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Temperature-Programmed Desorption/Surface Reaction (TPD/TPSR) Study of Fe-Exchanged ZSM-5 for Selective Catalytic Reduction of Nitric Oxide by Ammonia

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Temperature-programmed desorption (TPD) and temperature-programmed surface reaction (TPSR) were employed to study Fe-exchanged ZSM-5 for selective catalytic reduction (SCR) of NO with ammonia. TPD profiles of ammonia and NO_x showed that both NO_x and NH_3 adsorbed on Fe–ZSM-5. Physisorbed NO_x and NH_3 were not affected significantly by iron content. With increasing iron content, chemisorbed NO_x (mainly NO_2 bonded to iron sites) increased while chemisorbed NH_3 (mainly NH_4^+ on Brønsted acid sites) decreased due to substitution of protons by iron ions. The TPSR results indicated that ammonia adsorbed species were quite active in reacting with NO, O_2, $NO + O_2$, and NO_2 (producing H_2O, N_2 and/or N_2O), following the reactivity rank order $NO_2 \sim NO + O_2 > NO > O_2$. NO_x adsorbed species were also reactive to NH_3 at high temperatures. With NH_3 and NO_x coadsorbed on Fe–ZSM-5, TPSR with gaseous He, NO, and NO_2 showed two kinds of reactions for N_2 formation. One reaction near 55°C originated from decomposition of ammonium nitrite, which was not affected by Fe^{3+} content. The other reaction at higher temperatures (170–245°C) was due to an adsorbed complex, probably $[NH_4^+]_2NO_2$, reacting with NO or NO_2. A possible reaction path was proposed for NO reduction involving NO_2 and $[NH_4^+]_2NO_2$ as intermediates. Since the reactivity of $[NH_4^+]_2NO_2$ to NO (producing only N_2 at 170°C) was higher than that to NO_2 (producing both N_2 and N_2O at 200°C), it is reasonable to deduce that $[NH_4^+]_2NO_2$ prefers to react with NO and not NO_2, both of which are present in the SCR reaction. This may be the reason for N_2 being the only product for SCR on Fe–ZSM-5.

Key Words: **selective catalytic reduction; selective catalytic reduction of NO with ammonia; Fe-exchanged ZSM-5 catalyst; temperature-programmed desorption; temperature-programmed surface reaction.**

INTRODUCTION

Nitrogen oxides (NO, NO_2, and N_2O) from combustion of fossil fuels have been a major source of air pollution. Due to their implication in photochemical smog, acid rain, ozone depletion, and greenhouse effects, abatement of these NO_x emissions is increasingly urgent. An efficient technology for reducing NO_x emission from power plants is selective catalytic reduction (SCR) with ammonia in the presence of oxygen.

In the ammonia SCR reaction, catalysts with different compositions have been investigated (1). The commercial catalysts that are used today are V_2O_5 mixed with WO_3 and/or MoO_3 supported on TiO_2. More recently, H zeolites and ion-exchanged molecular sieves (pillared clays, ZSM-5, mordenite, Y zeolite, etc.) have received much attention for the SCR reaction (3–18). They were found to be more active than vanadia catalysts. In particular, Fe-exchanged ZSM-5 (Fe/Al = 0.19–0.43) showed nearly 100% NO conversions at 400–550°C under conditions with a high space velocity (GHSV = 4.6×10^5 h^{-1}) (14–16). This is much higher than the commercial $V_2O_5 + WO_3/TiO_2$ catalyst (67% NO conversion) under the same conditions (15). In addition, N_2 was the only detectable N-containing product and no N_2O was observed in the entire temperature range (250–600°C) for the Fe–ZSM-5 catalysts. This is different from vanadia catalysts, on which much N_2O and NO were detected when the reaction temperature was above 450°C due to oxidation of ammonia by oxygen (1, 2, 14).

