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Characterization of Fe-ZSM-5 Catalyst for Selective Catalytic Reduction of Nitric Oxide by Ammonia

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Fe-exchanged ZSM-5 (Fe/Al = 0.193), the most active catalyst known for the selective catalytic reduction (SCR) of NO with ammonia, was characterized by X-ray photoelectron spectroscopy (XPS), H_2 temperature-programmed reduction (H_2-TPR), electron spin resonance (ESR), and FT-IR spectroscopy. XPS and ESR results 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. 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. FT-IR spectra showed that NO molecules could be oxidized by O_2 to adsorbed N_2O_3, NO_2, and nitrate. The NO_x adspecies were not stable at above 300°C in He, but the adsorbed NO and NO_2 could be observed in flowing NO + O_2/He. NH_3 molecules were adsorbed on Brønsted acid and Lewis acid sites of Fe-ZSM-5 to generate, respectively, NH_4^+ ions (majority) and coordinated NH_3 (minority). The NH_4^+ ions with three hydrogen atoms (3H structure) bonded to AlO_4 tetrahedra of ZSM-5 were more stable at high temperatures (e.g., 300–400°C) than those with two bonds and the coordinated NH_3. The pretreatment by $SO_2 + O_2$ at 400°C increased the Brønsted acidity of the Fe-ZSM-5 due to formation of surface sulfate species of iron. This resulted in an enhancement of SCR activities by the presence of $H_2O + SO_2$ at high temperatures ($>$350°C). At 300°C, the NH_4^+ ions with 3H structure were active in reacting with NO and NO + O_2, but the reaction rate with NO + O_2 was much higher than that with NO. The results indicate that NH_4^+ ions with 3H structure as well as NO and NO_2 adspecies play an important role in the SCR reaction on the Fe-ZSM-5 catalyst. The role of Fe^{3+} is to oxidize NO to NO_2. Overexchange decreased the activity; the optimal Fe/Al ratio was 0.19–0.43. © 2000 Academic Press

Key Words: **selective catalytic reduction; SCR of NO with ammonia; Fe-exchanged ZSM-5 catalyst; characterization of Fe-ZSM-5; nitrogen oxides.**

INTRODUCTION

The removal of nitrogen oxides, including NO, NO_2, and N_2O, has received much interest in recent years because of its environmental importance. Selective catalytic reduction (SCR) with hydrocarbon or ammonia in the presence of excess oxygen is an efficient technology for reducing their emissions. Fe-exchanged ZSM-5 catalysts have been extensively studied for abating nitrogen oxides quite recently (1–15). Fe-ZSM-5 was first found to be active for SCR of NO with hydrocarbon by Sato *et al.*, but the activity was moderate (1). More recently, Feng and Hall (2) reported an overexchanged Fe-ZSM-5 (Fe/Al = 0.92) prepared by ion-exchange from oxalate salt. This catalyst was much more active than Cu-ZSM-5 and underexchanged Fe-ZSM-5 (i.e., ion-exchange level < 100%) for SCR of NO with isobutane as reductant. The overexchanged Fe-ZSM-5 was also stable under hydrothermal conditions and was resistant to sulfur dioxide. But unfortunately, these results were difficult to reproduce in the authors' laboratory later (3). Chen and Sachtler (4) subsequently studied the same reaction on overexchanged Fe-ZSM-5 (Fe/Al = 1) prepared by using anaerobic sublimation of volatile $FeCl_3$ to H-ZSM-5. They also reported a high activity and durability on the Fe-ZSM-5 for SCR with hydrocarbons. Because Fe-ZSM-5 has a high catalytic activity and a good hydrothermal stability and is resistant to sulfur dioxide, it has attracted intense interest. It has also been studied for SCR of NO with ammonia (5–9), N_2O decomposition (10–12), and N_2O reduction with hydrocarbon (13) and with ammonia (14).

In our previous work (5, 6), a series of Fe-exchanged molecular sieves (ZSM-5, mordenite, Y-zeolite, and MCM-41) were studied for SCR of NO with ammonia. It was found that Fe-ZSM-5 and Fe-MOR showed the highest activities among all known catalysts for the reaction. The maximum activity was obtained on the Fe-ZSM-5 with a moderate exchange level (Fe/Al = 0.19–0.43). For example, Fe-ZSM-5 (Fe/Al = 0.19) showed nearly 100% NO conversions at 400–550°C under conditions with a high space velocity (GHSV = 4.6×10^5 1/h). As compared with the commercial vanadia catalyst, the Fe-ZSM-5 catalyst was 5 times more active at 400°C and 7 times more active at 450°C, based on the first-order rate constants (6). This catalyst 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 (5). The SCR

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activity of the Fe-ZSM-5 was further improved by the presence of H_2O and SO_2 at high temperatures.

Although Fe-ZSM-5 has shown excellent performance for SCR of nitrogen oxides, only limited work has been performed in the characterization of this material (15–18). From H_2-TPR and NO adsorption experiments, Lobree *et al.* (18) concluded that the main form of Fe in the Fe-ZSM-5 catalysts was Fe^{3+} when the Fe/Al ratio was less than or equal to 0.19. An increase in Fe content above this level resulted in an increase of the concentrations of Fe^{2+} ions and FeO_x particles. For overexchanged Fe-ZSM-5, the state of Fe is still in debate. Chen and Sachtler proposed a paired oxygen-bridged active site $[(HO)Fe–O–Fe(OH)]^{2+}$ in their Fe-ZSM-5 (4). However, using *in situ* ESR experiments, Kucherov *et al.* (16) reported that most of the iron in the Fe-ZSM-5 existed as isolated FeO^+ ions in tetrahedral and distorted tetrahedral sites. More recently, based on the EXAFS (extended X-ray absorption fine structure spectroscopy) results, Joyner and Stockenhuber (17) suggested that Fe in Fe-ZSM-5 had an average composition of Fe_4O_4 and was in the form of nanoclusters. They also concluded that the small Fe_4O_4 clusters were more active (per iron atom) than iron ions for the hydrocarbon SCR reaction.

However, the above work mainly focused on the overexchanged Fe-ZSM-5 catalysts for hydrocarbon SCR reaction. To our knowledge, no characterization studies on Fe-ZSM-5 for the ammonia SCR reaction have been reported. Since the mechanisms for the two SCR reactions are different, it is necessary to understand the state of Fe in Fe-ZSM-5 and the adsorption behavior of reactants, e.g., NO and NH_3, on the catalyst. In this work, spectroscopic and other techniques have been applied to study the Fe-ZSM-5 catalyst. The techniques included XPS (X-ray photoelectron spectroscopy), H_2-TPR (temperature-programmed reduction), ESR (electron spin resonance), and FT-IR spectroscopy. The Fe-ZSM-5 with an Fe/Al ratio of 0.193 was chosen for the study because it showed the highest ammonia SCR activity in our previous work (6). The oxidation state and redox behavior of Fe as well as the interactions between Fe-ZSM-5 and various gases, e.g., NO, NO_2, $NO + O_2$, NH_3, H_2O, and SO_2, were studied.

