Journal of Catalysis **207,** 224–231 (2002)
doi:10.1006/jcat.2002.3528, available online at http://www.idealibrary.com on IDEAL®

Reaction Mechanism of Selective Catalytic Reduction of NO with NH_3 over Fe-ZSM-5 Catalyst

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

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

Received June 28, 2001; revised January 15, 2002; accepted January 15, 2002

Fe-exchanged ZSM-5 has been found previously to be much more active than commercial vanadia-based catalysts for selective catalytic reduction (SCR) of NO to N_2 with NH_3. The NO reduction mechanism is studied in this work using combined *in situ* FTIR (to observe surface-adsorbed species) and online mass spectrometry (to analyze reaction products). NH_3 adsorbs quickly on Fe-ZSM-5 to generate NH_4^+ ions, and the catalyst is quite active in oxidizing NO to NO_2 by O_2. The temperature-programmed surface reaction (TPSR) from 100 to 400°C shows that the reactivities of NH_4^+ with NO and NO_2 decrease in the order $NO + NO_2$ (1 : 1 ratio, producing N_2) > NO_2 (producing $N_2 + N_2O$) ≫ NO (producing N_2), with the same total NO_x concentration for the three cases. This trend is also observed in their reactivities at 200°C. It is concluded that both NO and NO_2 are involved in the reaction with NH_4^+ ions to form N_2. Also, the reactivity of NH_4^+ ions with $NO + O_2$ on Fe-ZSM-5 is much higher than that on H-ZSM-5, but the two catalysts show the same activity for the reaction between NH_4^+ and $NO + NO_2$. This suggests that NO_x reduction probably takes place on the Brønsted acid sites and that the role of Fe^{3+} irons is to oxidize NO to NO_2 by O_2. A possible reaction mechanism for NO reduction involves the reaction between one NO_2 molecule and two neighboring NH_4^+ ions to form an active intermediate $NO_2(NH_4^+)_2$, which subsequently reacts with another NO to produce N_2 and H_2O. The intermediate has been detected by FTIR with a band near 1602 cm^{-1}. © 2002 Elsevier Science (USA)

Key Words: **selective catalytic reduction; SCR of NO with ammonia; Fe-ZSM-5 catalyst; mechanism; NO_2.**

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) of NO with ammonia is the most efficient technology for abatement of NO from power plant exhaust gases. The main reaction of SCR is

$$4NH_3 + 4NO + O_2 = 4N_2 + 6H_2O. \quad [1]$$

This reaction implies 1 : 1 stoichiometry for NH_3 and NO. Many materials, such as mixed oxides and molecular sieves, have been found to be active for the ammonia SCR reaction (1). The commercial catalysts used today are V_2O_5-doped TiO_2, using WO_3 and/or MoO_3 as promoters. Although the vanadia-based catalysts have been commercialized, problems still remain, e.g., high activity for oxidation of SO_2 to SO_3 and toxicity of vanadia. Hence, there are continuing efforts to develop new catalysts.

Recently, H-zeolites and transition-metal ion-exchanged molecular sieves have received much attention as catalysts for the SCR reaction (2–13). They were reported to be more active than the vanadia catalysts. In particular, we found that Fe-ZSM-5 showed the highest activity among all known SCR catalysts. Compared with the commercial vanadia catalyst, the Fe-ZSM-5 catalyst was five times more active at 400°C and seven times more active at 450°C, based on the first-order rate constants (9). N_2 was the only detectable N-containing product, and no N_2O was observed in the entire temperature range (250–600°C) for Fe-ZSM-5 (8, 9). This is different from vanadia catalysts, with which N_2O was detected at high temperatures due to oxidation of ammonia by oxygen (1). In addition, we found that the presence of $H_2O + SO_2$ enhanced the SCR activity of Fe-ZSM-5 at above 400°C (9). We have attributed the enhancement to an increase in surface acidity and a decrease in NH_3 oxidation activity due to the formation of sulfate species from SO_2 oxidation (10–12). A stronger surface acidity was beneficial for decreasing ammonia oxidation (to NO) by oxygen (a competitive reaction for the SCR reaction). However, unfortunately, Sachtler and co-workers (13) misread our results and mistakenly reported that water (not SO_2) increased the acidity.

It was reported that both NO_x and NH_3 could adsorb onto the surface over ion-exchanged molecular sieves (2, 6, 8, 10, 11, 13–17). It is known that NH_3 molecules react with the protons of H-form zeolites to generate ammonium ions. NH_4^+ ions with two or three hydrogen atoms bonded to the AlO_4 tetrahedra of ZSM-5 were observed on H-ZSM-5 (15) and Fe-ZSM-5 (11) and they were stable at high temperatures (≤450°C). When NO + O_2 reacted with Fe-ZSM-5,

---

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

0021-9517/02 $35.00

adsorbed species of NO, NO_2, and nitrate (NO_3^-) were detected by IR, with NO_2 as the dominating species (11, 13, 16, 17). The NO was assigned to that adsorbed on Fe^{2+} sites, while NO_2 and NO_3^- species were adsorbed on Fe^{3+} sites. Our previous work showed that the NO_x-adsorbed species were not stable in a flow of He at above 300°C, but adsorbed NO and NO_2 could be observed in a flow of $NO + O_2$ at 200–400°C (11). The NH_4^+ ions were reactive with NO and $NO + O_2$, but the reaction rate with $NO + O_2$ was much higher than that with NO alone (11, 18). In addition, the NO_2 adsorbed species was also observed on Fe-exchanged TiO_2-pillared clay when $NO + O_2$ was introduced. The rate of reaction between NO_2 and NH_3 was much higher than that between NO and NH_3 (10). Also, the SCR activity correlated well with the formation rate of NO_2 (10, 11). These results suggest that NO, NO_2, and NH_4^+ species may play an important role in the SCR reaction on the Fe-exchanged molecular sieves. The SCR reaction on Fe-ZSM-5 probably takes place according to the reaction (11, 18)