For ammonia SCR reaction, the adsorption of reactants, i.e., NH_3 and NO, has been extensively investigated on different catalysts. As discussed in detail in recent reviews (1, 2), it is generally accepted that, for vanadia catalysts, the SCR reaction follows an Eley–Rideal-type mechanism; i.e., a strongly adsorbed ammonia species reacts with a gaseous NO molecule to form molecular N_2. Temperature-programmed desorption (TPD) and Fourier transform infrared (FTIR) experiments showed that NO does not adsorb on the surface of oxidized vanadia under reaction conditions (2). However, for molecular sieve-type catalysts, it was reported that both NO_x and NH_3 could adsorb on the catalysts (2, 3, 7, 10, 14, 19–22). On H-mordenite, Kiovsky *et al.* (3) observed that NO_2 was more reactive with NH_3 than NO and an increase in NO_2/NO ratio increased NO_x reduction activity. They suggested that NO_2 was an active intermediate for NO reduction by ammonia.

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Over H–ZSM-5, Eng and Bartholomew (10) also detected NO_2 formation and concluded that it played an important role in the ammonia SCR reaction. In addition, by using IR spectroscopy, Ito *et al.* (19) found that both nitrosonium ion (NO^+) and nitrito ion (NO_2^-) were formed on Ce-exchanged mordenite. NO^+ reacted with coordinated NH_3 at low temperatures and NO_2^- reacted with NH_4^+ ions at higher temperatures, producing N_2 and H_2O. In our previous studies, NO_2 was observed on Fe-exchanged TiO_2-pillared clay (Fe–TiO_2–PILC) (20) and Fe-exchanged ZSM-5 catalysts (14) when introducing $NO + O_2$/He. The reaction rate between NO_2 and NH_3 was much higher than that between NO and NH_3. Moreover, the SCR activity on the Fe–TiO_2–PILC catalyst correlated well with the rate of formation of NO_2 (20). Therefore, for molecular sieve catalysts, NO_2 plays an important role in the reduction of NO by ammonia in the presence of oxygen.

The aim of the present study is to gain new insights into the mechanism of NO reduction on Fe–ZSM-5 by using TPD and temperature-programmed surface reaction (TPSR). To obtain information on the acidity and redox properties of catalyst, TPD is used to study adsorption/desorption behavior of NH_3 and $NO + O_2$ on Fe–ZSM-5 with various iron contents. Since both NO_x and NH_3 can adsorb on Fe–ZSM-5, the following reactions are studied in the TPSR experiments: (1) NH_3-adsorbed species reacting with gaseous NO, O_2, $NO + O_2$, and NO_2, (2) NO_x-adsorbed species reacting with gaseous NH_3, and (3) $NO_x + NH_3$-coadsorbed species reacting with NO and NO_2. The relative reactivities between different surface species and gaseous species are evaluated and a possible reaction path for reducing NO is discussed.

EXPERIMENTAL

Preparation of Catalyst

NH_4–ZSM-5 (Si/Al = 10) was obtained from Air Products and Chemicals Inc. This material contained 0.07% Fe_2O_3 impurity. H–ZSM-5 was prepared by calcining NH_4–ZSM-5 at 500°C in air for 3 h. Fe(95)–ZSM-5 was obtained by ion exchange of 2 g H–ZSM-5 with a mixed solution that contained 200 ml of 0.1 M HCl and 0.73 g iron powder. During preparation of the catalyst, hydrochloric acid reacted with iron metal to generate ferrous ions and then Fe^{2+} ions exchanged with H–ZSM-5. To prevent oxidation of the ferrous ion to the ferric form, the ion exchange was performed under a helium flow at room temperature for 10 days. This method (16) is different from the procedure that was used in the Mobil patent (i.e., ZSM-5 was exchanged directly with a solution of ferrous salts above 55°C in an inert atmosphere) (17). Our method avoids hydrolysis of the Fe^{3+} ions, which are often present in ferrous salts as an impurity. Hence a high ion-exchange level without iron oxide formation could be obtained on Fe–ZSM-5 and, consequently, very high SCR activity was achieved (14), because iron ions in ZSM-5 were much more active than iron oxide for the NH_3 SCR reaction (14, 15). Fe(300)–ZSM-5 was prepared by sublimation of $FeCl_3$ vapor into H–ZSM-5 at 320°C for 2 h, followed by hydrolytic removal of chlorine, by following the procedure given by Chen and Sachtler (23). The catalysts obtained were first dried at 120°C in air for 12 h, then calcined at 500°C for 6 h. Fe^{2+} in the catalyst was oxidized to Fe^{3+} (24, 25). Finally, the samples obtained were pelleted and ground to 60–100 mesh. The Fe contents, measured by neutron activation analysis, were 2.40 wt% in Fe(95)–ZSM-5 and 6.69 wt% in Fe(300)–ZSM-5. For catalyst designation, the number in parentheses indicates the Fe-exchange level. The iron-exchange level was calculated as 3 × (number of iron ions)/(number aluminum ions) because most of the iron was in the ferric form on the catalysts (21–25). $FeCl_3$ (97.0%), iron powder, and HCl solution (2.00 M) were supplied by Fisher.

