at 30 min (Fig. 9). This result is consistent with their relative SCR activities.

To identify the species present on the catalyst under reaction conditions, IR spectra were recorded when Fe– MOR was heated from 300 to 450°C in a flow of 1000 ppm NO + 1000 ppm NH₃ + 2% O₂ at steady state. As shown in Fig. 10, the bands due to NH₄⁺ ions were observed at 3357, 3258, and 1433 cm⁻¹ at 300°C. Raising the temperature resulted in a decrease in the intensity of the NH₄⁺ bands. The NH₄⁺ ions were still observed at 450°C. In the temperature range studied, the IR bands due to NO_x adsorbed species were not detected. This suggests that the NO_x consumption rate (by NH₃) was much higher than the NO₂ formation rate from NO + O₂ under the reaction conditions. The observation of strong NH₄⁺ bands also indicates that NH₃ was in excess on the surface.

DISCUSSION

The present work indicated that Fe-exchanged zeolites were active for the SCR of NO with NH₃. The structure of zeolites had a strong effect on SCR activity. Under the same reaction conditions, SCR activity decreased in the sequence of Fe-MOR > Fe-HEU (clinoptilolite) > Fe-FER >Fe-beta > Fe-CHA. The Fe-MOR and Fe-HEU showed very high SCR activities, whereas the other catalysts were less active. For the Fe-MOR catalysts, NO conversion increased with iron content (Table 3). Since H-MOR showed very low NO conversions under the same conditions (at a high space velocity), it is clear that iron ions play a crucial role in the SCR reaction. Moreover, SCR activity on Fe-MOR was improved by the presence of SO_2 and $SO_2 + H_2O$ (Fig. 1). This observation is in agreement with our previous results obtained on Fe-exchanged pillared clay (22, 23) and ZSM-5 (15, 16). Nearly 100% NO conversion was obtained at 350-450°C with SO₂. This was close to the SCR performance obtained on Fe-ZSM-5 and was much higher than that of the commercial $V_2O_5 + WO_3/TiO_2$ catalyst (67% NO conversion at 400°C) under the same conditions (15, 16). In the presence of SO₂, the surface of the catalysts was sulfated and the sulfate species bonded to iron sites



FIG. 9. IR spectra taken at 300° C on passing 1000 ppm NO + 2% O₂/He over NH₃ presorbed on H–MOR (Si/Al = 6.4) for (a) 0, (b) 1, (c) 5, (d) 15, and (e) 30 min.



FIG. 10. IR spectra of Fe (59% exchange)–MOR (Si/Al = 6.4) in flowing 1000 ppm NH₃ + 1000 ppm NO + 2% O₂/He at (a) 300, (b) 350, (c) 400, and (d) 450° C.

were formed under the reaction conditions (23, 46). The sulfation increased the surface acidity (mainly Brønsted acidity) and decreased the activity for ammonia oxidation by O_2 so that more NH₃ could be used to reduce NO rather than react with O_2 (25). Therefore, SCR activity was enhanced. At 350–400°C, the Fe–MOR catalyst was stable and did not decrease its SCR activity during 9 h on stream in the presence of SO₂ (8).

Although iron cations were exchanged with NH₄-MOR as Fe²⁺ form, the TPR results indicated that most iron cations (\approx 72–74%) in the Fe–MOR were present as Fe³⁺ ions. Oxygen oxidized some Fe^{2+} to Fe^{3+} during calcination of the catalysts. Two TPR peaks were observed on Fe-MOR (Fig. 3), suggesting that Fe^{3+} ions occupied two sites in the catalysts. As shown in Fig. 11, mordenite has a onedimensional channel system bounded by twelve-member rings (main cage, 0.65×0.70 nm) with cross-links bounded by eight-member rings $(0.26 \times 0.57 \text{ nm})$ (55). The positions of cations are located mainly at the two cages (55, 56). For instance, one is near the center of the eight-member ring that connects the main cage with the smaller channel and the other is in the main cage far from the four-member ring. When Fe^{2+} ions were exchanged with the NH_4^+ in the mordenite, they preferred to occupy one cage (probably the main cage) first, and then exchanged with the NH_4^+ in another cage when this cage was full. The reduction temperatures of the Fe³⁺ ions in the two cages were different, possibly due to the different diffusion rates in the two cages for H₂ (with a kinetic diameter of 0.29 nm). The iron cations provide sites for NO_x adsorption, as discussed below.

