Catalytic Performance of Fe–ZSM-5 Catalysts for Selective Catalytic Reduction of Nitric Oxide by Ammonia

R. Q. Long and R. T. Yang[1]

Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136

A series of Fe-exchanged molecular sieves were studied as catalysts for the selective catalytic reduction (SCR) of NO with ammonia. It was found that Fe–ZSM-5 and Fe–mordenite catalysts were highly active for the SCR reaction. Nearly 100% NO conversions were obtained at 400–500°C under conditions with a high space velocity (GHSV $= 4.6 \times 10^5$ l/h). However, Fe–Y and Fe–MCM-41 with larger pore sizes showed lower activities for this reaction. For Fe–ZSM-5 catalysts, the SCR activity decreased with increasing Si/Al ratio in the zeolites. As the Fe-exchange level in the Fe–ZSM-5 catalysts was increased from 58 to 252%, NO conversion increased at lower temperatures (e.g., 300°C), but decreased at high temperatures (e.g., 600°C). Compared with the commercial vanadia catalyst, based on the first-order rate constants, the Fe–ZSM-5 catalyst was five times more active at 400°C and seven times more active at 450°C. It also functioned in a broader temperature window, produced only N_2 (rather than N_2O) and H_2O, and showed a substantially lower activity for oxidation of SO_2 to SO_3. © 1999 Academic Press

Key Words: selective catalytic reduction of NO with NH_3; Fe–ZSM-5 catalyst; Fe–mordenite catalyst; Fe–Y catalyst; Fe–MCM-41 catalyst.

INTRODUCTION

Nitrogen oxides (NO, NO_2, and N_2O) in the exhaust gases from combustion of fossil fuels remain a major source for air pollution. They contribute to photochemical smog, acid rain, ozone depletion, and greenhouse effects. The current technology for reducing nitrogen oxides emissions from power plants is selective catalytic reduction (SCR) of NO_x ($x = 1, 2$) with ammonia in the presence of oxygen. Many catalysts have been reported to be active for this reaction, such as vanadia and other transition metal oxides (e.g., CuO, Fe_2O_3, Cr_2O_3, Fe_2O_3–Cr_2O_3, Nb_2O_5, etc.), pillared clays, and zeolite-type catalysts (1, 2). Although the SCR technology based on vanadia catalysts has been commercialized, problems still remain, e.g., high activity for oxidation of SO_2 to SO_3, formation of N_2O at high temperatures, and

toxicity of vanadia. Hence there are continuing efforts in developing new catalysts.

H-zeolites and ion-exchanged molecular sieves have received much attention for SCR of NO_x by both hydrocarbon and ammonia in recent years. H-mordenite (MOR) was found active for SCR with ammonia by Pence and Thomas (3). Since that time, H-form, Cu-exchanged, and Fe-exchanged zeolites (e.g., mordenite, Y, ZSM-5) (4–10), pillared clays (11–13), MCM-41, and HMS (14) have been investigated by many groups. Our group first reported that pillared clays were active for the SCR reaction (11). Many transition metal ions (Cr^{3+}, Cu^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, etc.) have been exchanged with pillared clays (12). Among them, the Fe-exchanged pillared clays were the most active catalysts (12). Moreover, the SCR activity on the Fe-exchanged pillared clays was improved by the presence of H_2O and SO_2, which was attributed to an increase in surface acidity due to sulfation of the catalysts (13). Fe-exchanged zeolites also showed high activities for the SCR reaction. Komatsu *et al.* (9) studied the SCR of NO with NH_3 on Fe–ZSM-5, but the activity was only moderate. Its moderate activity could be related to the low iron content in the Fe–ZSM-5 catalyst because the Fe–ZSM-5 was prepared by exchanging Fe^{3+} with ZSM-5 so that only a low exchange level could be reached. More recently, Ma and Grunert (10) reported the preparation of an overexchanged Fe–ZSM-5 catalyst by sublimation of $FeCl_3$ vapor into H–ZSM-5, similar to that reported earlier by Chen and Sachtler (15). The catalyst showed a high SCR activity and was stable in the presence of H_2O and SO_2. However, the maximum NO conversion was still lower than that of overexchanged Cu–ZSM-5 under the same reaction conditions (10). The overexchanged Fe–ZSM-5 also showed a high activity for SCR of NO by isobutane, reported by Chen and Sachtler earlier (15).

Recently, we have also prepared a superior Fe-exchanged ZSM-5 (Si/Al $= 10$) catalyst that shows the highest activity among all known catalysts for SCR of NO by ammonia. Preliminary results on this catalyst have been reported elsewhere (16). In this paper, we present the catalytic performance of Fe–ZSM-5 (Si/Al $= 10$) in detail. For comparison, Fe-exchanged mordenite, Fe-exchanged Y zeolite and

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[1] To whom correspondence should be addressed. E-mail: yang@umich.edu.

Fe-exchanged MCM-41 as well as other Fe–ZSM-5 with different Si/Al ratios are also investigated. The relationship between the SCR activity and the structure of the molecular sieves is discussed. This catalyst is much more active than the commercial vanadia catalysts and does not have the deficiencies associated with the vanadia catalysts.

