Selective Catalytic Oxidation (SCO) of Ammonia to Nitrogen over Fe-Exchanged Zeolites

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

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

Fe-exchanged zeolites were prepared and studied as catalysts for selective catalytic oxidation (SCO) of ammonia to nitrogen in the presence of excess oxygen. Fe–ZSM-5, Fe–mordenite (MOR), and Fe–clinoptilolite (HEU) showed excellent SCO performance at a very high space velocity (GHSV $= 2.3 \times 10^5$ h^{-1}). Greater than 97% NH$_3$ conversion and nearly 100% N$_2$ selectivity were obtained. Among different zeolites, the catalytic performance decreased in the sequence of Fe–ZSM-5, Fe–MOR, Fe–HEU > Fe–Y, Fe–Beta > Fe–ferrierite, Fe–chabazite. High iron content, low Si/Al ratio, and low ammonia concentration were favorable for high activities for NH$_3$ oxidation to N$_2$. For the Fe-exchanged zeolites, there existed a good correlation between the N$_2$ selectivity for the SCO reaction and the activity for the SCR (selective catalytic reduction) of NO with ammonia; i.e., the higher the SCR activity, the higher the N$_2$ selectivity in SCO. The variable valence of iron cations might be beneficial to oxygen activation and thus result in the high SCO performance for the Fe-exchanged zeolites. A kinetic study indicated that the reaction was first order with respect to NH$_3$ and the apparent reaction activation energy (E_a) was 88 kJ/mol. © 2001 Academic Press

Key Words: selective catalytic oxidation (SCO) of NH$_3$; selective catalytic reduction (SCR) of NO; Fe-exchanged zeolites; Fe–ZSM-5; Fe–mordenite (MOR); Fe–clinoptilolite (HEU).

INTRODUCTION

The increasing problem of air pollution by N-contained compounds, such as NO, NO$_2$, N$_2$O, and NH$_3$, has led to more stringent emission control. The removal of ammonia from waste streams is becoming an increasingly important issue. It is known that many chemical processes use reactants containing ammonia or produce ammonia as a by-product. They are all plagued with ammonia slip problem. Selective catalytic oxidation (SCO) of ammonia to nitrogen is potentially an ideal technology for removing ammonia from oxygen-containing waste gases and consequently it is of increasing interest in recent years (1–10). Moreover, ammonia is used effectively in power plants for NO$_x$ ($x = 1, 2$) abatement by selective catalytic reduction (SCR, 4NH$_3$ +

4NO + O$_2$ = 4N$_2$ + 6H$_2$O). The commercial catalysts that are used today are V$_2$O$_5$ + WO$_3$ (or MoO$_3$) supported on TiO$_2$ (11). To control ammonia slip, most processes are carried out under the conditions of NH$_3$/NO < 1 ($\approx$0.9), which results in a decrease in NO reduction efficiency. For improving the NO reduction efficiency, the use of a stoichiometric or excess amount of ammonia is desirable. The SCO of ammonia can be applied to the SCR of NO in a secondary bed to oxidize the residual ammonia to N$_2$ (2).

Early results on ammonia oxidation showed that noble metals (e.g., Pt, Pd) were very active for oxidation of NH$_3$ to NO and N$_2$O, while transition metal oxides such as V$_2$O$_5$ could selectively convert NH$_3$ to N$_2$, but were much less active than the noble metals (1). For transition metal ion-exchanged Y zeolites, pulse reaction results showed that the activity for ammonia oxidation decreased in the following sequence: Cu–Y > Cr–Y > Ag–Y > Co–Y > Fe–Y > Ni–Y, Mn–Y, and the main product was nitrogen (1). However, the above experiments were performed at high NH$_3$ concentrations (>10%), which is not the case in the waste streams of interest (ppm levels). At 500 ppm NH$_3$ concentration, Gandhi and Shelef (3) found that CuMoO$_4$ was active for oxidation of NH$_3$ to N$_2$ at 450–550°C, but the activity and/or selectivity to N$_2$ were inhibited by water vapor. More recently, Li and Armor (2) reported that Pt, Rh, and Pd exchanged to ZSM-5 or supported on Al$_2$O$_3$ showed good SCO performance in a wet stream. The metal-ion-exchanged ZSM-5 was more active and also less affected by water than the corresponding Al$_2$O$_3$-supported catalysts. Also, the noble-metal catalysts were more active than V$_2$O$_5$/TiO$_2$ and Co–ZSM-5 (2). Over transition-metal oxides supported on γ-Al$_2$O$_3$, Amblard *et al.* (4) reported that Ni, Fe, and Mn were active for the SCO reaction. The SCO reaction was also investigated on other supported metal oxides, such as V$_2$O$_5$/TiO$_2$, CuO/TiO$_2$, and Cu–ZSM-5 (5), V$_2$O$_5$, MoO$_3$, and WO$_3$ on various supports (6), CuO/Al$_2$O$_3$ (7, 8), Cu–Mn/TiO$_2$ (9), and Cu, Co, and Ni oxides doped on SiO$_2$ (10). They all exhibited activities for nitrogen formation under various conditions.