$$2NH_4^+ + NO_2 + NO \rightarrow 2N_2 + 3H_2O + 2H^+. \qquad [2]$$

This is consistent with reaction [1] with an NH_3/NO ratio of 1 : 1. In fact, NO_2 has been considered as an intermediate for the ammonia SCR reaction on H-form zeolites. Kiovsky *et al.* (2) observed that, on H-MOR, NO_2 was more reactive than NO with NH_3, and an increase in the NO_2/NO ratio from 2 to 12 enhanced NO_x reduction activity significantly. Kiovsky *et al.* suggested that NO_2 was an active intermediate for NO reduction by ammonia. The difference in SCR activity for zeolites was due to their different rates of NO oxidation to NO_2 (2). However, Brandin *et al.* (4) observed that, an equimolar mixture of NO and NO_2 yielded a higher reaction rate on H-MOR, than either NO or NO_2 yielded in the feed. In addition, they proposed that NO^+, generated from NO oxidation by O_2, was the intermediate for the SCR reaction. The NO^+ could also result from the oxidation of NO by NO_2 when $NO + NO_2$ was used. But based on their negative correlation between SCR activity and the rate of NO oxidation to NO_2, they concluded that an ideal SCR catalyst would be one that could not oxidize NO to NO_2 (4). Eng and Bartholomew (15) also detected NO_2 formation over H-ZSM-5, and concluded that it played an important role in the ammonia SCR reaction.

Although these studies provided insights into the mechanism of NO reduction over molecular sieves, clear evidence supporting NO_2 and/or NO^+ as intermediates, especially on Fe-ZSM-5, was not obtained. There is still debate on the mechanism of SCR on H-form zeolites (2, 4, 15). The aim of the present study is to gain new insights into the mechanism of NO reduction on Fe-ZSM-5 by combining *in situ* FTIR and online mass spectrometer analyses. The *in situ* FTIR is used to observe the changes of surface-adsorbed species during the reactions. The online mass spectrometer is used to analyze the reaction products from the IR cell. A direct correlation between the reaction rate of adsorbed species and the N_2 formation rate is obtained. Since NO, NO_2, and NH_4^+ species may play an important role in the SCR reaction, the reactivities of NH_4^+ ions with NO, NO_2, and NO/NO_2 (1 : 1) with the same total NO_x concentration were studied. The results provide direct evidence that both NO and NO_2 participate in NO_x reduction and that $NO_2(NH_4^+)_2$ is a key intermediate. Finally, a reaction mechanism for the SCR reaction on Fe-ZSM-5 is proposed.

EXPERIMENTAL

Fe-ZSM-5 was prepared using a conventional aqueous ion-exchange technique. Two grams of NH_4-ZSM-5 (Si/Al ≈ 10) was added to 200 ml of 0.05 M $FeCl_2$ solution with constant stirring in air. After 24 h, the mixture was filtered and washed with deionized water. The obtained sample was then dried at 120°C overnight and calcined at 500°C for 6 h in air. Most Fe^{2+} ions in the catalyst were oxidized to Fe^{3+} ions (11). The Fe content, measured by neutron activation analysis, was 1.4 wt% in the Fe-ZSM-5, i.e., at the 50% ion-exchange level. H-ZSM-5 was obtained by calcining NH_4-ZSM-5 at 500°C for 4 h. The NH_4-ZSM-5 was supplied by Alsi-Penta Zeolithe Gmbh (Germany). $FeCl_2 \cdot 4H_2O$ (99%) was obtained from Aldrich.

Infrared spectra were recorded on a Nicolet Impact 400 FTIR 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 were first treated at 400°C in a flow of He for 30 min to remove adsorbed H_2O and other gases. Our previous H_2 TPR and ESR results indicated that the iron was still present mainly in the ferric form after this pretreatment (11). The samples were then cooled to desired temperatures, i.e., 350, 300, 250, 200, 150, and 100°C. At each temperature, the background spectrum was recorded in a flow of He and subtracted from the sample spectrum that was obtained at the same temperature. NH_3 adsorption was performed by treating the wafers with flowing 1.07% NH_3/He (500 ml/min) for 30 min and then purging with He for another 30 min. Subsequent to the ammonia adsorption step, the He flow was switched to different flows containing 1000 ppm NO, 1000 ppm NO_2, 500 ppm NO + 500 ppm NO_2, and 1000 ppm NO + 2% O_2. With increasing temperature (at 10°C/min) and/or time, IR spectra were recorded by accumulating 32 scans at a spectral resolution of 4 cm^{-1}. At the same time, the effluent gases from the IR cell were monitored continuously with a magnetic-deflection-type mass spectrometer (AERO VAC, Vacuum Technology Inc.). NH_3 ($m/e = 17$ minus the contribution of H_2O), H_2O ($m/e = 18$), N_2 ($m/e = 28$), and N_2O ($m/e = 44$) were recorded.

The gases were obtained by blending different premixed gases, using He as the diluent gas. The total gas flow rate was 500 ml/min (ambient conditions). The premixed gases (1.00% NO/He, 0.98% NO_2/He, and 1.07% NH_3/He), O_2 (99.5%), and He (99.995%) were supplied by Matheson without additional purification.