EXPERIMENTAL

Preparation of catalyst. The starting materials used for preparation of the catalysts are as follows. NH$_4$–ZSM-5 (Si/Al = 10) was obtained from Air Products and Chemicals Inc. The other NH$_4$-form molecular sieves were prepared from Na-form molecular sieves by exchanging with 0.5 M NH$_4$Cl solution (three times) at room temperature. ZSM-5 (Si/Al = 40) and ZSM-5 (Si/Al = 100) were kindly supplied by Exxon. Mordenite (MOR, Si/Al = 6.4) and Y zeolite (Si/Al = 2.4) were obtained from Zeolyst International Company and Strem Chemicals, respectively. Al–MCM-41 (Si/Al = 10) was prepared according to the procedure described elsewhere (17, 18). FeCl$_2 \cdot$ 4H$_2$O (99%), FeCl$_3$ (99%), and Fe(NO$_3$)$_3 \cdot$ 9H$_2$O (98.5%) were obtained from Aldrich. Iron powder and HCl solution (2.00 M) were supplied by Fisher.

Fe-exchanged catalysts were prepared mostly by using the conventional ion exchange procedure. In each experiment, 2 g NH$_4$–ZSM-5 (Si/Al = 10, 40, and 100), NH$_4$–MOR, or NH$_4$–Y was added to 200 ml of 0.05 M FeCl$_2$ solution with constant stirring. After 24 h, the mixture was filtered and washed five times with deionized water. Fe(93)–ZSM-5(10) was prepared by exchanging NH$_4$–ZSM-5 (Si/Al = 10) with FeCl$_2$ solution three times (for designation and analysis of the catalysts, please see Table 1).

In order to prepare overexchanged Fe–ZSM-5, two other methods were used. Fe(130)–ZSM-5(10) was obtained from exchanging 2 g H–ZSM-5 with a mixed solution that contained 200 ml 0.1 M HCl and 0.73 g iron powder. The ion exchange was performed at 50°C for 10 days in a flow of He, in order to prevent oxidation of the ferrous ion to the ferric form. Fe(252)–ZSM-5(10) was prepared by sublimation of FeCl$_3$ vapor into H–ZSM-5 at 320°C for 2 h, followed by hydrolytic removal of chlorine, by following the procedure given by Chen and Sachtler (15). H–ZSM-5 was prepared by calcining NH$_4$–ZSM-5 at 500°C for 3 h. Fe(85)–MCM-41(10) was prepared by exchanging H–Al–MCM-41 (Si/Al = 10) with a solution containing 200 ml 0.1 M HCl and 0.73 g Fe at room temperature for 3 days in a flow of He. The obtained catalysts were first dried at 120°C in air for 12 h and then calcined at 600°C for 6 h. Fe^{2+} in the catalysts was oxidized to Fe^{3+} (19). Finally, the obtained samples were 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 by 3 × (number of iron ions)/(number aluminum ions). The 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(58)–ZSM-5(10) indicates that the Fe-exchange level was 58% and Si/Al was 10.

Besides Fe-exchanged catalysts, 2.27 wt% Fe$_2$O$_3$/H–ZSM-5 and V$_2$O$_5$ + WO$_3$/TiO$_2$ catalyst (4.4 wt% V$_2$O$_5$ + 8.2 wt% WO$_3$/TiO$_2$) were also used for comparison. The catalysts were prepared by incipient wetness impregnation. The V$_2$O$_5$ + WO$_3$/TiO$_2$ catalyst had nearly identical SCR activity and behavior as that of the commercial

TABLE 1

Preparation Conditions and Iron Contents of Fe-Exchanged Molecular Sieve Catalysts

Sample	Si/Al	Fe content (wt%)	Ion-exchange extent (%)	Preparation condition
Fe(58)–ZSM-5(10)	10/1	1.59	57.7	Exchanging NH$_4$–ZSM-5 with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(93)–ZSM-5(10)	10/1	2.56	93.0	Exchanging NH$_4$–ZSM-5 with FeCl$_2$ solution for 24 h at room temperature (three times)
Fe(130)–ZSM-5(10)	10/1	3.58	130	Exchanging H–ZSM-5 with Fe + HCl solution at 50°C for 10 days in He
Fe(252)–ZSM-5(10)	10/1	6.94	252	Exchanging H–ZSM-5 with FeCl$_3$ vapor at 320°C
Fe(57)–ZSM-5(40)	40/1	0.43	57.3	Exchanging NH$_4$–ZSM-5 with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(65)–ZSM-5(100)	100/1	0.20	65.3	Exchanging NH$_4$–ZSM-5 with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(60)–MOR(6.4)	6.4/1	2.41	59.6	Exchanging NH$_4$–mordenite with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(67)–Y(2.4)	2.4/1	5.59	66.9	Exchanging NH$_4$–Y with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(85)–MCM-41(10)	10/1	2.33	84.7	Exchanging H–Al–MCM-41 with Fe + HCl solution at 25°C for 3 days in a flow of He

SCR catalyst supplied by a major catalyst manufacturer (20).