The aforementioned work was normally performed under a somewhat low space velocity (<10^5 h^{-1}). Recently,

we studied the SCO reaction on a series of transition-metal (Cr, Mn, Fe, Co, Ni, Cu, and Pd) ion-exchanged ZSM-5 (12). Results showed that the catalytic performance (i.e., NH_3 conversion and N_2 selectivity) increased in the following manner: Co–ZSM-5 $\approx$ Ni–ZSM-5 < Mn–ZSM-5 < H–ZSM-5 < Pd–ZSM-5 < Cr–ZSM-5 < Cu–ZSM-5 < Fe–ZSM-5 at a high gas hourly space velocity (GHSV = 2.3 × 10^5 h^{-1}). Near 100% of NH_3 conversion to N_2 was obtained at 450°C on Fe–ZSM-5. H_2O and/or SO_2 only decreased the NH_3 conversion slightly (12). In this paper, a comprehensive study on Fe-exchanged zeolites for the SCO reaction is presented. ZSM-5, mordenite, clinoptilolite, Y, Beta, ferrierite, and chabazite are used. In addition, the effects of iron content, Si/Al ratio, ammonia concentration, and space velocity on the catalytic performance are also studied.

EXPERIMENTAL

Preparation of catalyst. The starting materials used for the preparation of the catalysts are as follows. NH$_4$–ZSM-5 (Si/Al $\approx$ 10) was obtained from Alsi-Penta Zeolithe Gmbh (Germany). ZSM-5 (Si/Al = 40) and ZSM-5 (Si/Al = 100) were kindly supplied by Exxon. Mordenites (MOR, Si/Al = 6.4, 10, and 45), NH$_4$–Beta (Si/Al = 12.5), and NH$_4$–ferrierite (FER, Si/Al = 10) were obtained from Zeolyst International Co. Clinoptilolite (HEU, Si/Al = 5) and chabazite (CHA, Si/Al = 2) were provided from Steelhead Minerals and GSA Resources, respectively. Y zeolite (Si/Al = 2.4) was obtained from Strem Chemicals. The non-NH$_4$-form zeolites were first transformed to NH$_4$ zeolites by exchanging with 0.5 M NH$_4$Cl solution (four times) at room temperature. FeCl$_2 \cdot$ 4H$_2$O (99%) was 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 of NH$_4$-form zeolite 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(84)–MOR(6.4) was prepared by exchanging NH$_4$–mordenite (Si/Al = 6.4) with FeCl$_2$ solution three times. (For designation and analysis of the catalysts, please see Table 1). Fe(34)–ZSM-5(10) and Fe(95)–ZSM-5(10)

TABLE 1

Preparation Conditions and Iron Contents of Fe-Exchanged Zeolites

Sample	Si/Al	Fe content (wt%)	Ion-exchange extent (%)	Preparation conditions
Fe(34)–ZSM-5(10)	10/1	0.86	34	Exchanging NH$_4$–ZSM-5 with Fe + HCl solution at room temperature for 1 day in He
Fe(58)–ZSM-5(10)	10/1	1.6	58	Exchanging NH$_4$–ZSM-5 with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(95)–ZSM-5(10)	10/1	2.4	95	Exchanging NH$_4$–ZSM-5 with Fe + HCl solution at room temperature for 10 days in He
Fe(57)–ZSM-5(40)	40/1	0.43	57	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	Exchanging NH$_4$–ZSM-5 with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(56)–MOR(6.4)	6.4/1	2.1	56	Exchanging NH$_4$–mordenite with FeCl$_2$ solution for 2 h at room temperature (once)
Fe(60)–MOR(6.4)	6.4/1	2.4	60	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	84	Exchanging NH$_4$–mordenite with FeCl$_2$ solution for 24 h at room temperature (3 times)
Fe(73)–MOR(10)	10/1	1.8	73	Exchanging NH$_4$–mordenite with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(94)–MOR(45)	45/1	0.68	94	Exchanging NH$_4$–mordenite with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(81)–HEU(5)	5/1	3.5	81	Exchanging NH$_4$–clinoptilolite with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(67)–Y(2.4)	2.4/1	5.6	67	Exchanging NH$_4$–Y with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(72)–Beta(12.5)	12.5/1	1.6	72	Exchanging NH$_4$–Beta with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(21)–FER(10)	10/1	0.56	21	Exchanging NH$_4$–ferrierite with FeCl$_2$ solution for 24 h at room temperature (once)
Fe(56)–CHA(2)	2/1	6.0	56	Exchanging NH$_4$–chabazite with FeCl$_2$ solution for 24 h at room temperature (once)

were obtained from exchanging 2 g of NH_4–ZSM-5 (Si/Al = 10) with a mixed solution that contained 200 ml of 0.1 M HCl and 0.73 g of iron powder at room temperature for 1 and 10 days, respectively. During preparation of the catalysts, hydrochloric acid reacted with iron metal to generate ferrous ions and then Fe^{2+} ions exchanged with NH_4–ZSM-5. To prevent oxidation of the ferrous ion to the ferric form, ion exchange was performed under a helium flow (20 ml/min). The obtained catalysts were first dried at 120°C in air for 12 h and then calcined at 500°C for 6 h. Fe^{2+} in the catalysts was oxidized to Fe^{3+} (13). 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 of aluminum atoms). 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(34)–ZSM-5(10) indicates the Fe-exchange level is 34% and Si/Al ratio is 10.