TPD and TPSR Studies

TPD and TPSR experiments were carried out in a fixed-bed quartz reactor with an inner diameter of 10 mm. The temperature was controlled by an Omega programmable temperature controller (CN-2010). Before the experiment, 100 mg sample was pretreated in He at 500°C for 1 h to remove adsorbed H_2O and other gases. As reported by Lobree *et al.* (21), Fe^{2+} began to form at 500°C by autoreduction of Fe^{3+} in Fe–ZSM-5 with $Fe/Al > 0.19$, similar to that in Cu–ZSM-5 (26). However, our previous H_2-TPR and ESR results indicated that the iron was still present mainly in the ferric form after this pretreatment (25). After the sample was cooled to room temperature, the He flow was switched to a flow of 1000 ppm NH_3/He for 1.5 h. Mass spectra showed that the intensity of ammonia had stabilized. The reactor was then purged with He for another 1 h. For the TPD experiment, He was passed through the reactor and ammonia TPD was performed by ramping the temperature at 10°C/min to 600°C. For the TPSR experiments, subsequent to the ammonia adsorption step, the He flow was switched to different flows of 1000 ppm NO/He, 2% O_2/He, 1000 ppm NO + 2% O_2/He, or 1000 ppm NO_2/He. At the same time, the reactor was ramped at 10°C/min to 600°C. A magnetic deflection-type mass spectrometer (AERO VAC, Vacuum Technology Inc.) was used to monitor continuously the effluent from the reactor, which contained NH_3 (mass 17 minus the contribution of H_2O), H_2O (mass 18), N_2 (mass 28), NO_x (mass 30), O_2 (mass 32), and N_2O (mass 44). It is noted that an NO_2 signal at mass 46 was not detected with our mass spectrometer. Even when 1000 ppm NO_2/He was used, the intensity of mass 46 was still too weak to be detected (but the mass 30 signal was strong). Therefore, we used mass 30 as the signals for NO_x ($NO + NO_2$) in this work.

For NO_x adsorption, the sample was first treated with He at 500°C for 1 h followed by exposure to 1000 ppm NO + 2% O_2/He for 1 min, and then cooled to room temperature in flowing NO + O_2 in 1 h. The subsequent procedure was the same as that used in the ammonia TPD and TPSR experiments described above, except that 1000 ppm NH_3/He was used in the TPSR experiment.

The TPSR experiments between adsorbed NO_x and NH_3 as well as the reactions of adsorbed $NO_x + NH_3$ with gaseous NO and NO_2 were also studied. In these cases, after the He-treated sample (at 500°C) was cooled to room temperature, it was exposed to 1000 ppm NO + 1000 ppm NH_3 + 2% O_2/He for 1.5 h. The reactor was then purged with He for another 1 h. Subsequently, the sample was heated linearly to 600°C in different flows of He, 1000 ppm NO/He or 1000 ppm NO_2/He. The effluent gases were analyzed continuously with the mass spectrometer.

The gases were obtained by blending different premixed gases, using He as the diluent gas. The gas concentration was calibrated by standard gas with the mass spectrometer. The total gas flow rate was 500 ml/min (ambient conditions). The premixed gases (1.01% NO/He, 0.98% NO_2/He, and 1.00% NH_3/He) and He (99.995%) were supplied by Matheson without additional purification. The mass spectrum showed that about 0.05% H_2O vapor was present in the 1.00% NH_3/He cylinder.