RESULTS

TPSR of NH_4^+ on Fe-ZSM-5. The reactivities of NH_4^+ ions with NO, NO_2, and NO + NO_2 were studied first using temperature-programmed surface reaction (TPSR). When Fe-ZSM-5 was treated with 1.07% NH_3/He at 100°C, a strong IR band at 1461-cm^{-1} and a very weak band at 1612 cm^{-1} were observed (Fig. 1A). The 1461-cm^{-1} band is assigned to NH_4^+ ions that are chemisorbed on the Brønsted acid sites, whereas the weak band at 1612 cm^{-1} is due to NH_3 coordinately linked to Lewis acid sites (11, 19). It can be seen from the spectrum that there are many more Brønsted acid sites than Lewis acid sites on the Fe-ZSM-5. Also, four other IR bands were observed at 3353, 3290, 3052, and 2800 cm^{-1} (not shown). The first two bands can be assigned to NH_4^+ ions with three hydrogen atoms bonded to three oxygen ions of AlO_4 tetrahedra (3H structure). The other two bands are due to NH_4^+ ions with two hydrogen atoms bonded to AlO_4 tetrahedra (2H structure) (11, 15, 20). The NH_4^+ ions with the 3H structure are more stable than those with the 2H structure (11). Since NH_4^+ ions are the dominating ammonia species at high temperatures and coordinated NH_3 is not stable above 200°C when the ammonia SCR reaction takes place (11, 18), we will focus on the reactivities of NH_4^+ ions with NO_x. When 1000 ppm NO was passed over the sample, the above IR bands decreased with increasing temperature (10°C/min) (Fig. 1A). Meanwhile, NH_3 desorption was detected by the mass spectrometer (Fig. 1B). The NO adsorbed species which was observed at 1876 cm^{-1} in our previous work (11) when NO was introduced into the fresh Fe-ZSM-5, was not seen, probably due to the coverage of the surface by NH_3. At above 320°C, the reaction between NO and NH_4^+ ions occurred, producing a trace amount of N_2 and H_2O. N_2O formation was not detected (Fig. 1B), which suggests that NH_4^+ ions are less active when reacting with NO at low temperatures. This is consistent with our previous catalytic performance result that NO reduction activities by NH_3 were very low (3–5%) at 350 and 400°C in the absence of O_2 (9).

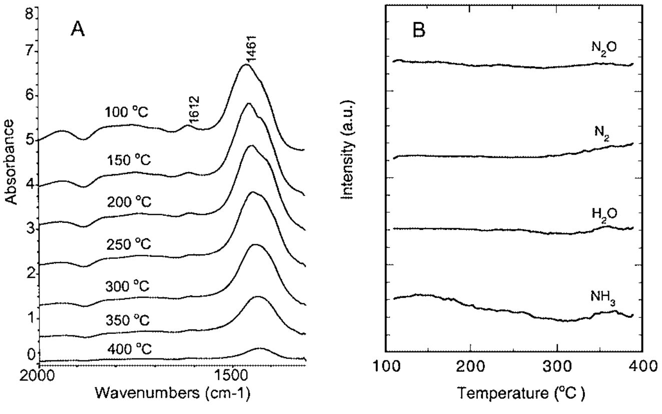

FIG. 1. (A) IR spectra and (B) product gas analysis of NH_3-adsorbed Fe-ZSM-5 heated in a flow of 1000 ppm NO/He at 10°C/min.

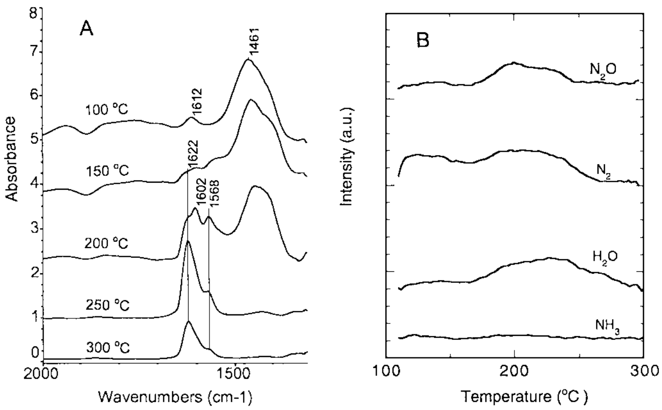

FIG. 2. (A) IR spectra and (B) product gas analysis of NH_3-adsorbed Fe-ZSM-5 heated in a flow of 1000 ppm NO_2/He at 10°C/min.

The TPSR results of NH_4^+ with NO_2 are shown in Fig. 2. When 1000 ppm NO_2 was introduced onto the NH_3-adsorbed Fe-ZSM-5 and the temperature was increased, the NH_4^+ band at 1461 cm^{-1} decreased. At 200°C, three new bands appeared at 1622, 1602, and 1568 cm^{-1} (Fig. 2A). The bands at 1622 and 1568 cm^{-1} are attributed to adsorbed NO_2 and nitrate species, respectively (11, 13, 16, 17, 21). The 1602 cm^{-1} band is due to another type of NO_2 species. It was present when both NO_2 adsorbed species and NH_4^+ ions were on the surface; i.e., it appeared at 200°C after NO_2 formation and then vanished at 250°C upon the consumption of NH_4^+. This band may be due to an intermediate for the reaction between NO_2 and NH_4^+ ions. When NO_2 molecules react with NH_4^+ ions, electrons transfer from the N atoms of NH_4^+ to NO_2. This enhances the electron density of NO_2 molecules and weakens the N–O bonds. Consequently, the NO_2 band shifts to lower wavenumbers (e.g., 1602 cm^{-1}). Since the pores in ZSM-5 are very small (0.52 × 0.57 nm), it is possible that the NO_2 is associated directly with NH_4^+ ions. We assign this intermediate to $NO_2(NH_4^+)_y$, where y is the molar ratio of NH_4^+ to NO_2 and changes with time/temperature. As shown in Fig. 2, the transfer of electrons from NH_4^+ to NO_2 also weakens the N–H bonds; thus, the NH_4^+ band at 1461 cm^{-1} shifts to lower wavenumbers and becomes broader. When the temperature was above 250°C, the NH_4^+ band disappeared, and only NO_2 and nitrate bands were seen on the surface. In the process, a large amount of N_2, N_2O, and H_2O was

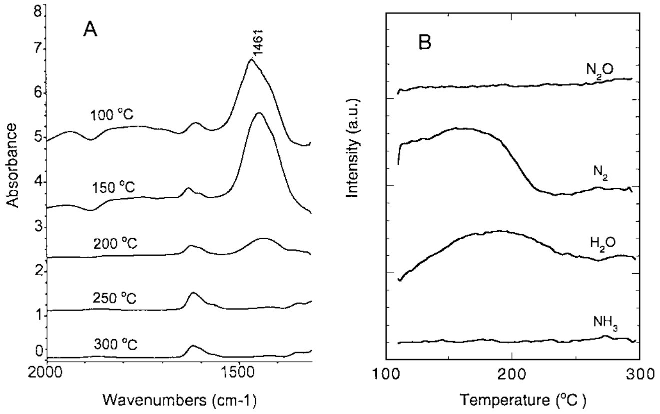

FIG. 3. (A) IR spectra and (B) product gas analysis of NH_3-adsorbed Fe-ZSM-5 heated in a flow of 500 ppm NO + 500 ppm NO_2/He at 10°C/min.