Catalytic performance measurement. The SCO activity measurement was carried out in a fixed-bed quartz reactor. The reaction temperature was controlled by an Omega (CN-2010) programmable temperature controller; 25–200 mg of catalyst was used in this work. The reactant gas was obtained by blending different gas flows. The typical reactant gas composition was as follows: 10–1000 ppm NH_3, 2% O_2, and balance He. The total flow rate was 500 ml/min (ambient conditions). The premixed gases (1.05% and 527 ppm NH_3 in He) were supplied by Matheson. A magnetic deflection type mass spectrometer (AERO VAC, Vacuum Technology Inc.) was used to monitor continuously the effluent gas from the reactor, which contained NH_3 ($m/e = 17$ minus the contribution of H_2O), H_2O ($m/e = 18$), N_2 ($m/e = 28$), NO ($m/e = 30$), O_2 ($m/e = 32$), and N_2O ($m/e = 44$). NO_2 ($m/e = 46$) was not detectable with this mass spectrometer. The concentrations of the unreacted NH_3 and the NO_x formed were also continually monitored with a chemiluminescent NO/NO_x analyzer (Thermo Electron Corp. Model 10) in which a high-temperature converter converted NH_3 to NO_x by the reaction $NH_3 + O_2 \rightarrow NO_x + H_2O$. The NH_3 conversion was calculated by $([NO] + 2[N_2] + 2[N_2O])/[NH_3]_0 \times 100\%$, where $[NH_3]_0$ is the initial NH_3 concentration. The selectivity is defined as the percentage conversion of ammonia to N_2, N_2O, and NO. The data were collected when the SCO reaction reached the steady state, typically after 20–180 min at each temperature.

RESULTS

SCO performance on different Fe-exchanged zeolites. The catalytic performance of Fe-exchanged zeolites for the SCO of NH_3 is summarized in Table 2. Under the conditions

TABLE 2

Catalytic Performance of Fe-Exchanged Zeolites

Catalyst[a]	Temp. (°C)	NH_3 conv. (%)	Selectivity (%)			N_2 yield %	TOF[b] × 10^3 (s^{-1})
			N_2	N_2O	NO		
Fe(58)–ZSM-5(10)	350	63	92	0	8	58	7.5
	400	95	98	0	2	93	11
	450	99	100	0	0	99	12
Fe(60)–MOR(6.4) (mordenite)	350	43	81	1	18	35	3.4
	400	77	90	1	9	69	6.1
	450	99	98	0	2	97	7.9
Fe(81)–HEU(5) (clinoptilolite)	350	72	90	1	9	65	3.9
	400	93	97	0	3	90	5.1
	450	98	100	0	0	98	5.3
Fe(67)–Y(2.4)	350	61	81	2	17	49	2.1
	400	86	84	1	15	72	2.9
	450	94	91	0	9	86	3.2
Fe(72)–Beta(12.5)	350	58	71	5	24	41	6.9
	400	72	82	4	14	59	8.6
	450	88	95	0	5	84	10
Fe(21)–FER(10) (ferrierite)	350	68	77	3	20	52	23
	400	81	47	4	49	38	27
	450	82	40	3	57	33	28
Fe(56)–CHA(2) (chabazite)	350	80	49	7	44	39	2.5
	400	80	50	4	46	40	2.5
	450	78	65	3	32	51	2.4

Note. Reaction conditions: 0.1 g of catalyst, $[NH_3] = 1000$ ppm, $[O_2] = 2\%$, He = balance, total flow rate = 500 ml/min, and GHSV = 2.3×10^5 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] Overall TOF (turnover frequency) is defined as the number of NH_3 molecules converted per Fe per second.

of 1000 ppm NH_3, 2% O_2, and GHSV = 2.3×10^5 h^{-1}, these catalysts showed various ammonia conversions at different temperatures. In all cases, N_2 was the main product for ammonia oxidation. Among them, Fe–ZSM-5, Fe–MOR, and Fe–HEU showed the highest NH_3 conversions to N_2 at 350–450°C. Only small amounts of N_2O and NO products were detected. Both NH_3 oxidation activity and N_2 selectivity increased with increasing temperature and reached nearly 100% N_2 yield at 450°C. By comparison, lower NH_3 conversions to N_2 were observed for Fe–Y and Fe–Beta catalysts, which also yielded more NO formation. As with the other catalysts, an increase in reaction temperature resulted in an increase in both NH_3 oxidation activity and N_2 selectivity. The maximum N_2 yield ($\approx 85\%$) was obtained at 450°C for the two catalysts. The lowest NH_3 conversions were obtained on Fe–FER and Fe–CHA. The ammonia oxidation activity did not vary significantly with temperature for the two catalysts. With increasing temperature, more NO was produced on Fe–FER. These results suggest that the structure of zeolite has a strong effect on the SCO of NH_3 to N_2

for the Fe-exchanged zeolites. It should be noted that these catalysts have different Si/Al ratios and iron contents, which also affect ammonia conversion and N_2 selectivity, as discussed below. The maximum N_2 yield by the Fe-exchanged zeolites decreased in the following sequence: Fe–ZSM-5, Fe–MOR, Fe–HEU > Fe–Y, Fe–Beta > Fe–FER, Fe–CHA. The selectivity for N_2O was very low for these catalysts. The SCO activity can also be represented quantitatively, turnover frequency (TOF). TOF is defined as the number of NH_3 molecules converted per Fe per second here (based on total Fe content). From the NH_3 conversions (Table 2) and Fe amounts (Table 1) on the above catalysts, TOFs were calculated and compared in Table 2. It seems that TOFs are affected mainly by Fe amounts; i.e., the higher the Fe contents, the lower the TOFs on the above catalysts.