Catalytic activity measurement. The SCR activity measurement was carried out in a fixed-bed quartz reactor. In this work, 50 mg (0.065 ml) catalyst was used. The flue gas was simulated by blending different gaseous reactants. Two sets of flowmeters were used to control the flow rates of the individual reactants. He, NH_3/He (premixed), and NO/He (premixed) gases were controlled by rotameters, whereas SO_2/He (premixed) and O_2 were controlled by mass flowmeters (FM 4575 Linde Division). The typical reactant gas composition was as follows: 1000 ppm NO, 1000 ppm NH_3, 2% O_2, 500 ppm SO_2 (when used), 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 (4.6×10^5 l/h). The premixed gases (1.01% NO in He, 1.00% NH_3 in He, and 0.99% SO_2 in He) were supplied by Matheson. Water vapor was generated by passing He through a heated gas-wash bottle containing deionized water. The tubings of the reactor system were wrapped with heating tapes to prevent formation and deposition of ammonium sulfate/bisulfate and ammonium nitrate. The NO and NO_2 concentrations were continually monitored by a chemiluminescent NO/NO_x analyzer (Thermo Electro Corporation, Model 10). 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. The products were also analyzed by a gas chromatograph (Shimadzu, 14A) at 50°C with a 5 A molecular sieve column for N_2 and Porapak Q column for N_2O. Hence the nitrogen balance and the product selectivities for N_2 and N_2O could be obtained. During the reaction, the temperature was increased stepwise from room temperature to 600°C. At each temperature step, i.e., 250, 300, 350, 400, 450, 500, 550, and 600°C, the data were recorded when the SCR reaction reached steady state after 5 min.

SO₃ analysis. To measure the amount of SO_3 from SO_2 oxidation during the SCR reaction, a conventional wet analysis method was adopted. With the same reactor used for measuring the catalyst SCR activity, the effluent was bubbled through a solution containing $BaCl_2$ and HCl. After 12- to 24-h runs at 375°C under the conditions of 1000 ppm NO, 1000 ppm NH_3, 2% O_2, 5% H_2O, 500 ppm SO_2, and GHSV = 4.6×10^5 l/h, SO_3 was quantitatively captured and precipitated as $BaSO_4$. Considering that a small amount of ammonium sulfates (resulting from the reaction of SO_3, H_2O and NH_3) might stay in the tubing between the SCR reactor and $BaCl_2$ solution, we washed the tubing with deionized water and collected in the $BaCl_2$ solution after the reaction. The $BaSO_4$ precipitate was collected on an ashless filter paper which was burned along with the precipitate in

a crucible, so the amount of the precipitate was accurately measured.

RESULTS

Catalytic performance of Fe–ZSM-5. The SCR activities of H–ZSM-5, Fe_2O_3/H–ZSM-5, Fe–ZSM-5, and $V_2O_5 + WO_3$/TiO_2 catalysts are shown in Fig. 1. Under the conditions with a high GHSV (4.6×10^5 l/h), H–ZSM-5(10) showed moderate activity. NO conversion increased from zero to 65% when the reaction temperature was increased from 250 to 600°C. This is in good agreement with the previous result that H–ZSM-5 was active for the SCR reaction at high temperatures (1, 2). After 2.27 wt% Fe_2O_3 was doped on the H–ZSM-5, NO conversions were improved at lower temperatures, but the highest NO conversion was only 70% at 550°C. However, when the same amount of iron ions were exchanged to ZSM-5, surprisingly high NO conversions were obtained on the Fe(58)–ZSM-5(10) catalyst, which also gave a broad temperature window (Fig. 1). Nearly 100% NO conversion was obtained at 400–550°C on the Fe–ZSM-5 catalyst. The above results indicate clearly that Fe^{3+} in the catalyst played an important role for the SCR reaction. By comparison, the
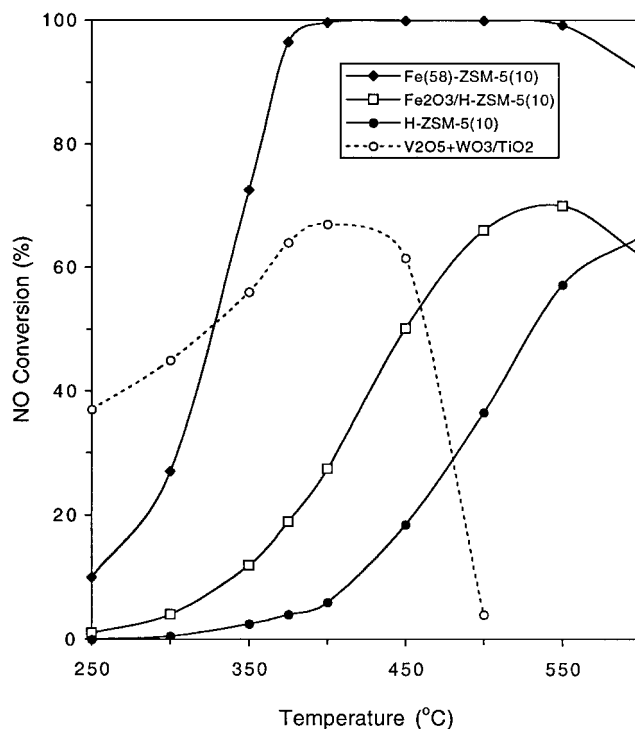