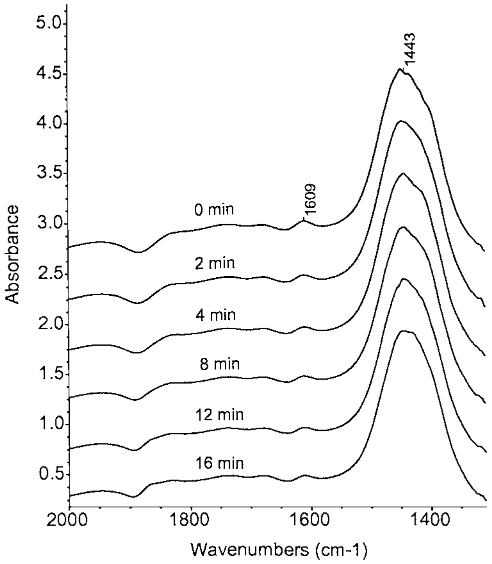

FIG. 4. IR spectra taken at 200°C upon passing 1000 ppm NO/He over NH_3-adsorbed Fe-ZSM-5 for 0–16 min.

produced (Fig. 2B). Almost no NH_3 desorption was detected by the mass spectrometer (Fig. 2B). These results indicate that NH_4^+ ions reacted with NO_2, producing N_2, N_2O, and H_2O, according to the reaction

$$2NH_4^+ + 2NO_2 \rightarrow N_2 + N_2O + 3H_2O + 2H^+. \qquad [3]$$

As shown in Fig. 3, when 500 ppm NO + 500 ppm NO_2 were passed over the NH_3-treated Fe-ZSM-5, the NH_4^+ band also decreased significantly with increasing temperature, and new bands due to NO_2 and nitrate species appeared at 1624 and 1570 cm^{-1}, respectively. At the same time, a very large amount of N_2 and H_2O was formed. No NH_3 desorption or N_2O formation was observed. The reaction takes place according to reaction [2]. By comparing the intensity of the NH_4^+ band at 200°C in Fig. 3A with that of the corresponding bands in Figs. 1A and 2A, it can be seen that the reactivity of NH_4^+ ions with NO + NO_2 is higher than that with NO or with NO_2 alone, although they have the same NO_x concentration. This conclusion can also be obtained from the temperatures for N_2 formation, e.g., 100–220°C for NO + NO_2, 100–260°C for NO_2, and above 320°C for NO.

Reactivities of NH_4^+ on Fe-ZSM-5 at 200°C. The IR spectra of the reaction between NH_4^+ ions and NO at 200°C are shown in Fig. 4. After 1000 ppm NO was passed over the NH_3-treated Fe-ZSM-5 for 16 min, the IR band due to NH_4^+ ions decreased slightly (approximately by 10%). The outlet gas analysis showed that almost no N_2, N_2O, or H_2O formation was observed by the mass spectrometer. This further proves that NO is quite inactive in reacting with NH_4^+ ions.

By comparison, when 1000 ppm NO_2 was passed over the sample, the NH_4^+ band decreased significantly (Fig. 5). The IR bands due to NO_2 (1624 cm^{-1}), nitrate (1573 cm^{-1}), and the intermediate $NO_2(NH_4^+)_y$ (1605 cm^{-1}) appeared after 2 min. Also, N_2, N_2O, and H_2O formation was detected by the mass spectrometer. The NH_4^+ band vanished in 14 min, and the catalyst surface was dominated by the adsorbed NO_2 and nitrate species.

The reactivity of NH_4^+ ions with NO + NO_2 is shown in Fig. 6. When 500 ppm NO + 500 ppm NO_2 were introduced into the IR cell at 200°C, the band at 1439 cm^{-1} decreased quickly. Meanwhile, a large amount of N_2 and H_2O was formed. Also, the NO_2-adsorbed species were seen at 1624 cm^{-1} in 1 min. After 7 min, the NH_4^+ band disappeared, and new IR bands due to $Fe^{2+}(NO)$ (weak, at 1876 cm^{-1})

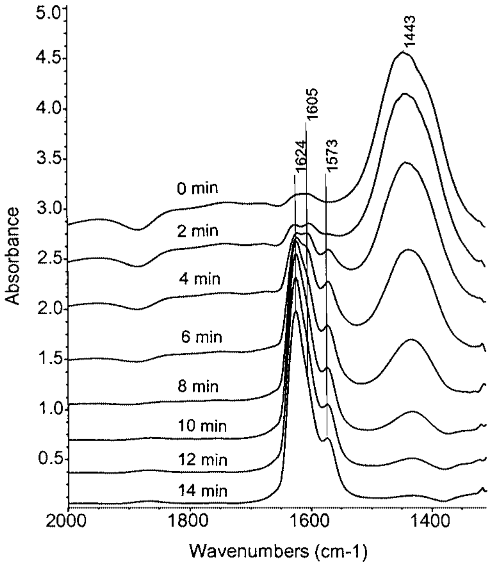

FIG. 5. IR spectra taken at 200°C upon passing 1000 ppm NO_2/He over NH_3-adsorbed Fe-ZSM-5 for 0–14 min.