Effect of Fe content on SCO performance. The effects of iron content on SCO performance for Fe–ZSM-5 and Fe–MOR are summarized in Tables 3 and 4, respectively. It can be seen that both NH_3 conversion and N_2 selectivity increased with iron content (with iron-exchange level <100%) at low temperatures for Fe–ZSM-5 (Table 3). At 450°C, the difference in NH_3 conversion was not detectable since almost all NH_3 was oxidized to N_2. Similar results were obtained on Fe–MOR, with a more significant increase in NH_3 conversion with iron content at low temperatures. With increasing temperature, more N_2 was produced and almost no N_2O or NO formation was observed at 450°C for the Fe–MOR with different iron contents. For the two kinds of catalysts, TOF decreased with Fe content except Fe–MOR at 350°C.

Effect of Si/Al ratio on SCO performance. The Si/Al ratio in zeolites affects their surface acidity and cation-

TABLE 3

Effect of Iron Content on SCO Performance for Fe–ZSM-5

Catalyst[a]	Temp. (°C)	NH$_3$ conv. (%)	Selectivity (%)			N$_2$ yield %	TOF[b] × 10^3 (s^{-1})
			N$_2$	N$_2$O	NO		
Fe(34)–ZSM-5(10)	350	63	85	0	15	54	14
	400	88	98	0	2	86	20
	450	99	100	0	0	99	22
Fe(58)–ZSM-5(10)	350	63	92	0	8	58	7.5
	400	95	98	0	2	93	11
	450	99	100	0	0	99	12
Fe(95)–ZSM-5(10)	350	78	92	0	8	72	6.2
	400	97	98	0	2	95	7.7
	450	99	100	0	0	99	7.9

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] Overall TOF (turnover frequency) is defined as the number of NH_3 molecules converted per Fe per second.

TABLE 4

Effect of Iron Content on SCO Performance for Fe–MOR

Catalyst[a]	Temp. (°C)	NH$_3$ conv. (%)	Selectivity (%)			N$_2$ yield %	TOF[b] × 10^3 (s^{-1})
			N$_2$	N$_2$O	NO		
Fe(56)–MOR(6.4)	350	31	76	2	22	24	2.8
	400	73	89	1	10	65	6.6
	450	99	97	0	3	96	9.0
Fe(60)–MOR(6.4)	350	43	81	1	18	35	3.4
	400	77	90	1	9	69	6.1
	450	99	98	0	2	97	7.9
Fe(84)–MOR(6.4)	350	65	85	2	13	55	4.0
	400	93	94	1	5	87	5.7
	450	98	100	0	0	98	6.0

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] Overall TOF (turnover frequency) is defined as the number of NH_3 molecules converted per Fe per second.

exchange capacity. The effect of Si/Al ratio on SCO performance was studied on Fe–ZSM-5 and Fe–MOR. Figure 1 shows the effect of Si/Al ratio on NH_3 conversion and N_2 selectivity for Fe–ZSM-5. The percentage of ion exchange was maintained approximately the same. With increasing Si/Al ratio from 10 to 40, NH_3 conversion and, especially N_2 selectivity, decreased significantly. A further increase in Si/Al ratio from 40 to 100 resulted in a slight decrease in the SCO performance. In addition, NH_3 conversion increased with temperature for all the Fe–ZSM-5 with different Si/Al ratios. However, the change for N_2 selectivity with temperature was different. For Fe–ZSM-5(40) and Fe–ZSM-5(100), N_2 selectivity decreased first and then increased with increasing temperature (Fig. 1), whereas for Fe–ZSM-5(10)
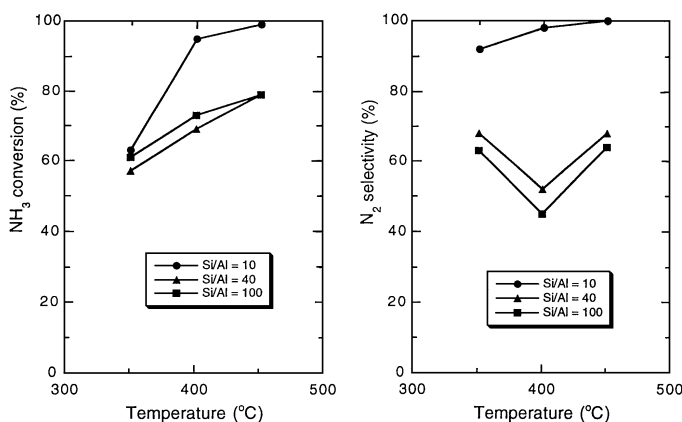

FIG. 1. Effect of Si/Al ratio on SCO performance over Fe(58% exchange)–ZSM-5(Si/Al = 10), Fe(57% exchange)–ZSM-5(Si/Al = 40), and Fe(65% exchange)–ZSM-5(Si/Al = 100) catalysts. Reaction conditions: 0.1 g of catalyst, [NH$_3$] = 1000 ppm, [O$_2$] = 2%, He = balance, total flow rate = 500 ml/min, and GHSV = 2.3 × 10^5 h^{-1}.
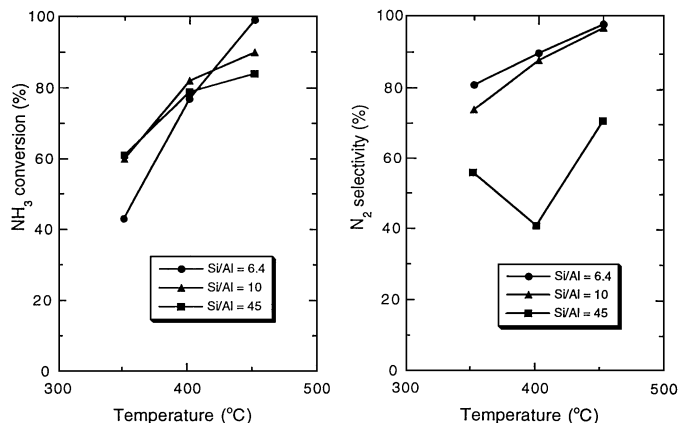
FIG. 2. Effect of Si/Al ratio on SCO performance over Fe(56% exchange)–MOR(Si/Al = 6.4), Fe(73% exchange)–MOR(Si/Al = 10), and Fe(94% exchange)–MOR(Si/Al = 45) catalysts. Reaction conditions are the same as those in Fig. 1.