EXPERIMENTAL

Catalyst preparation. Fe-ZSM-5 was prepared by using conventional ion-exchange procedure, as described in detail elsewhere (5). Two grams NH_4-ZSM-5 (Si/Al = 10, obtained from Air Products and Chemicals Inc.) was added to 200 ml of 0.05 M $FeCl_2$ (99%, Aldrich) solution with constant stirring. The ion exchange was carried out in air at room temperature, which is defferent from the procedure that Mobil Company used, i.e., ion-exchange in inert gas and at above 55°C (9). After 24 h, the mixture was filtered and washed 5 times with deionized water. The obtained solid was first dried at 120°C for 12 h, then calcined at 500°C for 6 h in air. The Fe content in the sample measured by neutron activation analysis was 1.59 wt%, i.e., Fe/Al = 0.193.

XPS analysis. The XPS experiment was carried out on a Perkin–Elmer PHI 5400 ESCA system at room temperature under 10^{-8}–10^{-9} Torr, using Mg $K\alpha$ radiation. Fe $2p_{3/2}$ binding energy was calibrated relative to the carbon impurity with a $C1s$ band at 284.7 eV.

TPR experiment. H_2-TPR was performed in a fixed-bed quartz reactor with an inner diameter of 10 mm. The temperature was controlled by an Omega (CN-2010) programmable temperature controller. In the experiment, 0.1 g Fe-ZSM-5 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., H_2O) on the catalyst. After the sample was cooled to room temperature in He, the reduction of the Fe-ZSM-5 was carried out from 30 to 700°C in a flow of 5.34% H_2/N_2 (27 ml/min) at 10°C/min. The consumption of H_2 was monitored continuously with a thermal conductivity detector. The water produced during reduction was trapped in a 5 Å molecular sieve column.

ESR analysis. ESR spectra were recorded on a Brucker EMX ESR spectrometer, under the conditions of a microwave power of 6.3 mW and a modulation amplitude of 5.0 G. Before the ESR experiment, Fe-ZSM-5 samples were first treated in various gases at different temperatures. The samples were then purged with He for 30 min at room temperature and sealed in Pyrex tubes under He atmosphere. The sealed samples were transferred to the ESR sample holder and the ESR spectra were recorded at 20°C.

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 diameter were prepared by pressing 20-mg samples and were loaded into a high-temperature IR cell with BaF_2 windows. The wafers could be pretreated *in situ* in the IR cell. Unless otherwise indicated, the wafers were first treated at 500°C in a flow of He for 15 min, and then cooled to desired temperatures, i.e., 400, 300, 200, 100, and 30°C. At each temperature, the background spectrum was recorded in flowing He and was subtracted from the sample spectrum that was obtained at the same temperature. In the experiment, the IR spectra were recorded by accumulating 100 or 16 scans at a spectral resolution of 4 cm^{-1}.

During the FT-IR experiments, the gas mixtures (i.e., NO/He, $NO + O_2$/He, NO_2/He, NH_3/He, H_2O/He, and $SO_2 + O_2$/He) had the same concentrations as those used in the activity measurements (5), i.e., 1000 ppm NO (when used), 1000 ppm NO_2 (when used), 1000 ppm NH_3 (when used), 2% O_2 (when used), 5% H_2O (when used), 500 ppm SO_2 (when used), and balance of He. The total gas flow rate was 500 ml/min (ambient conditions). The premixed gases

(1.01% NO/He, 0.98% NO_2/He, 1.00% NH_3/He, 0.99% SO_2/He, 5.0% O_2/He, and 5.34% H_2/N_2) were supplied by Matheson.

NO oxidation to NO_2. The experiment for NO oxidation to NO_2 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% O_2, and balance He. The total flow rate was 500 ml/min (ambient conditions). NO concentration was continually monitored by a chemiluminescent NO/NO_x analyzer (Thermo Electro Corp., Model 10). NO conversion to NO_2 was obtained by using the equation NO conversion to $NO_2 = (([NO_x] - [NO])/[NO_x]) \times 100\%$, where NO_x represents $NO + NO_2$.

RESULTS

XPS spectrum of Fe $2p_{3/2}$. Figure 1 shows the XPS spectrum of Fe $2p_{3/2}$ on the fresh Fe-ZSM-5. A broad XPS band centered at 711.7 eV was observed on the sample. This value is close to the binding energy of $2p_{3/2}$ of iron in Fe_2O_3 and $FeCl_3$ ($\approx$711 eV) (19), indicating that the iron in the Fe-ZSM-5 was mainly present as a valence of +3.

H_2-TPR profile of Fe-ZSM-5. Figure 2 is an H_2-TPR profile of Fe-ZSM-5 that was pretreated in He at 400°C. A peak at 385°C and a shoulder at 462°C were observed on the TPR profile, which can be attributed to the reduction of iron species at two different sites. Integration of the area of the TPR peaks yielded an H_2/Fe molar ratio of 0.45. This is 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 Fe^{2+} ions may also exist in the Fe-ZSM-5. Taking into account the facts that pure Fe_2O_3 will be reduced to metallic iron by H_2 at about 530°C and the ratio of H_2/Fe is 1.5 (4), it is likely that iron in the Fe-ZSM-5 existed in the form of Fe^{3+} ions.

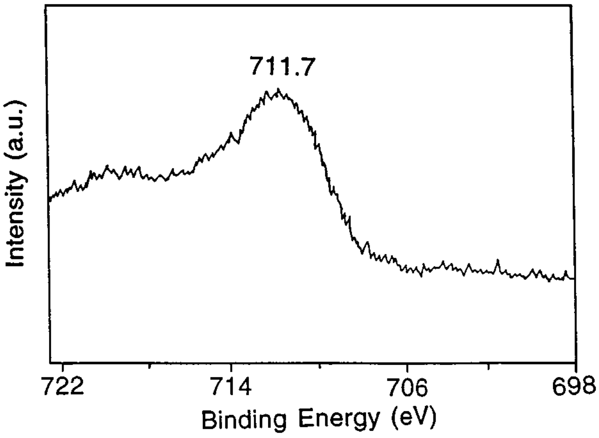

FIG. 1. XPS spectrum of Fe $2p_{3/2}$ on Fe-ZSM-5 catalyst.

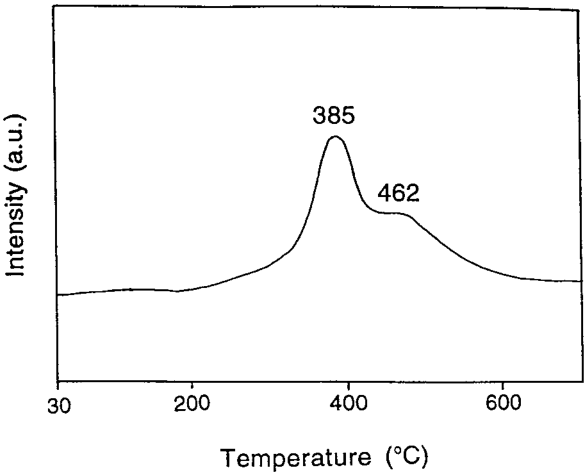

FIG. 2. H_2-TPR profile of Fe-ZSM-5 catalyst.