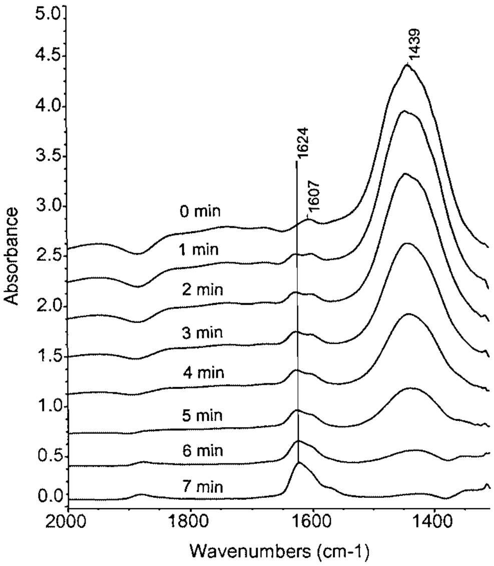

FIG. 6. IR spectra taken at 200°C upon passing 500 ppm NO + 500 ppm NO_2/He over NH_3-adsorbed Fe-ZSM-5 for 0–7 min.

(11, 16, 17) and nitrate (weak, at 1575 cm^{-1}) species were observed. The present results further verify that the reactivities with NH_4^+ ions decrease in the following sequence: $(NO + NO_2) > NO_2 > NO$ at 200°C.

The IR spectra of the reaction between NH_4^+ ions and $NO + O_2$ are shown in Fig. 7. After 1000 ppm NO + 2% O_2 were passed over the ammonia-adsorbed Fe-ZSM-5, the band attributed to NH_4^+ ions decreased significantly and vanished in 11 min. It is clear that oxygen increases the reaction rate between NO and NH_4^+ ions. The reaction products were N_2 and H_2O. New IR bands were seen at 1876 and 1618 cm^{-1} after 4 min, indicating formation of NO- and NO_2 adsorbed species, respectively.

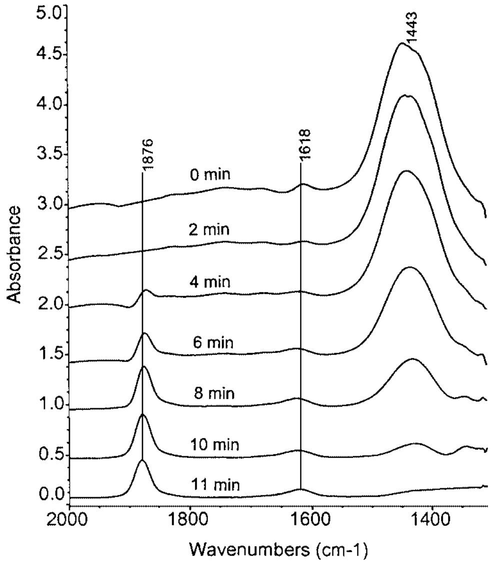

FIG. 7. IR spectra taken at 200°C upon passing 1000 ppm NO + 2% O_2/He over NH_3-adsorbed Fe-ZSM-5 for 0–11 min.

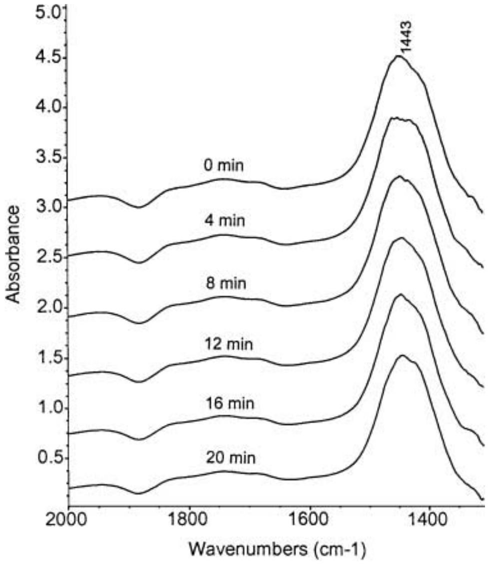

FIG. 8. IR spectra taken at 200°C upon passing 1000 ppm NO + 2% O_2/He over NH_3-adsorbed H-ZSM-5 for 0–20 min.

Reactivities of NH_4^+ on H-ZSM-5 at 200°C. The reactivities of NH_4^+ ions with $NO + O_2$ and $NO + NO_2$ on H-ZSM-5 were also studied. After the H-ZSM-5 was treated with 1.07% NH_3 at 200°C, the NH_4^+ band was also seen at 1443 cm^{-1} (Fig. 8). When 1000 ppm NO + 2% O_2 were passed over the sample, the intensity of the NH_4^+ band decreased only by ca. 12% in 20 min. The formation of N_2, N_2O, or H_2O was not detected by mass spectrometry. It is clear that $NO + O_2$ is much less active on H-ZSM-5 than that on Fe-ZSM-5 when reacting with NH_4^+ ions.

By comparison, after 500 ppm NO + 500 ppm NO_2 were passed over the NH_3-adsorbed H-ZSM-5, the NH_4^+ band decreased quickly (Fig. 9), suggesting that the NH_4^+ ions on H-ZSM-5 are quite reactive with $NO + NO_2$. At the same time, a large amount of N_2 and H_2O was detected in the outlet gas. The NH_4^+ band disappeared in 7 min.

Figure 10 compares the decreases in the relative peak areas of the NH_4^+ band at around 1443 cm^{-1} on H-ZSM-5 and Fe-ZSM-5 in different flowing gases at 200°C. It can be seen clearly that the reactivity of NH_4^+ ions with NO + O_2 on Fe-ZSM-5 is much higher than that on H-ZSM-5 (Fig. 10A) but they are almost the same in a flow of NO + NO_2 (Fig. 10B). Also, $NO + NO_2$ is more reactive than $NO + O_2$ with NH_4^+. These results support the conclusion that the role of Fe^{3+} ions on Fe-ZSM-5 is to oxidize NO to NO_2 in the SCR reaction.