N_2 selectivity increased with increasing temperature from 350 to 450°C. The effect of Si/Al ratio on the SCO performance for Fe–MOR is shown in Fig. 2. Similar to that for Fe–ZSM-5, the N_2 selectivity decreased significantly with increasing Si/Al ratio (from 6.4 to 45) for Fe–MOR, but the change for NH_3 conversion was not consistent with the decrease in Si/Al ratio.

Effect of NH_3 concentration on SCO activity. In various waste gases, the ammonia concentration varies from a few ppm to several thousand ppm. For instance, the NH_3 concentration (or "ammonia slip") is several ppm (typically 5 ppm) in the effluent from the selective catalytic reduction process of NO in power plants. The effect of ammonia concentration on SCO activity for Fe(58)–ZSM-5(10) was studied. As shown in Fig. 3, when ammonia concentration was decreased, ammonia conversion increased significantly, particularly at low temperatures. The ammonia conversion reached above 95% at 300–450°C when the inlet ammonia concentration was 10 ppm, i.e., less than 0.5 ppm NH_3 was in the outlet. The major product was nitrogen under 10–1000 ppm NH_3 concentration. The SCO activity also increased with increasing temperature. At high temperatures (e.g., 450°C), almost all of the NH_3 was converted to N_2 under the conditions with 10–1000 ppm NH_3.

Effect of space velocity on SCO performance. Fe(95)–ZSM-5(10) was used for this study. The catalyst amount was increased from 25 to 200 mg, under the conditions of $[NH_3] = 1000$ ppm, $[O_2] = 2\%$, balance = He, and total flow rate = 500 ml/min. The corresponding gas hourly space velocity (GHSV) was decreased from approximately 9.0×10^5 h^{-1} to 1.1×10^5 h^{-1}. As shown in Fig. 4, both ammonia conversion and N_2 selectivity were decreased with increasing space velocity on Fe(95)–ZSM-5(10). Lower SCO performance was obtained at higher space velocities. The major product was nitrogen (>80%) at 300–400°C.
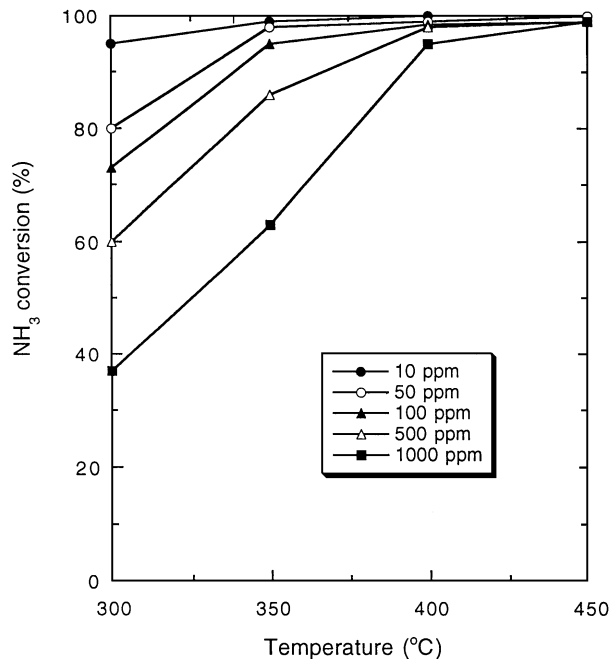

FIG. 3. Effect of NH_3 concentration on SCO activity over Fe(58% exchange)–ZSM-5(Si/Al = 10). Reaction conditions: 0.1 g of catalyst, $[NH_3] = 10$–1000 ppm, $[O_2] = 2\%$, He = balance, total flow rate = 500 ml/min, and GHSV = 2.3×10^5 h^{-1}.

DISCUSSION

The results discussed above show that Fe-exchanged zeolites are highly active for the SCO of ammonia to nitrogen. The catalytic performance, especially N_2 selectivity, was found to decrease in the follower manner: Fe–ZSM-5, Fe–MOR, Fe–HEU > Fe–Y, Fe–Beta > Fe–FER, Fe–CHA (Table 2). More than 97% NH_3 conversion and nearly 100% N_2 selectivity were obtained on Fe–ZSM-5, Fe–MOR, and
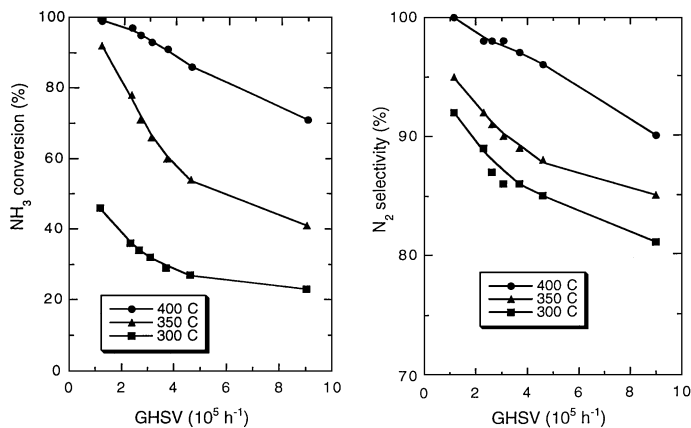