ESR spectra of Fe-ZSM-5. After Fe-ZSM-5 was treated in He at 400°C for 30 min and then cooled to room temperature, a strong narrow line at $g = 4.29$ was observed on the ESR spectrum (Fig. 3a), which can be assigned to Fe^{3+} ions in tetrahedral coordination (16). Also, a weak signal was detected at $g \approx 2.0$ originating from aggregated Fe^{3+} ions (not shown). The aggregated Fe^{3+} ions might come from the hydrolysis of residual ferric ions in $FeCl_2$ solution during the ion-exchange process. It is noted that the sample was sealed in a Pyrex tube and the empty Pyrex tube also showed a signal at $g = 4.29$, but the intensity was only one fourth as strong as that of the Fe-ZSM-5. When the catalyst was heated from 30 to 700°C in flowing 5.34% H_2/N_2 (similar to the above H_2-TPR experiment) and then cooled to room temperature, the Fe^{3+} signal at $g = 4.29$ decreased significantly (Fig. 3b). The intensity of the signal was almost the same as that of the empty Pyrex tube. This indicates a reduction of Fe^{3+} ions. When the H_2-reduced sample was treated at 500°C in 5.0% O_2/He for 15 min, the signal at $g = 4.29$ increased again (Fig. 3c), suggesting that O_2 oxidized iron back to tetrahedral Fe^{3+} reversibly. The intensity of the Fe^{3+} signal in the O_2-treated sample was slightly stronger than that in the He-treated sample (Fig. 3a), suggesting that more tetrahedral Fe^{3+} ions formed. The above H_2-TPR and ESR data suggest that the redox cycle between Fe^{3+} and Fe^{2+} is reversible.

FT-IR study. The IR spectrum of Fe-ZSM-5 at room temperature is shown in Fig. 4. A strong band at 3610 cm^{-1} and several weaker bands at 3740, 1982, 1872, and 1635 cm^{-1} were observed. The strong band at 3610 cm^{-1} has been attributed to OH stretching of the Brønsted acid (17, 18). The high Al/Si ratio in the ZSM-5 (Al/Si = 1/10) resulted in a strong Brønsted acidity. The weak band at 3740 cm^{-1} can be assigned to hydroxyl stretching vibration of the Si–OH group at crystal termination (20). The bands at 1982 and

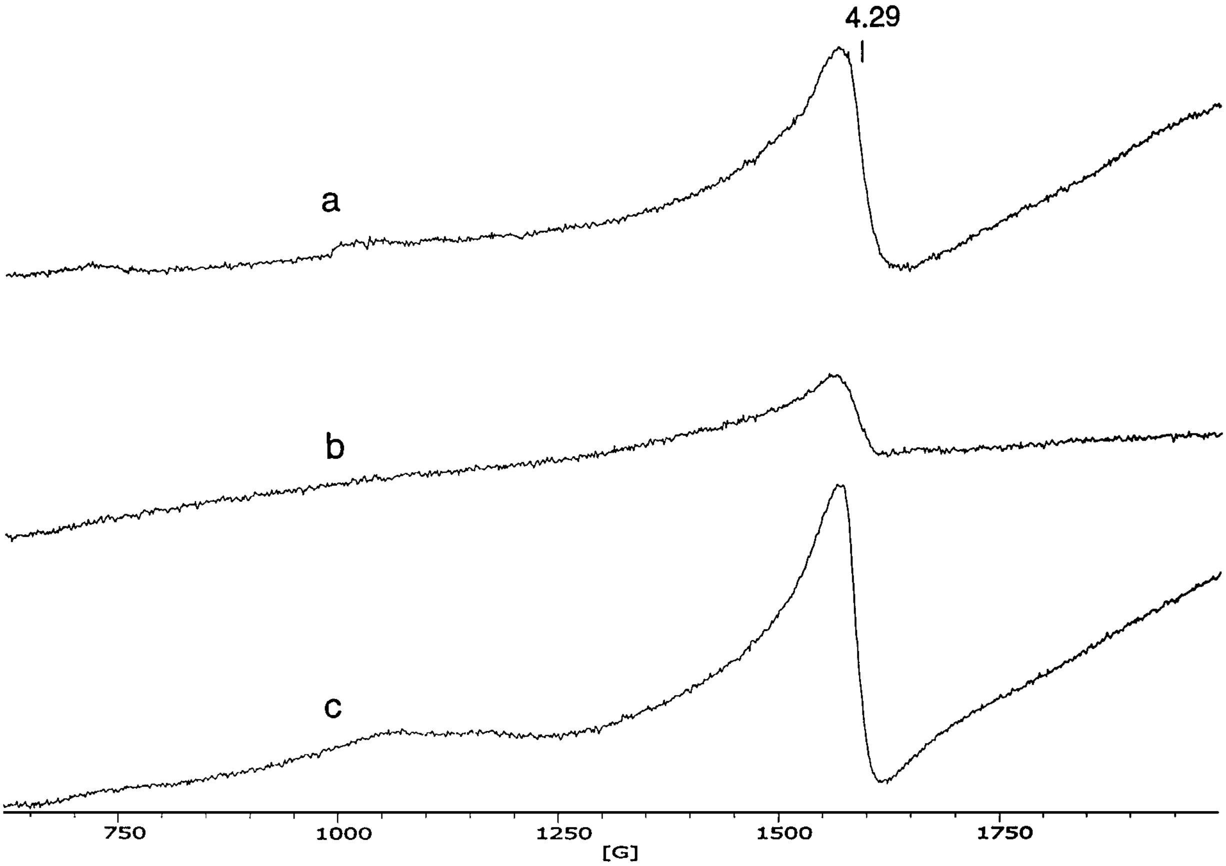

FIG. 3. ESR spectra of Fe-ZSM-5 catalyst at 25°C: (a) after treatment in He at 400°C for 30 min; (b) after reduction by 5.34% H_2/N_2 from 30 to 700°C, and then (c) reoxidation by 5.0% O_2/He at 500°C for 15 min.

1872 cm^{-1} are due to the zeolite overtone bands (17). The 1635 cm^{-1} band is likely due to adsorbed H_2O.

The adsorption of NO, NO + O_2, and NO_2 on Fe-ZSM-5 was studied first. Figure 5 shows the IR spectra after the catalyst was treated with these gases for 30 min followed by purging with He for 15 min at room temperature. When 1000 ppm NO/He was introduced to the sample, a strong peak was observed at 1876 cm^{-1}. This band is close to the vibration frequency of gas-phase NO (1880 cm^{-1}) and has been assigned to Fe^{2+} mononitrosyls [Fe^{2+}(NO)] (15, 17, 18). After the NO-treated sample was purged with He for 15 min, the band at 1876 cm^{-1} disappeared and two small peaks were observed at 1617 and 1575 cm^{-1} (Fig. 5a), which can be assigned to adsorbed NO_2 and nitrate species, respectively (15, 21–23). This suggests that NO molecules are weakly adsorbed and some of them were oxidized to NO_2 and nitrate species by the residual O_2 species weakly adsorbed on the catalyst. On the spectrum of NO + O_2 adsorbed on Fe-ZSM-5, three intense bands at 1682, 1614, and 1575 cm^{-1} were detected (Fig. 5b). The new band at 1682 cm^{-1} is probably due to adsorbed N_2O_3 species since it is close to the IR band at 1690 cm^{-1} for gaseous N_2O_3 (24). Oxygen improved NO adsorption, clearly due to oxidation of NO to NO_2 and nitrate species. The NO_x adspecies, with much stronger intensities, were also observed on the NO_2 adsorbed Fe-ZSM-5 (Fig. 5c), suggesting stronger adsorption for NO_2 than for NO.