FIG. 1. Catalytic activities for SCR of NO by ammonia on H–ZSM-5(Si/Al = 10), 2.27 wt% Fe_2O_3/H–ZSM-5(Si/Al = 10), Fe(58% ion exchange)–ZSM-5(Si/Al = 10), and 4.4 wt% $V_2O_5 + 8.2$ wt% WO_3/TiO_2 catalysts. Reaction conditions: 50 mg (0.065 ml) catalyst, 1000 ppm NO, 1000 ppm NH_3, 2% O_2, balance He, and GHSV = 4.6×10^5 l/h (based on ambient conditions).

commercial $V_2O_5 + WO_3/TiO_2$ catalyst showed substantially lower NO conversions under the same conditions, and the NO conversions decreased sharply when the temperature was above 450°C (Fig. 1) due to oxidation of ammonia by oxygen (1, 2). The SCR activity can also be represented quantitatively by first-order rate constant (k) (since the reaction is known to be first order with respect to NO under stoichiometric NH_3 conditions on a variety of catalysts (1)). By assuming plug flow reactor (in a fixed bed of catalyst) and free of diffusion limitation, the rate constant can be calculated from the NO conversion (X) by

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

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 reaction conditions, first-order rate constants could be calculated. The k values of Fe(58)–ZSM-5(10) were 2078 and 2793 cm^3/g/s at 400 and 450°C, respectively. They are about five and seven times as active as the commercial catalyst (417 cm^3/g/s at 400°C and 386 cm^3/g/s at 450°C). In addition, on the Fe(58)–ZSM-5(10) catalyst, no N_2O was detected in the entire temperature range of 250–600°C, with only N_2 and H_2O as the reaction products. With the $V_2O_5 + WO_3/TiO_2$ catalyst, a significant amount of N_2O was formed at high temperatures (e.g., 5% of N_2O yield was obtained at 375°C). The nitrogen balance in this work was above 95%. The maximum SCR activity on the Fe–ZSM-5 catalyst was also superior to any other catalysts reported in the literature.

Effect of Fe content on SCR activity over Fe–ZSM-5 (10) catalysts. The effect of the Fe content on the SCR activity is summarized in Table 2. At low temperatures (e.g., 300°C), both NO conversion and first-order rate constant (k) increased with increasing Fe content on the Fe–ZSM-5(10) catalysts. However, at higher temperatures (>550°C), they dropped more rapidly with an increase in Fe content. This may be related to oxidation of NH_3 by O_2 at high temperatures because a high iron content on the catalyst may be beneficial to oxidation of NH_3. At 400–500°C, NO conversion reached nearly 100% on the Fe–ZSM-5(10) catalysts with 58–130% of the Fe-exchange level. Also, no N_2O was detected by GC during the reaction for these catalysts. The SCR activity can also be represented quantitatively by turnover frequency (TOF). TOF is defined as the number of NO molecules converted per Fe per second (based on total Fe content). From the NO conversions and Fe amounts on the above catalysts, TOFs were calculated and compared in Table 2. It is clearly seen that TOF decreased with increasing Fe content on the above Fe–ZSM-5(10) catalysts.

Effect of Si/Al ratio on SCR activity over Fe–ZSM-5 catalysts. It is known that the Si/Al ratio in zeolites affects

TABLE 2

Catalytic Performance of Fe–ZSM-5(10) Catalysts in the Absence of H_2O and SO_2[a]

Catalyst[b]	Temperature (°C)	NO Conversion to N_2 (%)	$k^c \times 10^{-3}$ (cm^3/g/s)	TOF[d] $\times 10^3$ (s^{-1})
Fe(58)–ZSM-5(10)	300	27.0	0.101	6.49
	350	72.5	0.450	17.4
	400	99.6	2.08	23.9
	450	>99.9	2.79	24.0
	500	>99.9	2.99	24.0
	550	99.2	2.22	23.8
	600	92.0	1.23	22.1
Fe(93)–ZSM-5(10)	300	33.0	0.128	4.92
	350	82.0	0.597	12.2
	400	99.0	1.73	14.8
	450	>99.9	2.79	14.9
	500	>99.9	2.99	14.9
	550	95.6	1.26	14.2
	600	91.0	1.18	13.6
Fe(130)–ZSM-5(10)	300	35.0	0.138	3.73
	350	85.4	0.670	9.11
	400	99.1	1.77	10.6
	450	>99.9	2.79	10.7
	500	>99.9	2.99	10.7
	550	98.6	1.97	10.6
	600	91.5	1.20	9.79
Fe(252)–ZSM-5(10)	300	57.0	0.270	3.13
	350	97.0	1.22	5.34
	400	99.7	2.19	5.48
	450	95.0	1.21	5.22
	500	90.0	0.995	4.95
	550	86.0	0.905	4.73
	600	67.0	0.541	3.68

[a] Reaction conditions: 0.05 g catalyst, [NO] = [NH_3] = 1000 ppm, [O_2] = 2%, He = balance, total flow rate = 500 ml/min, and GHSV = 4.6 × 10^5 l/h.