FIG. 4. Effect of space velocity on SCO performance over Fe(95% exchange)–ZSM-5(Si/Al = 10). Reaction conditions: 0.025–0.2 g of catalyst, $[NH_3] = 1000$ ppm, $[O_2] = 2\%$, He = balance, total flow rate = 500 ml/min, and GHSV = 1.1–9.0×10^5 h^{-1}.

Fe–HEU at 450°C under the condition of GHSV $= 2.3 \times 10^5 \, h^{-1}$. In our previous work (12), we also studied the effects of H_2O and SO_2 on the SCO performance over the Fe–ZSM-5 catalyst. Results showed that when 500 ppm SO_2 and/or 4% H_2O were added to the reactants, NH_3 conversion decreased only slightly; 94% NH_3 conversion could be obtained at 500°C (12). Cu–ZSM-5 is also known as a good SCO catalyst (5, 12), which showed similar SCO performance under the same conditions without H_2O or SO_2 as compared to that with Fe–ZSM-5 (12). However, H_2O and SO_2 inhibited NH_3 conversion significantly for Cu–ZSM-5. Only 65–73% NH_3 conversions were observed at 450–500°C in the presence of H_2O and SO_2 (12). For the Fe-exchanged zeolites, the difference in the SCO performance may be related to differences in pore structure and pore size for different zeolites, different iron contents and surface acidities for the Fe-exchanged zeolites. ZSM-5 has a unique pore structure that consists of two interecting channel systems: one straight and the other sinusoidal and perpendicular to the former. Both channel systems have 10-membered 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-membered rings (0.6–0.7 nm). Clinoptilolite is a member of the heulandite (HEU) family. The HEU has two main channels parallel to the c direction, one formed by a 10-membered ring (0.44–0.72 nm) and the other by an 8-member ring. It appears that zeolites with narrow, channel pore structures favor ammonia oxidation to nitrogen.

The catalytic performance results also showed that high iron content (Tables 3 and 4), low Si/Al ratio (Figs. 1 and 2), low ammonia concentration (Fig. 3), and low space velocity (Fig. 4) were favorable for high NH_3 conversion and high N_2 selectivity. It is known that ammonia molecules can adsorb on the Brønsted acid and Lewis acid sites of zeolites to generate, respectively, NH_4^+ ions and coordinated NH_3. Our previous IR results showed that the NH_4^+ ions (at 3353 and 3290 cm^{-1}) with three hydrogen atoms (3H structure) bonded to AlO_4 tetrahedra of ZSM-5 were stable at high temperatures (e.g., 300–400°C), whereas that with two bonds (at 3050 and 2795 cm^{-1}) and the coordinated NH_3 (at 1276 cm^{-1}) vanished above 300°C (13). The NH_4^+ ions with 3H structure might play an important role in ammonia oxidation to N_2 for zeolite-type catalysts. The zeolites with low Si/Al ratios have stronger Brønsted acidity and higher cation capacity than those with high Si/Al ratios. Strong Brønsted acidity is clearly favorable for ammonia adsorption and activation. After Fe^{2+} ions were exchanged to zeolites, they were oxidized to Fe^{3+} ions by O_2 during calcination. Our previous XPS and ESR data (13) on Fe–ZSM-5 indicated that iron cations were present mainly as Fe^{3+} ions with tetrahedral coordination, along with a small amount of Fe^{2+} and aggregated Fe^{3+} ions. Also, the Fe^{3+} ions could be partially reduced to Fe^{2+} ions by H_2 at 300–600°C, but the oxidation was reversible when O_2 was introduced into the reduced catalyst at 500°C (13). The variable valence of iron cations in the Fe-exchanged zeolites might be beneficial to oxygen adsorption and activation under the SCO reaction conditions, but this point needs to be verified by further spectroscopic characterization. The oxygen adspecies, e.g., O_2^-, $O_2^{\delta-}$ $(1 < \delta < 2)$, and O_2^{2-}, have been observed on O_2-adsorbed Fe_2O_3 by IR spectroscopy (14). The high cation capacities would lead to more iron ions in the Fe-exchanged zeolites with low Si/Al ratios (Table 1), which provide more active sites for oxygen adsorption and activation. Consequently, high activities for ammonia oxidation to N_2 are expected on the catalysts with the low Si/Al ratios and high iron contents.