After the Fe-ZSM-5 that was treated with NO + O_2 was heated to 100°C in He, the bands at 1682 and 1575 cm^{-1} either disappeared or decreased sharply, while the band at 1614 cm^{-1} (due to NO_2 adspecies) increased slightly and shifted to 1624 cm^{-1} (Fig. 6b). This suggests that N_2O_3 and nitrate adspecies desorbed or transformed to NO_2 adspecies. As the temperature was further increased, the 1624 cm^{-1} band also decreased. All of the bands vanished at 400°C (Fig. 6e). However, when the Fe-ZSM-5 was heated in flowing 1000 ppm NO + 2% O_2/He, the IR spectra were different, as shown in Fig. 7. At 200°C, three bands due to weakly adsorbed NO (1876 cm^{-1}), NO_2 (1624 cm^{-1}), and nitrate (1575 cm^{-1}) adspecies were detected (Fig. 7a). When the temperature was increased to 300–400°C, the 1575 cm^{-1} band due to nitrate species vanished, while the bands at 1876 and 1624 cm^{-1} due to, respectively, NO and NO_2 adspecies decreased and were then split into two pairs of bands at 1906 and 1852 cm^{-1} as well as at 1629 and 1600 cm^{-1}, respectively (Figs. 7b and 7c). This indicates that the NO and

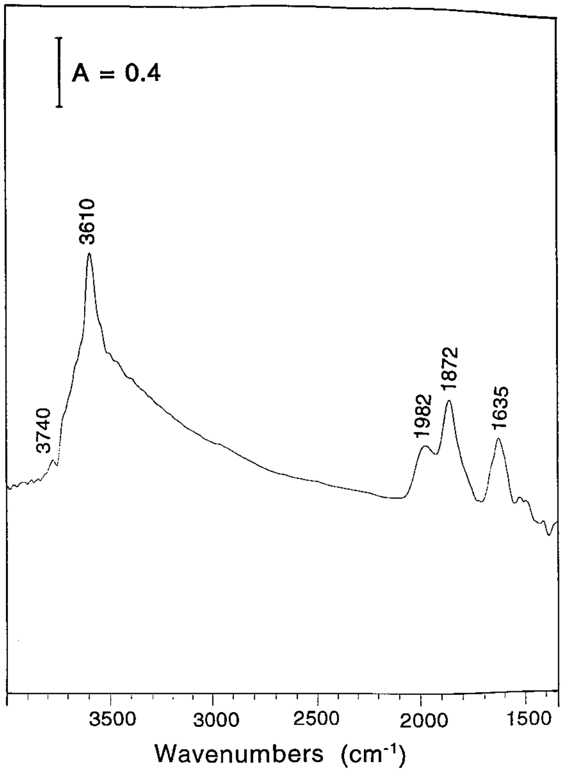

FIG. 4. IR spectrum (100 scans) of Fe-ZSM-5 catalyst at 30°C, with empty cell as background.

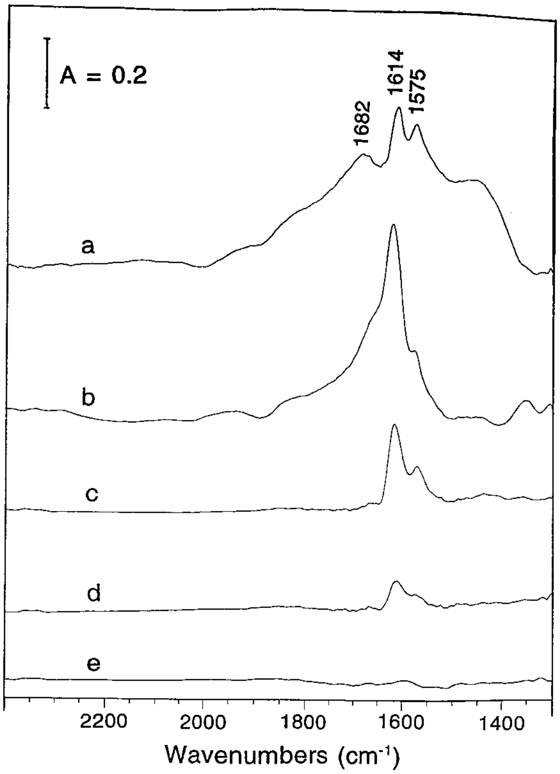

FIG. 6. IR spectra (100 scans) of Fe-ZSM-5 treated in flowing 1000 ppm NO + 2% O_2/He at 30°C for 30 min and then purged by He at (a) 30, (b) 100, (c) 200, (d) 300, and (e) 400°C.

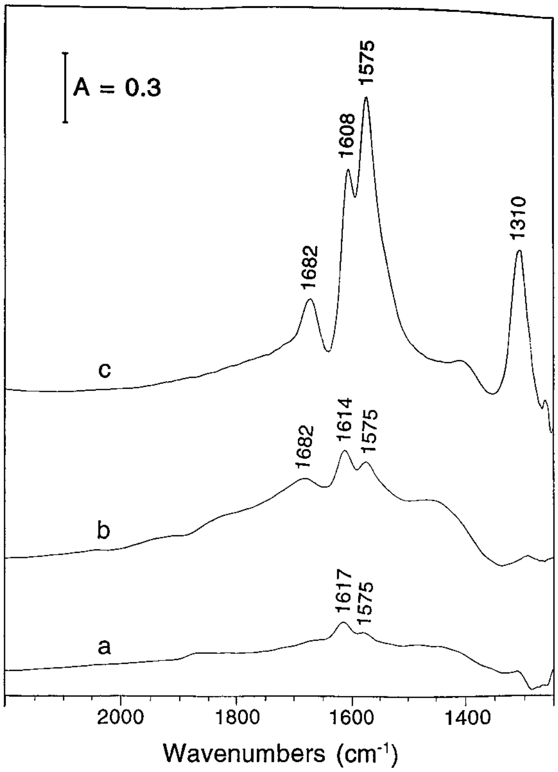

FIG. 5. IR spectra (100 scans) of Fe-ZSM-5 treated with (a) 1000 ppm NO/He, (b) 1000 ppm NO + 2% O_2/He, and (c) 1000 ppm NO_2/He, for 30 min followed by purge with He for 15 min at 30°C.

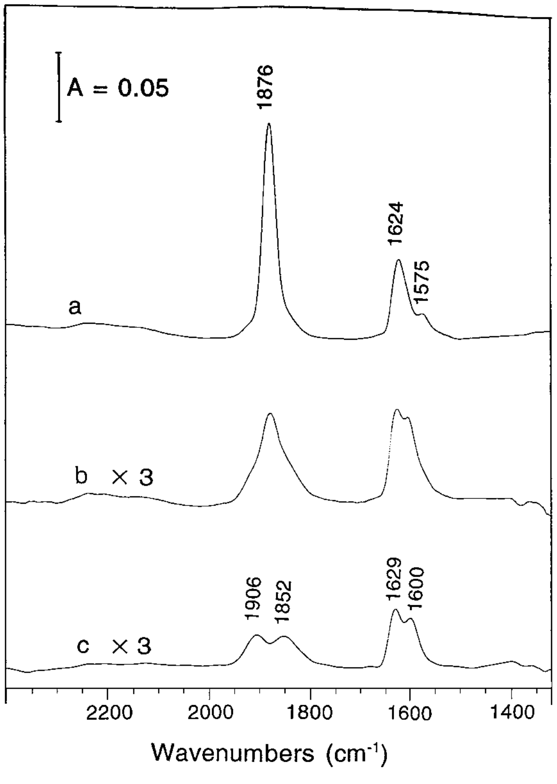

FIG. 7. IR spectra (100 scans) of Fe-ZSM-5 treated in flowing 1000 ppm NO + 2% O_2/He at (a) 200, (b) 300, and (c) 400°C.