The FT-IR spectra indicated that adsorbed NO, N₂O₃, NO₂, and nitrate species were formed after Fe-MOR catalysts were treated with $NO + O_2$ (Figs. 6 and 7). This is similar to the results obtained on Fe-ZSM-5 (41-43, 46), but different from that obtained on vanadia-based catalysts. Most researchers agreed that nitrogen oxides do not adsorb on fully oxidized vanadia (1-3). Since NO_x species were not detected on H-MOR (Fig. 7), they were bonded to iron sites in the Fe-MOR. NO was reported to adsorb on the Fe^{2+} sites and the other NO_x species were adsorbed on the Fe^{3+} sites (43, 46, 57, 58). NO adsorption was very weak. It disappeared when the sample was purged with He. The NO_2 and nitrate species came from the reaction between oxygen adsorbed species and gaseous NO (43). The NO₂ was the dominant species at 200-300°C. The concentrations of the NO_x adsorbed species increased with iron content in the catalysts (Fig. 7). Since Fe–MOR catalysts were much more active than H-MOR for the SCR reaction (Table 3), it is clear that the NO_x adsorbed species played an important role in NO reduction.

When Fe-MOR was treated in flowing NH₃/He, NH₃ molecules were adsorbed on the Brønsted acid sites to



FIG. 11. Framework topology of mordenite.

form NH_4^+ ions (Fig. 4). Although coordinated NH_3 was also detected, its concentration was much lower than that of NH_4^+ . The NH_4^+ ions are present in two forms: a 3H structure (three hydrogen atoms bonded to the AlO₄ tetrahedra) and a 2H structure (two hydrogen atoms bonded to the AlO₄ tetrahedra). NH_4^+ ions with the 3H structure are more stable than those with the 2H structure at high temperatures and they were still observed at 400°C in He (Fig. 4). This also indicates that NH_4^+ ions were more stable than NO_x adsorbed species at high temperatures because NO_x desorbed below 400°C (Fig. 6). As expected, the replacement of NH_4^+ by iron ions decreased the concentration of NH_4^+ (Fig. 5). The NH_4^+ ions on the Fe–MOR were active in reacting with $NO + O_2$. They were consumed completely when introducing NO + O_2 in 5 min at 300°C (Fig. 8). By comparison, when passing $NO + O_2$ over the ammonia adsorbed H–MOR, the NH_4^+ bands vanished after 30 min. This suggests that Fe^{3+} in Fe–MOR promoted the reaction between NO + O_2 and NH⁺₄ ions, probably due to an increase in NO_x formation (Fig. 7). This phenomenon was in good agreement with our SCR results showing that Fe-MOR was much more active than H-MOR. The presence of iron cations in the zeolite increased NO oxidation to NO₂ by O₂. As shown in Fig. 12, H–MOR showed very low



FIG. 12. Oxidation activity of NO to NO₂ by O₂ on H–MOR (Si/Al = 6.4) and Fe (59% exchange)–MOR (Si/Al = 6.4) under the following conditions: 50 mg of catalyst, 1000 ppm NO, 2% O₂, and 500 ml/min total flow rate. The empty-tube conversion under the same conditions was below 1.5% at 300–450°C.

activity for oxidizing NO to NO₂ under the conditions of 1000 ppm NO, 2% O₂, and GHSV = 4.6×10^5 h⁻¹. When iron ions were exchanged to H-MOR, the NO conversions to NO₂ were increased significantly, from 2-3% to 10-13% at 300-400°C. At above 450°C, NO conversion was close to the thermal equilibrium value. We have verified that the formation of NO₂ will promote the reaction between NH_4^+ ions and NO on Fe–ZSM-5. The reaction between NH_4^+ and $NO + NO_2$ is faster than those between $NH_4^+ + NO_2$ and between $NH_4^+ + NO$ under the conditions with the same NO_x concentration (59). In addition, under the reaction conditions, i.e., with NO, O₂, and NH₃ at high temperatures, the surface of Fe–MOR was covered mainly by NH_4^+ ions. NO_x adsorbed species were not observed (Fig. 10). This indicates that the reaction of NH_4^+ ions with NO_x was much faster than that of NO_x formation from $NO + O_2$. As soon as NO_x was generated, it was consumed by NH₄⁺ ions so that the steady state concentration of NO_x was below the detection limit of our IR spectrometer. This suggests that NO oxidation to NO₂ is a slow step for the SCR reaction.