It is interesting to note that Fe-exchanged zeolites also showed excellent activity for the selective catalytic reduction (SCR) of NO to N_2 with ammonia as reductant (15, 16). The reactivity of NH_3 with $NO + O_2$ was much higher than that with O_2 (17). Our previous work indicated that almost all of the NO was reduced to N_2 by ammonia on Fe–ZSM-5 and Fe–MOR at 400–550°C under the condition of GHSV $= 4.6 \times 10^5 \, h^{-1}$ (15, 16). These two catalysts were much more active than Fe–Y, which is in line with their relative SCO performance (e.g., N_2 selectivity) obtained in this work. Moreover, with increasing Si/Al ratio from 10 to 100 in Fe–ZSM-5, the maximum SCR activity decreased sharply from 99 to 30% (16), while the SCO performance, especially N_2 selectivity, also decreased significantly (Fig. 1). When the SCR activity is compared with SCO performance for the various Fe-exchanged zeolites, it can be seen that there is a good correlation between the SCR activity and the N_2 selectivity for the SCO reaction; i.e., the higher the SCR activity, the higher the N_2 selectivity. This conclusion indicates that when NO (the main by-product) is generated during the SCO reaction, it can be further reduced to N_2 by unreacted ammonia through the SCR reaction. Similar results were also obtained on V_2O_5/TiO_2, which showed both high SCR activity and SCO N_2 selectivity (1, 2, 5, 6, 11). For the SCO reaction, two pathways for oxidation of NH_3 to N_2 have been proposed in the literature. One is a direct route by the recombination of $2NH_2$ species to NH_2–NH_2 and then oxidation of NH_2–NH_2 to N_2 (18). The other is a two-step route that involves oxidation of NH_3 to NO_x and then reduction of NO_x to N_2 by NH_3 (1, 6, 19). According to our catalytic performance results, it seems that SCO reaction on the Fe-exchanged zeolites takes place by the two-step route; i.e., NO is an intermediate for N_2 formation. NH_3 was first oxidized to NO by O_2. This reaction occurs either on the catalyst surface or in the gaseous phase or both. Our empty-tube results showed that NH_3 conversions were 23–55% at 350–450°C under the condition of GHSV $= 2.3 \times 10^5 \, h^{-1}$, with NO as the predominant product (12). Subsequently, the NO reacts with unreacted NH_3

to produce N_2 through the SCR reaction. Therefore, good SCR catalysts are expected to have high N_2 selectivities for the SCO reaction. At low temperatures, the reactivity between NH_3 and NO_x was not high enough to convert all of the NO to N_2. For example, 72% of NO conversion was obtained on $Fe(58)$–ZSM-5(10) at 350°C (16). With increasing temperature, the SCR activity increased significantly. Almost all of the NO was reduced to N_2 by NH_3 at 400–450°C (16). Hence, very low NO selectivity would be expected at high temperatures for the SCO reaction. This led to the fact that N_2 selectivity for the SCO reaction increased with temperature on most of the Fe-exchanged zeolites.

In addition, the steady-state kinetics of the SCO reaction are worthy of a discussion. As shown in Fig. 4, SCO activity decreased with increasing space velocity at 300–400°C. Since this reactor can be considered as an integral reactor, if the reaction is assumed to be first order with respect to NH_3 and is free of diffusion limitation (as verified below), the apparent rate constant (k_a) and NH_3 conversion (X) will have the following relationship,

$$k_a = -\frac{F_0}{[NH_3]_0 W} \ln(1 - X), \qquad [1]$$

where F_0 is the molar NH_3 feed rate, $[NH_3]_0$ is the molar NH_3 concentration at the inlet (at the reaction temperature), and W is the catalyst amount (g). At the same temperature and the same NH_3 concentration, $-\ln(1 - X)$ should
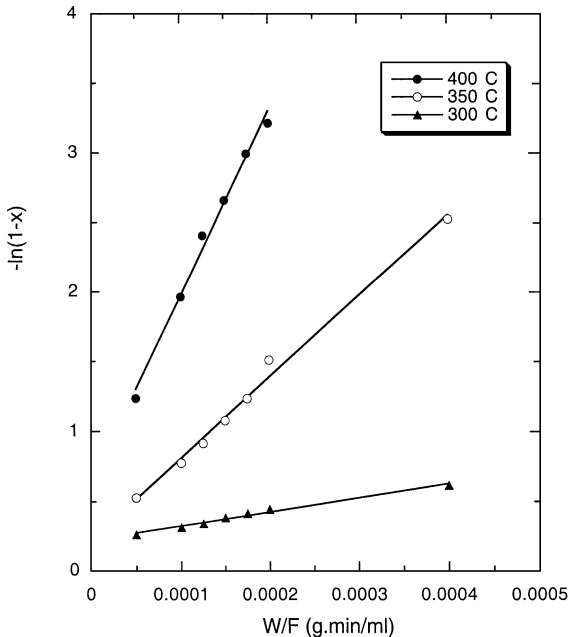

FIG. 5. First-order plots with respect to NH_3 for the data of Fig. 4, where W is the catalyst amount, F is the molar feed rate of ammonia, and X is the conversion.

TABLE 5

Apparent Rate Constant (k_a) and Intrinsic Rate Constant (k) for Fe-Exchanged ZSM-5