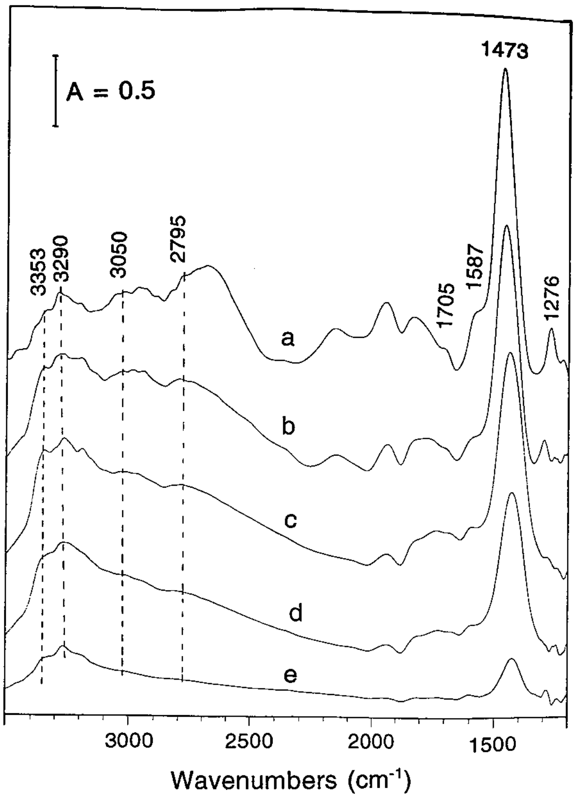

FIG. 8. IR spectra (100 scans) of Fe-ZSM-5 treated in flowing 1000 ppm NH_3/He at 30°C for 30 min and then purged by He at (a) 30, (b) 100, (c) 200, (d) 300, and (e) 400°C.

NO_2 adspecies were still present on the catalyst in flowing NO + O_2/He at high temperatures.

The IR spectra of ammonia adsorbed on Fe-ZSM-5 at different temperatures are shown in Fig. 8. After the sample was treated in flowing 1000 ppm NH_3/He for 30 min and then purged with He for 15 min at 30°C, a strong band at 1473 cm^{-1} and weaker bands at 3353, 3290, 3050, 2795, 1705, 1587, 1276, and 2600–2900 cm^{-1} were observed (Fig. 8a). The broad band between 2600 and 2900 cm^{-1} is attributed to physisorbed ammonia. The bands at 1705 and 1473 cm^{-1} are due to the symmetric and asymmetric bending vibrations, respectively, of NH_4^+ that is chemisorbed on the Brønsted acid sites, while the bands at 1587 and 1276 cm^{-1} can be assigned to asymmetric and symmetric bending vibrations, respectively, of the N–H bonds in NH_3 coordinately linked to Lewis acid sites (25). The bands at higher wavenumbers are attributed to the N–H stretching vibration of NH_4^+ ions located at the AlO_4 tetrahedra of the ZSM-5 framework. The bands at 3353 and 3290 cm^{-1} can be assigned to NH_4^+ ions with three hydrogen atoms bonded to three oxygen ions of AlO_4 tetrahedra (3H structure), while the bands at 3050 and 2795 cm^{-1} are due to the NH_4^+ ions with two hydrogen atoms bonded to AlO_4 tetrahedra (2H structure) (21, 26). The above results indicate that there are many more Brønsted acid sites than Lewis acid sites on the Fe-ZSM-5. With increasing temperatures, the intensities of the 3353 and 3290 cm^{-1} bands increased first (at the expense of the 3050 and 2795 cm^{-1} bands), passing through a maximum at 200°C, and then decreased at higher temperatures (Figs. 8b–8e). This suggests an NH_4^+ transformation from 2H structure to 3H structure at higher temperatures. The intensities of all other bands decreased with increasing temperature, as shown in Figs. 8b–8e, indicating desorption of NH_3. The IR bands at 1587 and 1276 cm^{-1} due to coordinated NH_3 disappeared at 200°C, whereas those due to NH_4^+ ions with 3H structure (at 3353, 3290, and 1473 cm^{-1}) were still detected at 400°C in He (Fig. 8e). This result indicates that NH_4^+ ions with 3H structure are more stable at high temperatures than the other ammonia adspecies.

When Fe-ZSM-5 was treated with 5% H_2O/He for 30 min at room temperature, a strong broad band was observed at 1633 cm^{-1} (Fig. 9a), indicating that H_2O molecules were adsorbed on the catalyst. However, the H_2O adsorption was not very strong. After the H_2O-adsorbed catalyst was heated to 300°C in flowing He, the IR band at 1633 cm^{-1} vanished. When the fresh Fe-ZSM-5 was treated at 400°C for 30 min in flowing 500 ppm $SO_2 + 2\%$ O_2/He and then purged with He for 15 min, a peak at 1363 cm^{-1} appeared (Fig. 9b), suggesting the formation of sulfate species on the

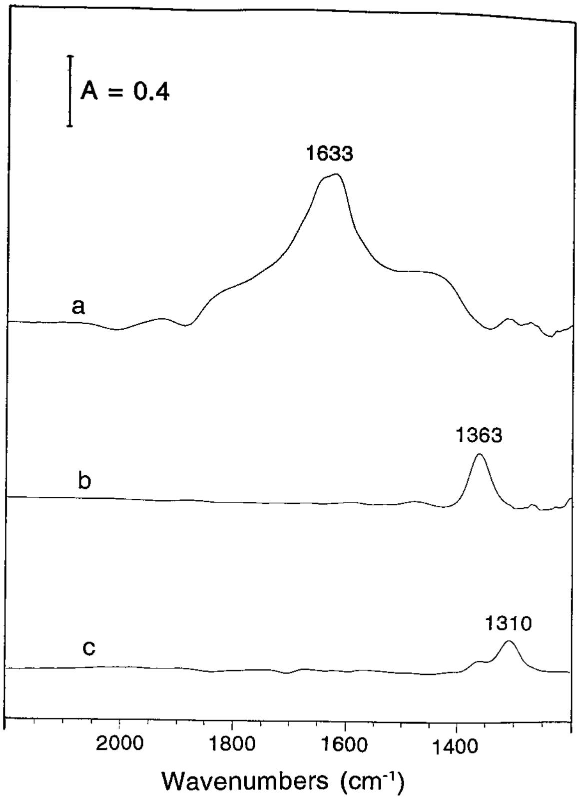

FIG. 9. IR spectra (100 scans) of Fe-ZSM-5 catalyst: (a) after 5% H_2O/He adsorption for 30 min and then purge with He for 15 min at 30°C; (b) after treatment by $SO_2 +$ O_2/He for 30 min and then purge with He for 15 min at 400°C, and then (c) cooling to 30°C.

Fe^{3+} sites of the Fe-ZSM-5 catalyst (27). The 1363 cm^{-1} band comes from asymmetric S=O stretching frequencies of an “organic” sulfate species which has covalent S=O double bonds (27). When the temperature was decreased to room temperature, the intensities of the “organic” sulfate bands (1363 cm^{-1}) decreased, while a new band at 1310 cm^{-1} formed (Fig. 9c). The band at 1310 cm^{-1} is attributed to a chelating bidentate inorganic SO_4^{2-} bond to iron which has ionic SO bonds with a partial double-bond character (27). This suggests a structural transformation from “organic” sulfate to inorganic sulfate with decreasing temperature.