RESULTS

TPD of Ammonia

The TPD profiles of ammonia on H–ZSM-5, Fe(95)–ZSM-5, and Fe(300)–ZSM-5 are shown in Fig. 1. Ammonia desorption was observed over a wide temperature range for these samples. Two main peaks (both broad) were found at 160 and 390°C. Our previous FTIR spectra (25) showed that, after Fe–ZSM-5 was treated in flowing 1000 ppm NH_3/He, physisorbed NH_3 (at 2600 and 2900 cm^{-1}), coordinated NH_3 (minority, at 1587 and 1276 cm^{-1}), and NH_4^+ ions (majority, at 3353, 3290, 3050, 2795, 1705, and 1473 cm^{-1}) were generated. With increasing temperatures, the IR bands due to physisorbed and coordinated NH_3 disappeared below 300°C, whereas those due to NH_4^+ ions with three hydrogen atoms bonded to three oxygen ions of AlO_4 tetrahedra (3H structure) (at 3353, 3290, and 1473 cm^{-1}) were still detected at 400°C in He (25). This suggests that the NH_4^+ ions with 3H structure were more stable at high temperatures than the other ammonia adsorbed species. Therefore, it is reasonable to assign the ammonia species desorbed at 160°C to physically adsorbed NH_3 and coordinated NH_3 and that desorbed at 390°C to the NH_4^+ ions with 3H structure. Further evidence for the assignments was obtained by a separate TPD experiment on NH_4–ZSM-5. In this experiment, no NH_3 desorption peak near 160°C was seen, but a peak at 390°C was observed. With increasing Fe content, the NH_3 desorption peak at 390°C decreased significantly, which was due to the fact that the Brønsted acid protons of ZSM-5 were substituted by Fe^{2+} or Fe^{3+}. During the ammonia TPD experiments, no oxidation products (such as N_2, N_2O, or NO_x) were detected.

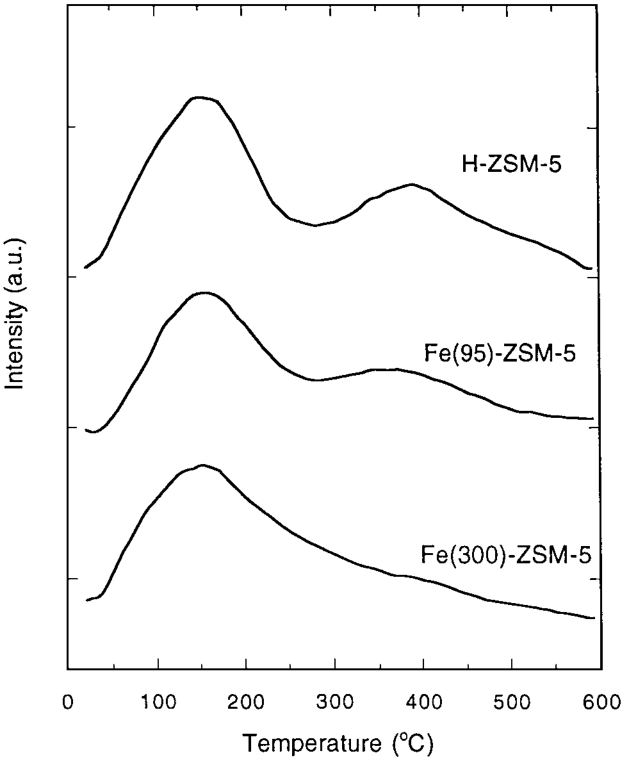

FIG. 1. TPD profile of NH_3 from H–ZSM-5 and Fe–ZSM-5 catalysts (number in parentheses indicates Fe-exchange level). The samples were first treated with NH_3/He at 25°C (see details in text).