[b] The number in the first parentheses indicate % ion exchange, and that in the second is Si/Al ratio.

[c] First-order rate constant, defined by Eq. [1]. All numbers need to be multiplied by 1000.

[d] TOF (turnover frequency) is defined as the number of NO molecules converted per Fe per second.

their acidity–basicity and cation exchange capacity. The effect of Si/Al ratio on SCR activity over Fe–ZSM-5 catalysts was studied. As shown in Fig. 2, the ratio of Si/Al had a strong effect on NO conversion for the Fe–ZSM-5 catalysts. With an increase in Si/Al ratio, NO conversions decreased rapidly in the temperature range of 250–600°C (Fig. 2). High NO conversions were obtained over Fe(58)–ZSM-5 (Si/Al = 10), but very low NO conversions were obtained on Fe(65)–ZSM-5 (Si/Al = 100). These results indicate that the Fe–ZSM-5 catalysts with low Si/Al ratio are favorable to a high NO conversion.

SCR activities on different Fe-exchanged molecular sieves. The SCR activity on other different Fe-exchanged molecular sieves (Fe–MOR, Fe–Y and Fe–MCM-41) were also

studied in this work. The results are shown in Fig. 3. Like Fe(58)–ZSM-5(10), Fe(60)–MOR(6.4) catalyst also showed high activities and a broad temperature window. Also, no N_2O was detected in the entire temperature range. In comparison, Fe(67)–Y(2.4) was less active than the above two catalysts. The lowest SCR activity was found on Fe(85)–MCM-41(10) catalyst. The maximum NO conversion on the Fe–MCM-41 catalyst was only 25.5% at 550°C under the condition with 4.6×10^5 l/h. The above results suggest that the structure of molecular sieves has a strong effect on the SCR activity.

Effect of oxygen on SCR activity. The effect of oxygen concentration on NO conversion is shown in Fig. 4. In the absence of oxygen, NO conversions were low at 350 and 450°C for the Fe(58)–ZSM-5(10) catalyst. However, when a small amount of oxygen was added to the reactants, NO conversions were increased sharply (Fig. 4), indicating a promoting role of oxygen for the SCR reaction. At 350°C, NO conversion increased with increasing oxygen concentration from 0 to 4%. However, at 450°C, nearly 100% NO conversions were obtained in the presence of oxygen. Also, no N_2O was detected during the reaction.

Effect of $H_2O + SO_2$ on SCR activity. Because resistance to H_2O and SO_2 is an important factor for SCR catalysts, we studied the effect of H_2O and SO_2 on the
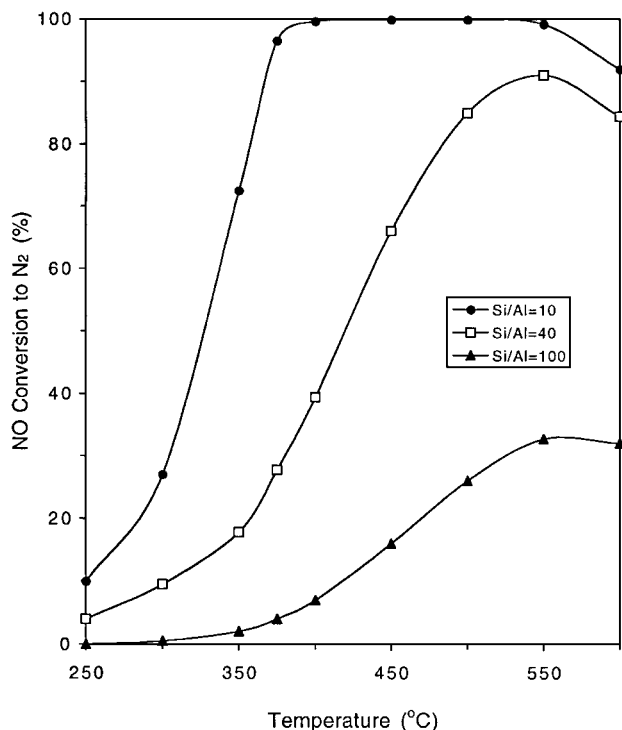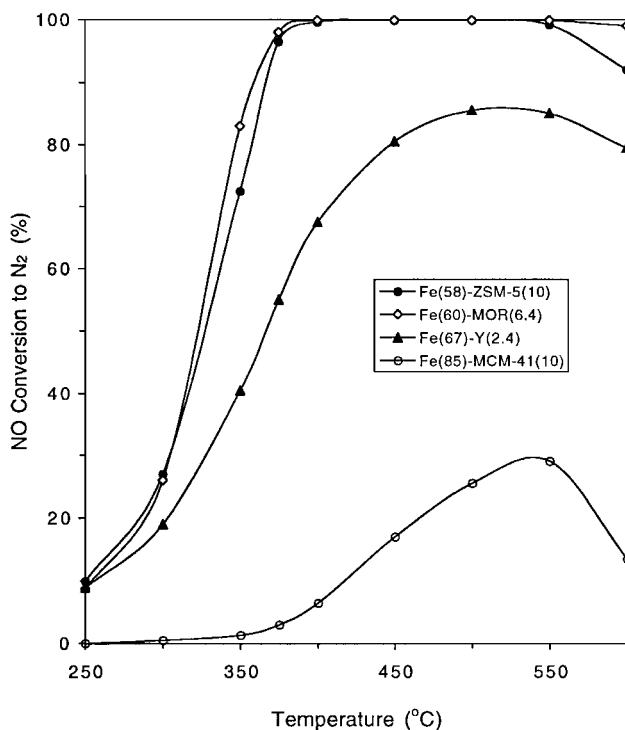