IR spectra of Fe-ZSM-5 in a flow of $NO + NH_3 + O_2$. To identify the species present on the catalyst under reaction conditions, IR spectra were recorded when Fe-ZSM-5 was

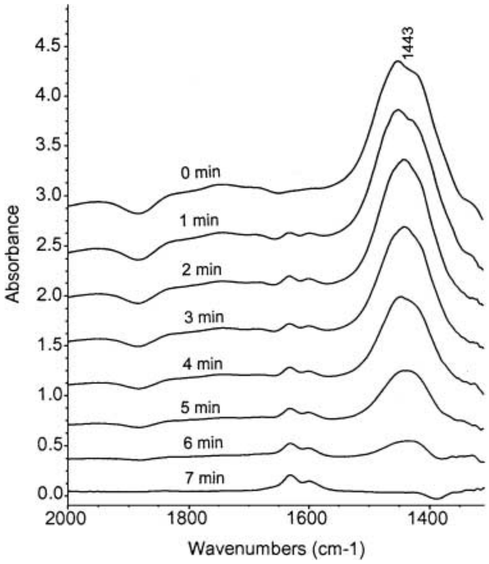

FIG. 9. IR spectra taken at 200°C upon passing 500 ppm NO + 500 ppm NO_2/He over NH_3-adsorbed H-ZSM-5 for 0–7 min.

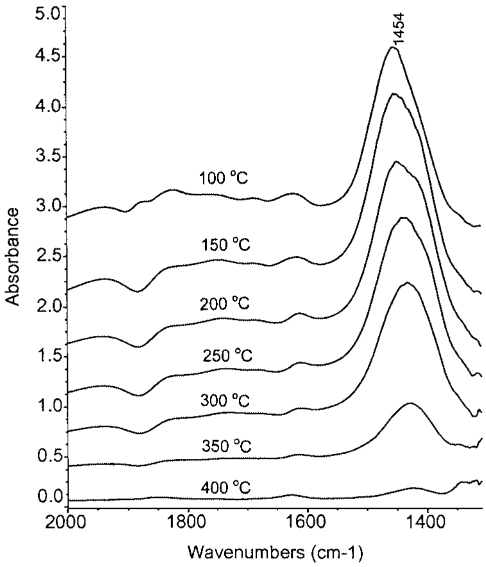

FIG. 11. IR spectra of Fe-ZSM-5 in a flow of 1000 ppm NO + 1000 ppm NH_3 + 2% O_2/He at 100–400°C.

heated from 100 to 400°C in a flow of 1000 ppm NO + 1000 ppm NH_3 + 2% O_2 at steady state. As shown in Fig. 11, the band due to NH_4^+ ions was observed at 1454 cm^{-1} at 100°C. Raising the temperature resulted in a decrease in the intensity of the NH_4^+ band. The NH_4^+ ions were still observed at 400°C. In the temperature range studied, the IR bands due to NO_x adsorbed species were not detected. This suggests that the NO_2 consumption rate (by NH_3) was much higher than the NO_2 formation rate from NO + O_2 under the reaction conditions. The observation of a strong NH_4^+ band also indicates that NH_3 was present in excess. The formation of N_2 and H_2O was observed with the mass spectrometer. Our previous catalytic performance results also showed that 0–99% NO conversions were obtained at 100–400°C under similar reaction conditions with a GHSV of 4.6×10^5 h^{-1} (9).

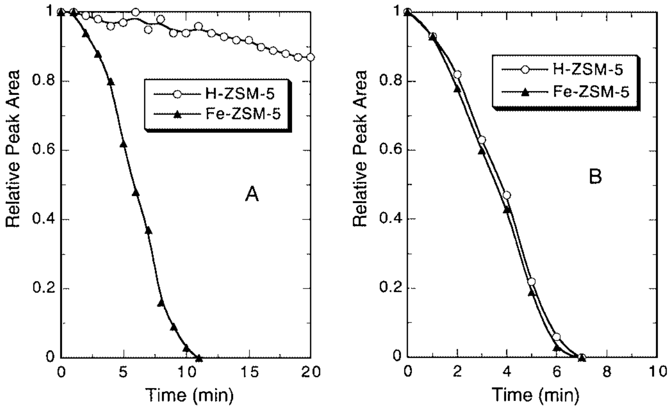

FIG. 10. Changes in peak areas of IR band near 1443 cm^{-1} (due to NH_4^+ ions) on H-ZSM-5 and Fe-ZSM-5 at 200°C in a flow of (A) 1000 ppm NO + 2% O_2/He and (B) 500 ppm NO + 500 ppm NO_2/He.

DISCUSSION

Fe-ZSM-5 has been widely studied as catalyst for both the ammonia SCR reaction and the hydrocarbon SCR reaction. Our previous results showed that, although iron cations were exchanged with NH_4-ZSM-5 in the Fe^{2+} form, most iron cations in the Fe-ZSM-5 were present as Fe^{3+} ions with tetrahedral coordination, with only a small amount of both Fe^{2+} and aggregated Fe^{3+} ions (11). As expected, the replacement of NH_4^+ (or H^+) by iron cations resulted in a decrease in the number of Brønsted acid sites. However, even when all of the protons were replaced by $FeCl_2^+$ in $FeCl_3$, a substantial number (ca. 40%) of Brønsted acid sites remained on the overexchanged Fe-ZSM-5 after hydrolysis (16). These protons provide sites for ammonia adsorption, generating NH_4^+ ions. The foregoing data of TPSR and activity at 200°C showed that the reactivity of NH_4^+ ions with NO was very low below 320°C (Figs. 1 and 4). However, the addition of O_2 increased the activity significantly (Fig. 7), which is in good agreement with the SCR activity on Fe-ZSM-5 (9). The improvement is related to the formation of NO_2 from oxidation of NO by O_2, because Fe-ZSM-5 is highly active in oxidizing NO to NO_2 (11) and NO_2 is much more reactive than NO with NH_4^+ ions (Figs. 1, 2, 4, and 5). Although NO_2 is highly active in reacting with NH_4^+ ions, the formation of N_2 and N_2O is not consistent with our previous SCR result that N_2 was the only N-containing product for NO reduction (8, 9). This suggests that NO_2 is not the only reactant to react with NH_3 during the SCR reaction. Moreover, the previous results indicate that the reactivity of NH_4^+ with $NO + NO_2$ was much higher than that with NO_2 alone with the same total NO_x concentration (Figs. 3 and 6), producing only N_2. All of these results support strongly that NO is also involved in the reaction with NH_4^+ ions for the SCR reaction.