According to the above results, it seems that the NO reduction path on the Fe–MOR is similar to that on Fe-exchanged pillared clay (45) and Fe–ZSM-5 (59). The SCR reaction most probably takes place according to the following steps:

$$2NH_{3(g)} + 2H^{+} - 2NH_{4(a)}^{+}, \qquad [2]$$

$$NO_{(g)} + 1/2O_{2(a)} - NO_{2(a)},$$
 [3]

$$NO_{2(a)} + 2NH_{4(a)}^{+} - NO_{2}(NH_{4}^{+})_{2(a)},$$
 [4]

$$NO_2(NH_4^+)_{2(a)} + NO_{(g)} - \cdots \rightarrow 2N_{2(g)} + 3H_2O_{(g)} + 2H^+.$$
[5]

This is a somewhat simplified mechanism. During the SCR reaction, gaseous NH₃ molecules are adsorbed quickly on the Brønsted acid sites to form NH₄⁺ ions. Also, NO molecules are oxidized to NO_2 on Fe^{3+} sites by O_2 . Then one molecule of NO₂ diffuses to two adjacent NH_4^+ ions to form an active complex $NO_2(NH_4^+)_2$. The active complex subsequently reacts with one molecular NO to produce N_2 and H_2O and thus completes the catalytic cycle. The oxidation of NO to NO₂ is probably the ratedetermining step. H-MOR showed strong surface acidity but very low activity for the oxidation of NO to NO₂; its SCR activity was therefore very low. After it was exchanged with iron, the iron ions increased the oxidation rate of NO to NO₂ significantly and hence a much higher SCR activity was expected on Fe-MOR. It is noted that although the nitrate species with an IR band near 1570 cm^{-1} was also observed on the fresh Fe-MOR when introducing $NO + O_2$, it might not be an intermediate for the SCR reaction. This is because the nitrate species comes from oxidation/disproportionation of NO₂, but NO₂ is consumed

very quickly by NH_4^+ ions during the SCR reaction. It is difficult to further convert NO2 to nitrate species in the presence of NH₃. Additionally, mordenite with a low Si/Al ratio will have strong Brønsted acidity (which is favorable for NH₃ adsorption) and large ion-exchange capacity (which increases iron content in Fe-MOR and thus enhances NO oxidation to NO₂). Hence, SCR activity increased with a decrease in the Si/Al ratio of Fe-MOR (Fig. 1). In addition, NO reduction needs NH_4^+ pairs (reaction [2]). A small pore diameter in zeolites will promote the formation of NH_4^+ pairs and thus be beneficial to NO reduction. However, a small pore size clearly decreases pore diffusion rate and thus decreases SCR activity. Therefore, an appropriate pore diameter in zeolites, e.g., 0.5-0.7 nm in ZSM-5, mordenite, and clinoptilolite, seems to be good for high SCR activity.

CONCLUSIONS

Based on the above results, it can be concluded that Fe-exchanged mordenite and clinoptilolite were highly active for the ammonia SCR reaction, whereas Fe-exchanged beta, ferrierite, and chabazite were less active. SCR activity was improved by the presence of SO_2 and $SO_2 + H_2O$. Near 100% NO conversion was obtained on Fe-MOR at a high space velocity (GHSV = $4.6 \times 10^5 \text{ h}^{-1}$). The iron cations in the catalysts were present mainly as Fe³⁺ ions. Adsorbed NO, N2O3, NO2, and nitrate species were observed when introducing $NO + O_2$ to Fe–MOR. They were bonded to the iron sites. NH3 molecules were adsorbed on Brønsted acid sites to form NH_4^+ ions. The NH_4^+ ions on Fe–MOR were active in reacting with $NO + O_2$ at high temperatures, but those on the H-MOR were less active. The present results indicate that NH_4^+ , NO, and NO₂ species play an important role in the SCR reaction. A possible reaction scheme for NO reduction was proposed involving NO₂ as an intermediate.

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