FIG. 3. Catalytic performance for SCR of NO by ammonia on Fe-exchanged molecular sieve catalysts. Reaction conditions are the same as in Fig. 1.
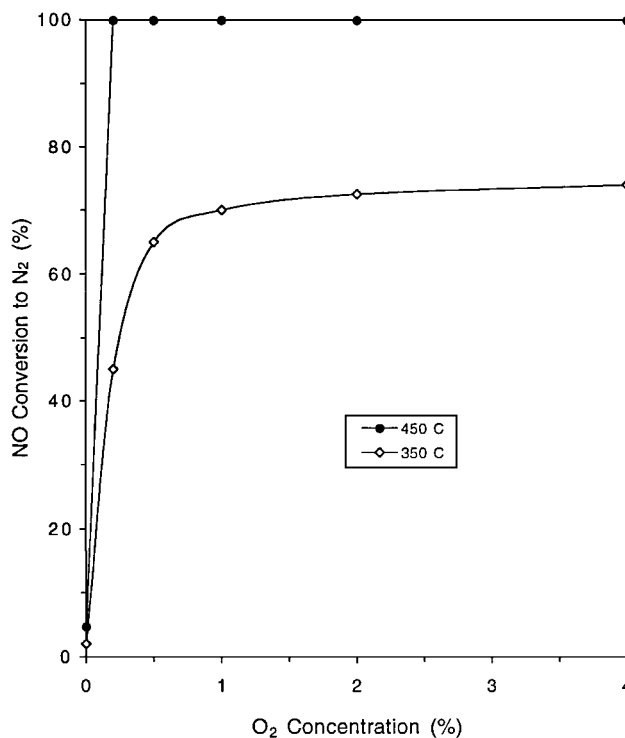

FIG. 2. Effect of Si/Al ratio on NO conversion over Fe(58% exchange)–ZSM-5(Si/Al = 10), Fe(57% exchange)–ZSM-5(Si/Al = 40), and Fe(65% exchange)–ZSM-5(Si/Al = 100) catalysts. Reaction conditions are the same as in Fig. 1.

FIG. 4. Effect of O_2 concentration on catalytic performance for SCR of NO by ammonia on Fe(58% exchange)–ZSM-5(Si/Al = 10) catalyst. Reaction conditions: 50 mg catalyst, 1000 ppm NO, 1000 ppm NH_3, 0–4% O_2, balance He, and GHSV = 4.6×10^5 l/h (ambient conditions).

TABLE 3

Catalytic Performance of Fe–ZSM-5(10) Catalysts in the Presence of H_2O and SO_2[a]

Catalyst[b]	Temperature (°C)	NO Conversion to N_2 (%)	$k^c \times 10^{-3}$ (cm³/g/s)	TOF[d] $\times 10^3$ (s⁻¹)
Fe(58)–ZSM-5(10)	300	20.0	0.072	4.81
	350	70.0	0.419	16.8
	400	>99.9	2.60	24.0
	450	>99.9	2.79	24.0
	500	>99.9	2.99	24.0
	550	>99.9	3.18	24.0
	600	94.0	1.37	22.6
Fe(130)–ZSM-5(10)	300	30.0	0.114	3.21
	350	81.8	0.594	8.75
	400	>99.9	2.60	10.7
	450	>99.9	2.79	10.7
	500	>99.9	2.99	10.7
	550	>99.9	3.18	10.7
	600	95.0	1.46	10.1

[a] Reaction conditions: 0.05 g catalyst, [NO] = [NH₃] = 1000 ppm, [O₂] = 2%, [H₂O] = 5%, [SO₂] = 500 ppm, He = balance, total flow rate = 500 ml/min, and GHSV = 4.6×10^5 l/h.

[b] The number in the first parentheses indicates % ion exchange, and that in the second Si/Al ratio.

[c] First-order rate constant, defined by Eq. [1].

[d] TOF (turnover frequency) is defined as the number of NO molecules converted per Fe per second.

catalytic performance over the Fe–ZSM-5 catalysts (Table 3). At low temperatures (e.g., 300°C), NO conversions, first-order rate constants (k), and TOFs decreased in the presence of H_2O and SO_2 on Fe(58)–ZSM-5(10) and Fe(130)–ZSM-5(10) catalysts. However, at high temperatures, it was found that H_2O and SO_2 increased SCR activities and also widened the temperature windows for the two catalysts (Tables 2 and 3). This phenomenon is similar to that observed on Fe-exchanged pillared clay catalysts (13).