At 200°C, the reactivity of NH_4^+ ions with $NO + O_2$ on Fe-ZSM-5 was much higher than that on H-ZSM-5 (Fig. 10A), which is consistent with their respective SCR activities (9). The addition of iron ions to ZSM-5 increased the activities dramatically. The increase is related to the increase in NO oxidation to NO_2. In our previous work (11), we found that H-ZSM-5 showed very low activity for oxidizing NO to NO_2. When iron ions were exchanged to H-ZSM-5, the NO conversion to NO_2 was increased significantly from 4–6% to 20–30%, under the conditions of 300–400°C, 1000 ppm NO, 2% O_2, and GHSV $= 4.6 \times 10^5$ h^{-1}. The formation of NO_2 promotes the reaction between NH_4^+ ions and NO. In fact, the reactivities of NH_4^+ with $NO + NO_2$ were almost the same on the H-ZSM-5 and Fe-ZSM-5 catalysts (Fig. 10B). It seems that Fe^{3+} ions on Fe-ZSM-5 did not participate in the NO_x reduction reaction. The reaction probably took place on the Brønsted acid sites, because NH_4^+ ions are difficult to move at 200°C. The role of Fe^{3+} ions is to oxidize NO to NO_2.

The previously described results showed that both NO_x adsorbed species and NH_4^+ ions were observed on Fe-ZSM-5 when $NO + O_2$ and NH_3 were introduced separately. However, under our reaction conditions, i.e., with NO, O_2, and NH_3 at high temperatures, the surface of Fe-ZSM-5 was covered mainly by NH_4^+ ions. NO_x adsorbed species were not observed (Fig. 11), which suggests that the reaction of NH_4^+ ions with $NO_2 + NO$ was much faster than that of NO_2 formation from $NO + O_2$. As soon as NO_2 was generated, it was consumed by NH_4^+ ions, so that the steady-state concentration of NO_2 was below the detection limit of our IR spectrometer. In addition, the observation of NH_4^+ ions also suggests that the SCR reaction took place with excess NH_4^+, except at high temperatures when NH_3 conversion reached 100%. In the reaction between NH_4^+ and NO_2, an intermediate $NO_2(NH_4^+)_y$ was observed with an IR band near 1602 cm^{-1} (Figs. 2 and 5). In the SCR reaction, the steady-state NH_4^+/NO_2 ratio is much larger than 1 because of the excess NH_4^+ ions as compared to NO_2 (Fig. 11). Since the reaction between $NO_2(NH_4^+)_y$ and NO needs only two NH_4^+ ions (reaction [2]), the excessive NH_4^+ ions remain on the catalyst and do not participate in NO_x reduction. The $NO_2(NH_4^+)_y$ will actually be $NO_2(NH_4^+)_2$ in the SCR reaction. The transfer of electrons from NH_4^+ to NO_2 weakens both N–H and N–O bonds. This is an activation process for NH_4^+ ions and NO_2. The intermediate $NO_2(NH_4^+)_2$ was not observed during the SCR reaction (Fig. 11) and the reaction between NH_4^+ ions and $NO + NO_2$ (Figs. 3 and 6), probably due to a faster reaction of $NO_2(NH_4^+)_2$ with NO than with NO_2 (18).

According to the above results, we proposed a simplified mechanism for a NO reaction with ammonia on Fe-ZSM-5, as shown in Fig. 12.

During the SCR reaction, gaseous NH_3 molecules are adsorbed quickly onto the Brønsted acid sites to form NH_4^+ ions, and NO molecules are oxidized to NO_2 on Fe^{3+} sites by O_2. This is a slow reaction. Then one molecule of NO_2 diffuses to two adjacent NH_4^+ ions to form the active complex, $NO_2(NH_4^+)_2$. The small pore size in ZSM-5 facilitates the formation of this complex. The active complex subsequently reacts with one molecule of NO to produce N_2 and H_2O, thus completing the catalytic cycle. The total reaction is the same as reaction [1]. This reaction scheme is similar to that on H-ZSM-5 (15) and Fe-exchanged TiO_2-pillared clay (10), but different from that on V_2O_5-based catalysts, where N_2 comes from the reaction between ammonia-adsorbed species and gaseous NO (1, 22–27). On Fe-ZSM-5, the oxidation of NO to NO_2 is probably the rate-determining step for the SCR reaction. The oxidation of NO should be near first order with respect to NO. It follows that the overall reaction should also be first order, as verified in our kinetic studies (28). Also, the coverage of surface by NH_3 under the reaction conditions is in agreement with the reactions being zero-order with respect to NH_3 (28). H-ZSM-5 showed strong surface acidity but very low activity in the oxidation of NO to NO_2; its SCR activity was therefore very low. After being ion exchanged with iron, the iron ions increased the oxidation rate of NO to NO_2 significantly (11); hence, a much higher SCR activity was expected on Fe-ZSM-5 (9). The active complex $NO_2(NH_4^+)_2$ could also react with NO_2 to produce N_2 and N_2O, e.g., when NO_2 was the only reactant (Figs. 2 and 5). However, in the presence of NO, this intermediate prefers to react with NO rather than with NO_2, because the reactivity of $NO_2(NH_4^+)_2$ with NO is much higher than that with NO_2 according to our previous TPSR results (18). This explains why N_2 was the only N-containing product for the SCR reaction on Fe-ZSM-5. It is noted that, although the nitrate species with an IR band near 1573 cm^{-1} was also observed on the fresh Fe-ZSM-5 when $NO + O_2$ was introduced (11), it might not be an intermediate for the SCR reaction. This is because the nitrate species comes from oxidation/disproportionation of NO_2, but NO_2 is consumed very quickly by NH_4^+ ions during the SCR reaction. It is difficult to further convert NO_2 to nitrate species in the presence of NH_3. On the contrary, if nitrate species were formed, it would react with NH_4^+ or NH_3 to generate ammonium nitrate; then NH_4NO_3 would decompose quickly to N_2O and H_2O, according to the reaction

$$NH_4NO_3 \rightarrow N_2O + 2H_2O. \qquad [4]$$

It is well known that reaction [4] is the reaction by which

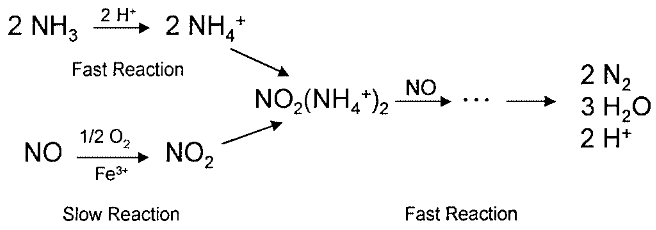

FIG. 12. Reaction scheme of SCR of NO with ammonia on Fe-ZSM-5.