When the H_2O-adsorbed Fe-ZSM-5 was treated in flowing 1000 ppm NH_3/He, the band at 1633 cm^{-1} due to adsorbed H_2O decreased continually; at the same time, two new bands at 1473 and 1276 cm^{-1} due to NH_4^+ ions and coordinated NH_3 appeared. After the sample was treated for 30 min, the IR band due to adsorbed H_2O vanished completely, while only ammonia adspecies (1704, 1587, 1473, and 1276 cm^{-1}) were observed (Fig. 10b). This indicates that ammonia adsorption is stronger than H_2O adsorption on the catalyst, which can be attributed to its stronger basicity than H_2O. Integration of the 1473 cm^{-1} band area showed an increase in Brønsted acidity by approximately 8% as compared to the fresh catalyst (Fig. 10a). After the Fe-ZSM-5 (that was pretreated by $SO_2 + O_2$/He at 400°C) adsorbed NH_3 for 30 min at room temperature, the sulfate band at 1310 cm^{-1} shifted to 1274 cm^{-1}. Meanwhile, a strong band at 1473 cm^{-1} and two weaker bands at 1704 and 1587 cm^{-1} appeared (Fig. 10c). Electron transfer from the adsorbed ammonia to the sulfate species resulted in a decrease in the S–O vibration frequencies. The band at 1276 cm^{-1} due to symmetric vibration of the NH_3 coordinated to Lewis acid sites was overlapped by the sulfate band at 1274 cm^{-1}. Integration of the 1473 cm^{-1} band area indicated an increase in Brønsted acidity by approximately 23% as compared to the fresh Fe-ZSM-5 catalyst (Fig. 10a). The surface sulfate species increased the Brønsted acidity of the Fe-ZSM-5.

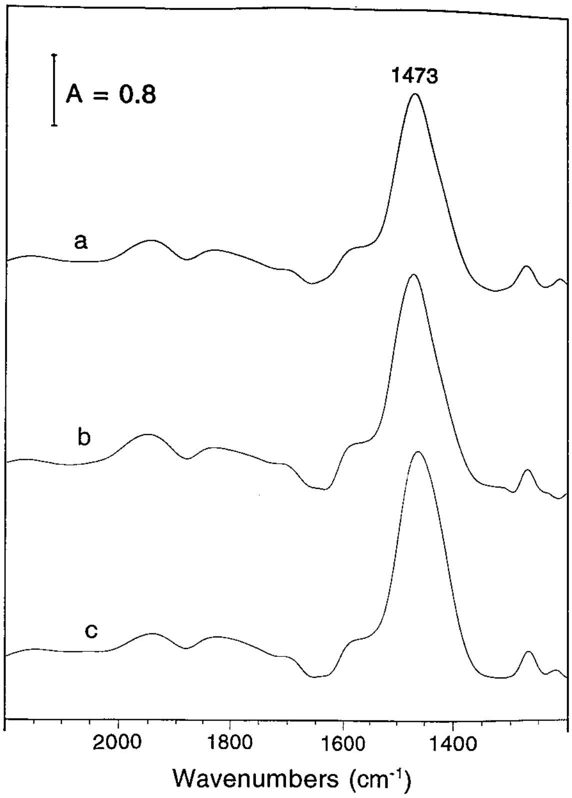

FIG. 10. IR spectra (100 scans) of 1000 ppm NH_3/He adsorption on (a) fresh, (b) H_2O preadsorbed, and (c) $SO_2 + O_2$ pretreated (400°C) Fe-ZSM-5 catalyst at room temperature.

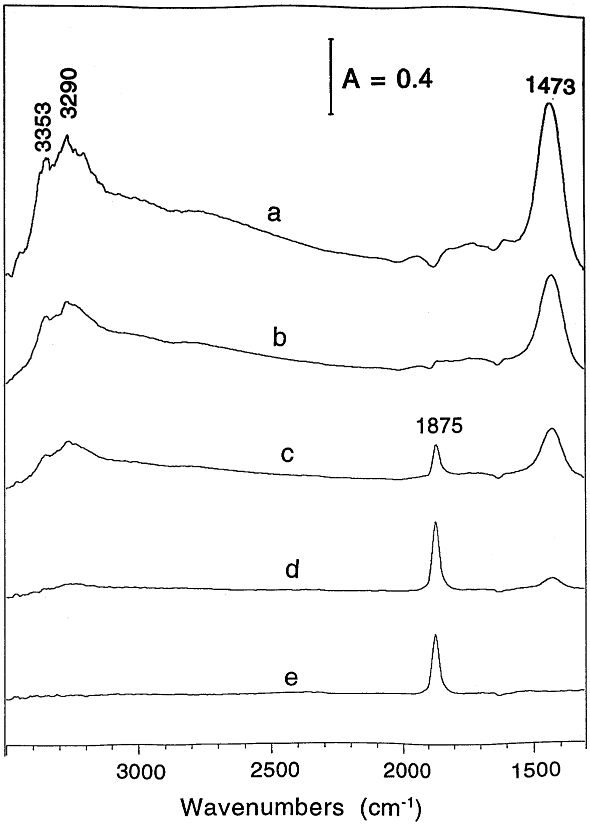

FIG. 11. IR spectra (16 scans) taken at 300°C upon passing 1000 ppm NO over the NH_3 presorbed on Fe-ZSM-5 for (a) 0, (b) 2, (c) 5, (d) 10, and (e) 15 min.

The reactions of ammonia adspecies with NO and NO + O_2 were also studied. Fe-ZSM-5 was first treated with NH_3/He for 30 min followed by He purge at 300°C. NO/He was then introduced into the cell and IR spectra were recorded as a function of time (Fig. 11). As noted above, NH_4^+ ions with 3H structure (3353, 3290, and 1473 cm^{-1}) were generated after Fe-ZSM-5 was treated with NH_3/He, and their IR bands did not decrease in flowing He for 30 min. After 1000 ppm NO/He was passed over the sample

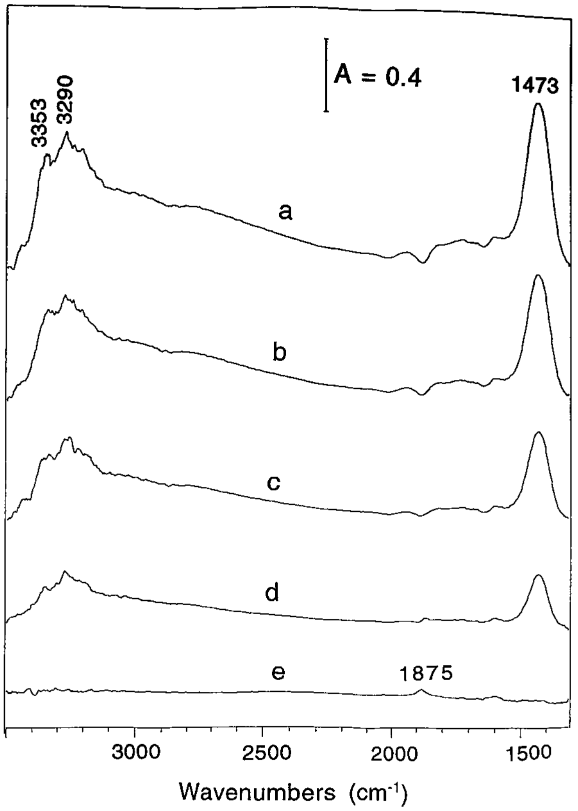

FIG. 12. IR spectra (16 scans) taken at 300°C upon passing 1000 ppm NO + 2% O_2 over the NH_3 presorbed on Fe-ZSM-5 for (a) 0, (b) 1, (c) 2, (d) 3, and (e) 5 min.