SO₂ oxidation activity. Using the wet chemical method described in the foregoing to quantitatively measure the amounts of SO_3 generated in the reaction effluents, SO_2 conversions at 375°C for Fe(58)–ZSM-5(10) and $4.4\%V_2O_5 + 8.2\%WO_3/TiO_2$ were obtained. The conversion for SO_2 to SO_3 was 0.7% for Fe(58)–ZSM-5(10), which was much lower than that (3.8%) on the vanadia catalyst under the same reaction conditions.

DISCUSSION

The present work has shown that the Fe–ZSM-5(10) catalysts have higher activities than all known catalysts for SCR reaction of NO with ammonia. Nearly 100% NO conversion was obtained under a high space velocity (GHSV = 4.6×10^5 l/h) (Fig. 1 and Tables 2 and 3). NO conversions on Fe–ZSM-5 catalysts were also much higher than that

on H–ZSM-5 and Fe_2O_3 doped H–ZSM-5 catalysts under the same reaction conditions (Fig. 1), indicating that Fe^{3+} in the catalysts played an important role for the SCR reaction. This is similar to our previous result that Fe-exchanged TiO_2–pillared clay (Fe–TiO₂–PILC) catalysts were more active than Fe_2O_3/TiO_2–PILC and TiO_2–PILC catalysts for the SCR reaction (13, 20). At low temperatures, H_2O and SO_2 decreased the SCR activities for Fe–ZSM-5 catalysts, whereas they improved the catalytic activities at high temperatures (Tables 2 and 3). As compared with the commercial vanadia catalyst, the Fe–ZSM-5(10) catalysts were much more active; they functioned in a broader temperature window and produced only N_2 (rather than N_2O) and H_2O; they also showed a substantially lower activity for the oxidation of SO_2 to SO_3.

For Fe–ZSM-5(10) catalysts, when the Fe-exchange level was increased from 58 to 252%, the NO conversion increased at lower temperatures (e.g., 300°C) but decreased at high temperatures (>500°C, Table 2). Whereas the TOF decreased with increasing iron content in the Fe–ZSM-5(10) catalysts. This is in good agreement with our previous result on Fe–TiO₂–PILC catalysts that NO conversion at high temperatures decreased with an increase in iron content (13), but is contrary to the result reported by Ma and Grunert (10) that the SCR activity on Fe–ZSM-5 with an exchange degree of <100% was inferior to that on the overexchanged Fe(300)–ZSM-5(14). Overexchanged Fe–ZSM-5 catalysts have attracted much attention for the SCR of NO with hydrocarbon because they were highly active and resistant to H_2O and SO_2 as compared with the Cu–ZSM-5 catalysts. Feng and Hall (19) first reported that Fe(183)–ZSM-5(19) prepared by ion-exchange from oxalate salt was an active and durable SCR catalyst with isobutane as the reductant. The SCR activity of Fe(183)–ZSM-5(19) was much higher than that of underexchanged Fe–ZSM-5 catalysts (i.e., ion-exchange level <100%). Chen and Sachtler (15) studied the same reaction on Fe(300)–ZSM-5 catalysts prepared by using anaerobic sublimation of volatile $FeCl_3$ to H–ZSM-5. They also reported high activity and durability of the overexchanged Fe–ZSM-5 catalysts for SCR with hydrocarbons. Using the procedure of Chen and Sachtler (15), Ma and Grunert (10) prepared an overexchanged Fe(300)–ZSM-5(14) catalyst and investigated its catalytic performance for the SCR of NO with ammonia. They also concluded that the SCR activity of the overexchanged catalyst was superior to that of underexchanged Fe–ZSM-5 catalysts obtained by conventional aqueous exchange. However, the maximum NO conversion on the Fe(300)–ZSM-5(14) in their work was below 85% under the condition with a lower space velocity of 3.04×10^5 l/h, which was significantly lower than that (near 100%) on the Fe(58)–ZSM-5(10) catalyst obtained at a higher space velocity (4.6×10^5 l/h) in this work. It is noted that, although overexchange is important for Fe–ZSM-5 catalysts to obtain a high activity for SCR with hydrocarbons (15, 19), it

may not be necessary for SCR with ammonia. The mechanisms for these two SCR reactions are different. The SCR reaction with hydrocarbons generally involves the adsorption/oxidation of nitrogen oxides and hydrocarbons. The surface acidity of catalyst does not play an important role and no direct relationship between catalytic activity and acidity has been found for this reaction (21, 22). For the SCR of NO with ammonia, the reaction path involves the adsorption of ammonia on the Brønsted or Lewis acid sites and reaction between the ammonia adspecies and nitrogen oxides (1, 2). In this reaction, surface acidity is important because strong acidity is beneficial to NH_3 adsorption. Much work has demonstrated that there is a direct correlation between SCR activity and surface acidity for many catalysts (e.g., V_2O_5/TiO_2, pillared clay and zeolite catalysts), and an increase in surface acidity improves the catalytic activity (1, 2, 13, 20, 23–25). The results obtained in this study indicated that a higher Fe-exchange level did not result in a higher acidity. However, a higher iron content may increase the activity for oxidation of ammonia by oxygen at high temperatures. This will result in a decrease in NO conversion at high temperatures over the Fe–ZSM-5(10) catalysts with higher iron contents. Komatsu *et al.* (26) reported that the oxidation activity of ammonia by oxygen increased with copper content on Cu–ZSM-5 and the catalysts with higher copper contents also showed lower NO conversions at high temperatures for the SCR reaction of NO with ammonia.