N_2O is prepared commercially. The absence of N_2O in the SCR products (8, 9) verifies that nitrate is not an intermediate. In addition, NO reduction needs adjacent NH_4^+ ions (Fig. 12). Small pores and low Si/Al ratios in zeolites will promote the formation of the NH_4^+ ions. Meanwhile, zeolites with low Si/Al ratios will also have large ion-exchange capacities, which increase iron contents on the Fe-exchanged zeolites and thus enhance NO oxidation to NO_2. Therefore, Fe-ZSM-5 with Si/Al ratio = 10 showed much better performance than other Fe-exchanged zeolites with larger pores and higher Si/Al ratios in our previous work (9).

CONCLUSIONS

Based on the above results, it can be concluded that (1) the reactivities of NH_4^+ ions (preadsorbed on Fe-ZSM-5) with NO and NO_2 decrease in the following order: $NO + NO_2 > NO_2 \gg NO$; (2) the reactivity of NH_4^+ ions with $NO + O_2$ on Fe-ZSM-5 is much higher than that on H-ZSM-5, but the two catalysts show the same activity for the reaction between NH_4^+ and $NO + NO_2$; (3) the SCR reaction needs two kinds of sites: the Brønsted acid sites for ammonia adsorption and the metal ion sites (i.e., Fe^{3+} ions) for NO oxidation to NO_2; (4) a possible reaction mechanism is proposed for NO reduction involving NO_2 and $NO_2(NH_4^+)_2$ as intermediates, and these two intermediates have been detected by *in situ* FTIR; (5) NO_x reduction takes place on the Brønsted acid sites.

ACKNOWLEDGMENT

This work was supported by the NSF under Grant CTS-0095909.

REFERENCES

1. Bosch, H., and Janssen, F., *Catal. Today* **2**, 369 (1988).
2. Kiovsky, J. R., Koradia, P. B., and Lim, C. T., *Ind. Eng. Chem. Prod. Res. Dev.* **19**, 218 (1980).
3. Kucherov, A. V., Montreuil, C. N., Kucherova, T. N., and Shelef, M., *Catal. Lett.* **56**, 173 (1998).
4. Brandin, J. G. M., Andersson, L. A. H., and Odenbrand, C. U., *Catal. Today* **4**, 187 (1989).
5. Yang, R. T., Chen, J. P., Kikkinides, E. S., Cheng, L. S., and Cichanowicz, J. E., *Ind. Eng. Chem. Res.* **31**, 1440 (1992).
6. Amiridis, M. D., Puglisi, F., Dumesic, J. A., Millman, W. S., and Topsøe, N. Y., *J. Catal.* **142**, 572 (1993).
7. Long, R. Q., and Yang, R. T., *J. Catal.* **186**, 254 (1999).
8. Long, R. Q., and Yang, R. T., *J. Am. Chem. Soc.* **121**, 5595 (1999).
9. Long, R. Q., and Yang, R. T., *J. Catal.* **188**, 332 (1999).
10. Long, R. Q., and Yang, R. T., *J. Catal.* **190**, 22 (2000).
11. Long, R. Q., and Yang, R. T., *J. Catal.* **194**, 80 (2000).
12. Long, R. Q., Chang, M. T., and Yang, R. T., *Appl. Catal. B* **33**, 97 (2001).
13. Sun, Q., Gao, Z. X., Chen, H. Y., and Sachtler, W. M. H., *J. Catal.* **201**, 89 (2001).
14. Ito, E., Mergler, Y. J., Nieuwenhuys, B. E., Calis, H. P. A., van Bekkum, H., and van den Bleek, C. M., *J. Chem. Soc., Faraday Trans.* **92**, 1799 (1996).
15. Eng, J., and Bartholomew, C. H., *J. Catal.* **171**, 27 (1997).
16. Lobree, L. J., Hwang, I.-C., Reimer, J. A., and Bell, A. T., *J. Catal.* **186**, 242 (1999).
17. Lobree, L. J., Hwang, I.-C., Reimer, J. A., and Bell, A. T., *Catal. Lett.* **63**, 233 (1999).
18. Long, R. Q., and Yang, R. T., *J. Catal.* **198**, 20 (2001).
19. Topsøe, N. Y., *J. Catal.* **128**, 499 (1991).
20. Teunissen, E. H., van Santen, R. A., Jansen, A. P. J., and van Duijneveldt, F. B., *J. Phys. Chem.* **97**, 203 (1993).
21. Li, Y., and Armor, J. N., *J. Catal.* **150**, 388 (1994).
22. Busca, G., Lietti, L., Ramis, G., and Berti, F., *Appl. Catal. B* **18**, 1 (1998).
23. Went, G. T., Leu, L. J., Rosin, R. R., and Bell, A. T., *J. Catal.* **134**, 492 (1992).
24. Ozkan, U. S., Cai, Y., and Kumthekar, M. W., *J. Catal.* **149**, 390 (1994).
25. Odenbrand, C. U. I., Bahamonde, A., Avila, P., and Blanco, J., *Appl. Catal. B* **5**, 117 (1994).
26. Topsøe, N.-Y., Dumesic, J. A., and Topsøe, H., *J. Catal.* **151**, 241 (1995).
27. Long, R. Q., and Yang, R. T., *J. Catal.* **196**, 73 (2000).
28. Huang, H. Y., Long, R. Q., and Yang, R. T., Submitted for publication.