for 2–5 min, the bands attributed to NH_4^+ ions decreased. At the same time, a new band was observed at 1875 cm^{-1} (Fig. 11c). As mentioned above, the band at 1875 cm^{-1} was due to weakly adsorbed NO species on Fe^{2+} sites. These results indicate that the reaction between NH_4^+ ions and NO occurred. With increasing time, the NH_4^+ bands were further decreased and vanished at 15 min, while only NO adspecies was detected (Fig. 11e). The IR spectra of the reaction between ammonia adspecies and NO + O_2/He at 300°C are shown in Fig. 12. By comparison, after NO + O_2/He was passed over the ammonia adsorbed Fe-ZSM-5 for 1 min, the bands attributed to NH_4^+ ions decreased significantly. All of the NH_4^+ ions bands vanished in 5 min. At the same time, a weak peak was observed at 1875 cm^{-1}, suggesting formation of adsorbed NO species on Fe^{2+} sites. The above results indicate that oxygen increased the reaction rate between NO and NH_4^+ ions. Oxygen also oxidized some ferrous ions to ferric ions and thus decreased the formation of NO adspecies bonded to Fe^{2+} ions.

DISCUSSION

The above XPS, H_2-TPR, and ESR results indicate that, although iron cations were exchanged with NH_4-ZSM-5 in Fe^{2+} form, most iron cations in the Fe-ZSM-5 are present as Fe^{3+} ions with tetrahedral coordination, besides a small amount of Fe^{2+} and aggregated Fe^{3+} ions. Oxygen oxidized Fe^{2+} to Fe^{3+} during calcination of the catalyst. An equilibration of $Fe^{2+} \Leftrightarrow Fe^{3+}$ exists in the Fe-exchanged ZSM-5. Oxidation or reduction treatment will, respectively, increase or decrease the ratio of Fe^{3+}/Fe^{2+}. The Fe^{3+} ions were reduced to Fe^{2+} ions in flowing H_2/N_2 at high temperatures. But when the reduced catalyst was treated by 5% O_2/He at 500°C, the Fe^{2+} ions were oxidized back to tetrahedral Fe^{3+} ions. This is different from the result reported on the overexchanged Fe-ZSM-5 that was prepared by sublimation of $FeCl_3$ vapor into H-ZSM-5 (16). In that case, when the overexchanged Fe-ZSM-5 was treated in flowing 1% H_2/He at 400°C, the oxidation of Fe^{2+} to tetrahedral Fe^{3+} ions by 10% O_2/He was irreversible, resulting in a loss of the ESR signal due to tetrahedral Fe^{3+} ions and the appearance of a new broad signal due to α-Fe_2O_3 aggregates (16). The iron cations in the underexchanged Fe-ZSM-5 seem to be more stable under redox treatment than those in the overexchanged Fe-ZSM-5.

The FT-IR spectra indicate that NO, NO_2, and nitrate species were adsorbed on Fe-ZSM-5 catalyst after the sample was treated, respectively, with NO/He, NO + O_2/He, and NO_2/He (Figs. 5–7). This is similar to the results obtained on CuO/Al_2O_3 and zeolite catalysts (28–30), but different from that obtained on vanadia-based catalysts. Most researchers agreed that nitrogen oxides do not adsorb on the fully oxidized vanadia (31, 32). NO adsorption was weak, which may be due to low Fe^{2+} concentration in the catalyst because NO is bonded more strongly to Fe^{2+} than to Fe^{3+} (33, 34). The presence of O_2 increased NO adsorption, forming N_2O_3, NO_2, and nitrate adspecies. The NO_2 and nitrate species resulted from the reaction between adsorbed O_2 and gaseous NO (35). NO_2 adsorption was much stronger than NO adsorption. With increasing temperature, the bands due to nitrogen oxide adspecies decreased (Fig. 6). The NO_2 adspecies was the dominant species at 100–300°C. NO_x TPD experiments showed that the NO_2 adspecies was not observed on the NO_x adsorbed H-ZSM-5, and its concentration increased with iron content in the Fe-ZSM-5, suggesting that the NO_2 was bonded to iron sites (36). All of the IR bands due to nitrogen oxides adspecies vanished at 400°C in He. However, the adsorbed NO and NO_2 were still observed on the catalyst in flowing NO + O_2/He at 300–400°C (Fig. 7).

For the ammonia SCR reaction, it has been accepted that ammonia is adsorbed on the Brønsted or Lewis acid sites to form, respectively, NH_4^+ or coordinated NH_3, then gaseous or adsorbed nitrogen oxides react with them to form N_2 and H_2O, although some different mechanisms have been proposed (31, 32, 38–42). Hence surface acidity of the catalyst is important for ammonia SCR reaction because strong surface acidity is beneficial to ammonia adsorption. As shown in Fig. 4, many Brønsted acid sites exist on the Fe-ZSM-5. When the catalyst was treated in flowing NH_3/He, NH_3 molecules were adsorbed on these sites to form NH_4^+ ions (Fig. 8). The NH_4^+ ions are present in two forms, 3H structure (three hydrogen atoms bonded to the AlO_4 tetrahedra) and 2H structure (two hydrogen atoms bonded to the AlO_4 tetrahedra). The 3H structure is more stable than the 2H structure at high temperatures (>100°C). The NH_4^+ ions with 3H structure were still observed when the temperature was increased to 400°C in He, indicating a strong Brønsted acidity on the Fe-ZSM-5 (Fig. 8). By comparison, ammonia adspecies (both NH_4^+ ions and coordinated NH_3) on V_2O_5/TiO_2 were almost removed at around 300°C (25). This may be one of the reasons that Fe-ZSM-5 showed much higher SCR activity than vanadia catalysts. Furthermore, when Fe-ZSM-5 was treated by $SO_2 + O_2$/He, its Brønsted acidity increased. This was identified by an increase in the intensity of the 1473 cm^{-1} band (due to NH_4^+ ions) when ammonia was introduced into the sample (Fig. 10). The increase in the Brønsted acidity is in line with the improvement of the SCR activity at higher temperatures by H_2O and SO_2, as reported in our previous studies (5, 6). It is known that, when some metal oxides, such as Fe_2O_3, TiO_2, and ZrO_2, are treated by H_2SO_4 or $(NH_4)_2SO_4$ followed by calcination at high temperatures, or are treated by $SO_2 + O_2$ at high temperatures, their acidities will be increased significantly (43). After the Fe-ZSM-5 was treated at 400°C in flowing $SO_2 + O_2$/He, SO_2 was oxidized to SO_3 by O_2 and a sulfate species was formed. These were identified, respectively, in our previous SO_2 oxidation experiment (5) and the above IR experiment (Fig. 9). The sulfate ions bonded to iron show a characteristic IR absorption band at near 1375 cm^{-1} (27). In the case of sulfate ions, S=O has a covalent double bond and has a much stronger affinity to electrons as compared with that of a simple metal sulfate; hence, the Lewis acid strength of metal ions becomes substantially stronger by the inductive effect of S=O in the complex. When a water molecule is bonded to the Lewis acid site, the Lewis acid site becomes a Brønsted acid site. This will increase the Brønsted acidity of the catalysts that contain iron, in this case, Fe-ZSM-5. Consequently, the adsorption amount of ammonia is increased. This phenomenon is similar to that observed on Fe^{3+}-exchanged TiO_2-pillared clay catalysts, except that the increase in Brønsted acidity by $SO_2 + O_2$ for the Fe-ZSM-5 is less significant than that for the Fe-exchanged pillared clays (44, 45). This is due to a lower iron content in the former catalyst (1.59 wt% in Fe-ZSM-5 vs 4.32–20.1 wt% in Fe-exchanged pillared clays). The above result indicates a promoting role of surface sulfate species for the Fe-ZSM-5 and the importance of surface acidity for ammonia SCR reaction.