The above results also indicated that the ratio of Si/Al in ZSM-5 had a strong effect on NO conversion for the Fe–ZSM-5 catalysts. Although the ion-exchange level for Fe(58)–ZSM-5(10), Fe(57)–ZSM-5(40), and Fe(65)–ZSM-5(100) were close, NO conversions decreased sharply with increasing Si/Al ratio (Fig. 2). It is known that ZSM-5 with a lower Si/Al ratio has a higher Brønsted acidity so that a high SCR activity will be achieved on the Fe–ZSM-5 catalyst. For different Fe-exchanged molecular sieves, NO conversions were found to decrease in an order of Fe(58)–ZSM-5(10) ≈ Fe(60)–MOR(6.4) > Fe(67)–Y(2.4) ≫ Fe(85)–MCM-41(10) (Fig. 3). This indicates that the structure of the molecular sieve played an important role for the SCR reaction with ammonia. ZSM-5 has a unique pore structure that consists of two intersecting channel systems: one straight and the other sinusoidal and perpendicular to the former. Both channel systems have 10-member-ring elliptical openings (0.52–0.57 nm in diameter). The mordenite pore structure consists of elliptical and noninterconnected channels parallel to the *c*-axis of the orthorhombic structure. Their openings are limited by 12-member rings (0.6–0.7 nm). Y–zeolite is a faujasite-type zeolite with 1.5–3.0 of Si/Al ratio, whose large cavities of 1.3 nm in diameter (supercages) are connected to each other through apertures of 1.0 nm. By comparison, MCM-41, a new member of molecular sieve family, shows a regular hexagonal array of uniform pore openings with pore di-

mensions between 1.5 and 10 nm (27). The average pore diameter of the Al–MCM-41(10) was 4.3 nm (17). Hence, the pore sizes of the above molecular sieves increase according to the sequence ZSM-5 < MOR < Y < MCM-41, but the SCR activities on the above Fe-exchanged molecular sieves decreased in this order. However, large pore diameter is clearly beneficial to diffusion rates for the SCR reaction. This contradiction suggests that the SCR reaction could be free of diffusion limitation and the SCR reaction was achieved at pore openings near the crystallite surfaces. For the H–ZSM-5 catalyst, Eng and Bartholomew (28) proposed a scheme for reducing NO to N_2 by ammonia. One pair of NH_4^+ ions (i.e., two NH_3 molecules adsorbed onto neighboring Brønsted acid sites) reacts with one NO_2 molecule (resulting from oxidation of NO by O_2) to form a complex, which subsequently reacts with another NO molecule to produce N_2 and H_2O. They suggested that the oxidation of NO to NO_2 was the rate-limiting step for the reaction. According to the above catalytic performance results, it seems that Fe-exchanged molecular sieves also follow this reaction pathway. Fe^{3+} ions on the catalysts increased the oxidation rate of NO to NO_2 and thus increased the SCR activity significantly as compared with H–ZSM-5 (Fig. 1). A small pore diameter and a low Si/Al ratio in molecular sieves would promote the formation of NH_4^+ pairs so that Fe–ZSM-5(10) and Fe–MOR(6.4) catalysts showed high activities. On the contrary, pairs of NH_4^+ would be difficult to form on Fe-exchanged molecular sieves with large pore sizes and high Si/Al ratios (due to a lack of adjacent acid sites) thus very low SCR activities were obtained on Fe(85)–MCM-41(10) and Fe(65)–ZSM-5(100) catalysts.

Durability of the Fe–ZSM-5 catalysts in SO_2 and H_2O was discussed in our previous paper (16). In a 60-hour test of the Fe–ZSM-5 catalyst, the NO conversion decreased by nearly 20%. However, after the addition of Ce promoter, no decrease in its activity was observed (16).

CONCLUSIONS

The present work has shown that Fe–ZSM-5(Si/Al = 10) and Fe–MOR(Si/Al = 6.4) catalysts were highly active for the SCR reaction of NO with ammonia. Nearly 100% NO conversion was obtained at 400–550°C under conditions with a high space velocity (GHSV = 4.6×10^5 l/h). However, Fe–Y(Si/Al = 2.4) and Fe–MCM-41(Si/Al = 10) with larger pore diameters showed lower activities for this reaction. For Fe–ZSM-5 catalysts, the SCR activity also decreased with increasing Si/Al ratio in the zeolites. As compared with the commercial vanadia catalyst, the Fe–ZSM-5(10) catalysts were much more active; they functioned in a broader temperature window and produced only N_2 (rather than N_2O) and H_2O; they also showed a substantially lower activity for oxidation of SO_2 to SO_3.

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