Temperature (°C)	Apparent k_a (s^{-1})	Intrinsic k (s^{-1})	Effectiveness factor ε
400	2.6×10^3	$2.6\text{-}2.7 \times 10^3$	0.95–1.0
350	1.0×10^3	1.0×10^3	0.98–1.0
300	1.7×10^2	1.7×10^2	1.0

be proportional to W/F. According to the data shown in Fig. 4, the plots of $-\ln(1 - X)$ vs W/F are shown in Fig. 5. The linearity at 300, 350, and 400°C verified that the reaction order with respect to NH_3 is first order. The apparent rate constants (k_a) can be calculated from the slopes of the lines. They are 32.5, 202, and 503 cm^3/g/s, respectively, at 300, 350, and 400°C. Also, the apparent activation energy (E_a), obtained from the plot of $\ln(k_a)$ vs $1/T$ at 300–400°C, is 88 kJ/mol. If pore diffusion limitation exists in the SCO reaction, the apparent rate constant (k_a) is related to the intrinsic rate constant (k) by

$$r = -k_a[NH_3] = -k\varepsilon[NH_3] \quad \text{or} \quad k_a = k\varepsilon, \qquad [2]$$

where $[NH_3]$ is the concentration of NH_3 outside the pores and ε is the effectiveness factor (20). The effectiveness factor is given by

$$\varepsilon = \tanh\left(L\sqrt{\frac{k}{D}}\right) \bigg/ \left(L\sqrt{\frac{k}{D}}\right), \qquad [3]$$

where L is the pore length and D is the pore diffusivity. The above apparent rate constants, with units of cm^3/s/g, need to be converted to the units 1/s by dividing by the pore volume (21). The pore volume is 0.19 cm^3/g for ZSM-5. The converted rate constants (k_a) are given in Table 5. It is known that the pore diffusivity (D) in H–ZSM-5 for CH_4 is ca. 10^{-8} m^2/g at 334 K (22) and the sizes of NH_3, H_2O, NO, O_2, and N_2 molecules are close or smaller as compared with CH_4. It is reasonable to use 10^{-8}–10^{-9} m^2/g as an estimate for the pore diffusivities. The particle size of ZSM-5 is estimated at 0.5 μm. The intrinsic rate constants (k) and effective factors (ε) are calculated (21) for Fe–ZSM-5 at 300–400°C and are shown in Table 5. It can be seen that the effective factors are very close to 1, verifying that the SCR reaction is almost free of diffusion limitation.

CONCLUSIONS

Based on the above results, it can be concluded that Fe-exchanged zeolites are highly active for the SCO of ammonia to nitrogen at very high space velocities. The catalytic performance was found to decrease in the order of

Fe–ZSM-5, Fe–MOR, Fe–HEU > Fe–Y, Fe–Beta > Fe–FER, Fe–CHA. High iron content, low Si/Al ratio, low ammonia concentration, and low space velocity were favorable for high SCO performance. In addition, there exists a good correlation between the N_2 selectivity for the SCO reaction and the SCR activity of NO with NH_3 for the Fe-exchanged zeolites; i.e., the higher the SCR activity, the higher the SCO N_2 selectivity. The variable valence of iron cations might be beneficial to oxygen adsorption and activation and thus result in high SCO performance. The reaction order with respect to NH_3 was found to be first order and the apparent activation energy was 88 kJ/mol.

ACKNOWLEDGMENTS

REFERENCES

1. II'chenko, N. I., *Russ. Chem. Rev.* **45**, 1119 (1976).
2. Li, Y., and Armor, J. N., *Appl. Catal. B* **13**, 131 (1997).
3. Gandhi, H. S., and Shelef, M., *J. Catal.* **40**, 312 (1975).
4. Amblard, M., Burch, R., and Southward, B. W. L., *Appl. Catal. B* **22**, L59 (1999).
5. Sazonova, N. N., Simakov, A. V., Nikoro, T. A., Barannik, G. B., Lyakhova, V. F., Zheivot, V. I., Ismagilov, Z. R., and Veringa, H., *React. Kinet. Catal. Lett.* **57**, 71 (1996).
6. De Boer, M., Huisman, H. M., Mos, R. J. M., Leliveld, R. G., Vandillen, A. J., and Geus, J. W., *Catal. Today* **17**, 189 (1993).
7. Gang, L., van Grondelle, J., Anderson, B. G., and van Santen, R. A., *J. Catal.* **186**, 100 (1999).
8. Curtin, T., O'Regan, F., Deconinck, C., Knuttle, N., and Hodnett, B. K., *Catal. Today* **55**, 189 (2000).
9. Wollner, A., and Lange, F., *Appl. Catal. A* **94**, 181 (1993).
10. Dannevang, F., U.S. Patent 5,587,134, 1996.
11. Bosch, H., and Janssen, F., *Catal. Today* **2**, 369 (1988).
12. Long, R. Q., and Yang, R. T., *Chem. Commun.* 1651 (2000).
13. Long, R. Q., and Yang, R. T., *J. Catal.* **194**, 80 (2000).
14. Al-Mashta, F., Sheppard, N., Lorenzelli, V., and Busca, G., *J. Chem. Soc. Faraday Trans. I* **18**, 979 (1982).
15. Long, R. Q., and Yang, R. T., *J. Am. Chem. Soc.* **121**, 5595 (1999).
16. Long, R. Q., and Yang, R. T., *J. Catal.* **188**, 332 (1999).
17. Long, R. Q., and Yang, R. T., *J. Catal.* **198**, 20 (2001).
18. Ramis, G., Yi, L., and Busca, G., *Catal. Today* **28**, 373 (1996).
19. Amblard, M., Burch, R., and Southward, B. W. L., *Catal. Today* **59**, 365 (2000).
20. Thiele, E. W., *Ind. Eng. Chem.* **31**, 916 (1939).
21. Yang, R. T., Pinnavaia, T. J., Li, W., and Zhang, W., *J. Catal.* **172**, 488 (1997).
22. Caro, J., Bulow, M., Schirmer, W., Karger, J., Heink, W., and Pfeifer, H., *J. Chem. Soc. Faraday Trans. 1* **81**, 2541 (1985).