The above results suggest that both NO_x and NH_3 could adsorb on the Fe-ZSM-5, but formed NH_4^+ ions were more stable than NO_2 adspecies at high temperatures. The NH_4^+ ions were active in reacting with $NO + O_2$, and they were consumed completely with the introduction of 1000 ppm $NO + 2\%\ O_2$ in 5 min at 300°C. By comparison, when passing 1500 ppm $NO + 2.2\%\ O_2$ over the ammonia-adsorbed H-ZSM-5 at 300°C, Eng and Bartholomew (21) reported that NH_4^+ bands were still observed after 10 min. This suggests that Fe^{3+} in the Fe-ZSM-5 promoted the reaction between $NO + O_2$ and NH_4^+ ions, which is in good agreement with our previous performance results showing that Fe-ZSM-5 was much more active than H-ZSM-5 for the SCR reaction (6). The NH_4^+ ions on the Fe-ZSM-5 could also react with NO at 300°C, but the reaction rate was much lower than that with $NO + O_2$ (Figs. 11 and 12). The presence of O_2 improved significantly the reactivity between NO and NH_4^+ ions, which is consistent with the promoting role of oxygen for the SCR reaction (6). The enhancement may be related to the formation of NO_2 adspecies. Our TPSR (temperature programmed surface reaction) also showed that the reaction rate of $NO_2 + NH_4^+$ was much higher than that of $NO + NH_4^+$ on the Fe-ZSM-5 (36). NO_2 may be an intermediate for the SCR reaction. The NO reduction path on the Fe-ZSM-5 is probably similar to that on H-ZSM-5 (21) and Fe-exchanged TiO_2-pillared clay (46). It involves the reaction between one molecular

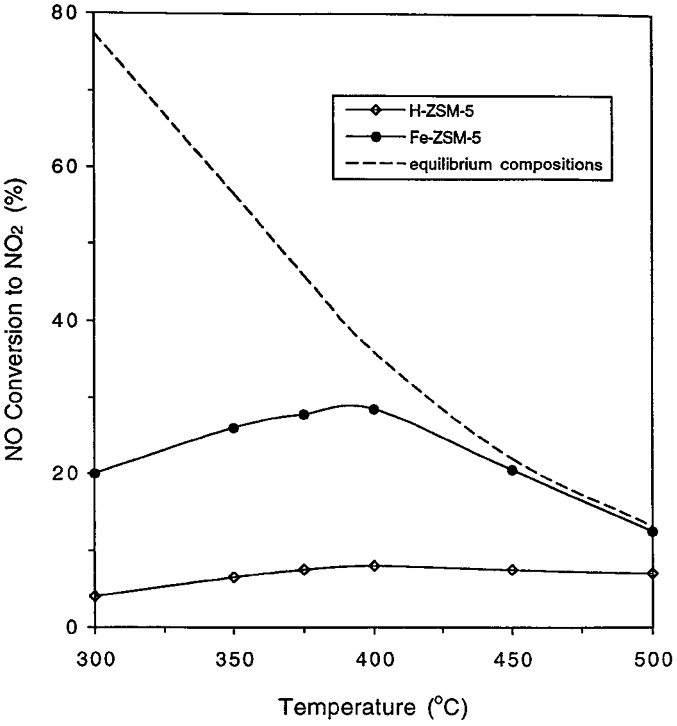

FIG. 13. Oxidation activity of NO to NO_2 by O_2 on H-ZSM-5 and Fe-ZSM-5 under the conditions of 50 mg sample, 1000 ppm NO, 2% O_2, and 500 ml/min total flow rate. The empty-tube conversion under the same conditions was below 1.5% at 300–450°C.

NO_2 and two NH_4^+ ions to form an active intermediate, which subsequently reacts with another gaseous or weakly adsorbed NO to produce N_2 and H_2O. Therefore, both NH_4^+ ions and NO_2 adspecies are important for NO reduction. As compared to H-ZSM-5, Fe^{3+} in the Fe-ZSM-5 enhances oxidation of NO to NO_2 and thus increases the SCR activity. As shown in Fig. 13, when 1000 ppm NO + 2% O_2 was passed over the catalysts, only 4–8% NO conversions to NO_2 were observed on H-ZSM-5 at 300–500°C, whereas much higher NO conversions were obtained on Fe-ZSM-5 under the same conditions. At the same time, ZSM-5 provides Brønsted acid sites to activate ammonia. However, the replacement of protons on ZSM-5 by iron ions will decrease its Brønsted acidity, as shown in our TPD experiments (36). Hence, an appropriate iron content in the Fe-ZSM-5 is favorable for a high SCR activity. This is in good agreement with our previous SCR performance in which the maximum NO conversion was obtained on the Fe-ZSM-5 with 1.59–3.58 wt% iron and a further increase of iron content decreased NO conversion at high temperatures (6).

CONCLUSIONS

Based on the above results, it can be concluded that the main form of Fe in the Fe-ZSM-5 (Fe/Al = 0.193) catalyst was Fe^{3+} with tetrahedral coordination, along with a small amount of Fe^{2+} and aggregated Fe^{3+} ions. The Fe^{3+} ions could be partially reduced to Fe^{2+} ions by H_2 at high temperatures (300–600°C), but the oxidation was reversible when O_2 was introduced to the reduced catalyst at 500°C. NH_3 molecules were adsorbed on the Brønsted acid and Lewis acid sites to generate, respectively, NH_4^+ ions (majority) and coordinated NH_3 (minority). The NH_4^+ ions with three hydrogen atoms bonded to the AlO_4 tetrahedra of ZSM-5 were more stable at high temperatures than those with two bonds. The pretreatment by $SO_2 + O_2$ at 400°C increased the Brønsted acidity of the Fe-ZSM-5 due to the formation of surface sulfate species of iron. This resulted in an enhancement of the SCR activities by $H_2O + SO_2$ at high temperatures (>350°C). NO molecules adsorbed only weakly on the Fe-ZSM-5, forming Fe^{2+} mononitrosyl species. In the presence of O_2, NO was oxidized to adsorbed N_2O_3, NO_2, and nitrate species. The adsorbed nitrogen oxides were not stable at above 300°C in He, but the NO and NO_2 adspecies could be observed in flowing NO + O_2/He. The adsorbed NH_4^+ ions were active in reacting with NO and NO + O_2 at 300°C, but the reaction rate with NO + O_2 was much higher than that with NO. The present results indicate that NH_4^+ ions as well as NO and NO_2 adspecies may all play an important role in the SCR reaction on the Fe-ZSM-5 catalyst.

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