TPD of NO_x

NO_x TPD experiments were also conducted on H–ZSM-5, Fe(95)–ZSM-5, and Fe(300)–ZSM-5. The results are shown in Fig. 2. Only one peak at 75°C was observed on H–ZSM-5, which probably came from physisorbed NO_x. It was reported that NO could be oxidized to NO_2 by O_2 and then stored on H–ZSM-5 (10, 18). As shown in Fig. 2, two desorption peaks at 75 and 310°C were detected on the Fe–ZSM-5 catalysts, which can be attributed to NO_x adsorbed at two different types of sites. Since the peak at 310°C was not observed on the H–ZSM-5, one can conclude that the NO_x was bonded to iron sites. The intensity of the peak at 310°C increased with iron content. Our previous FTIR spectra showed that N_2O_3 (1682 cm^{-1}), NO_2 (1614 cm^{-1}), and nitrate species (1575 cm^{-1}) were formed on the Fe–ZSM-5 that was treated with NO + O_2. N_2O_3 was not stable and decomposed below 100°C, while NO_2 was the dominant species at high temperatures (25). Hence, the peak at 75°C on Fe–ZSM-5 probably came from desorption of N_2O_3 and physisorbed NO_x, while the peak at 310°C was

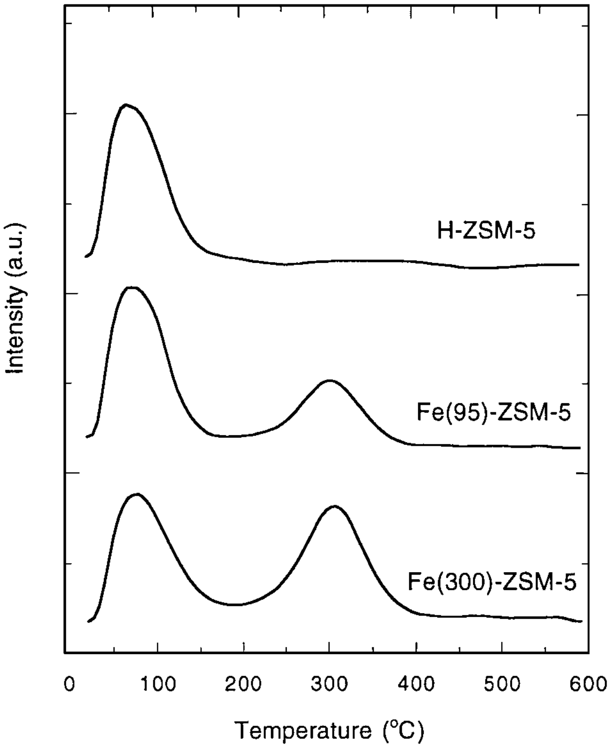

FIG. 2. TPD profile of NO_x from H–ZSM-5 and Fe–ZSM-5 catalysts (number in parentheses indicates Fe-exchange level). The samples were first treated with NO + O_2/He at 500°C (see details in text).

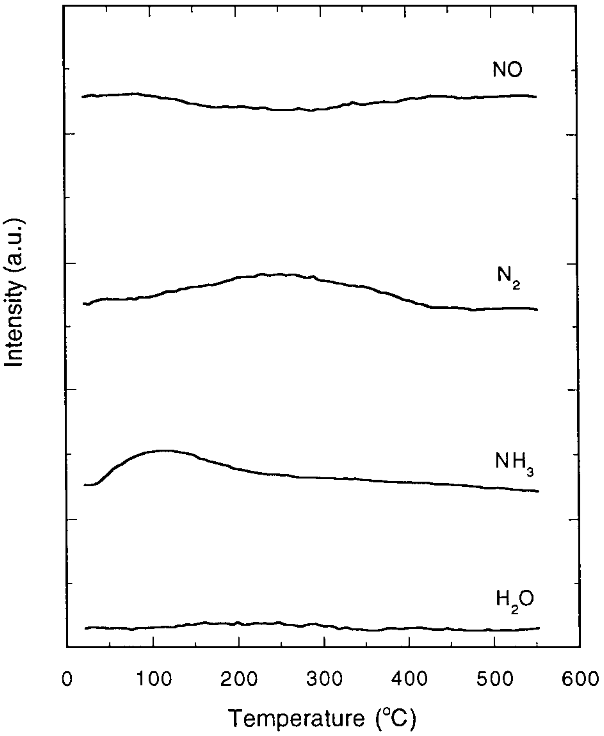

FIG. 3. TPSR profile in 1000 ppm NO/He following exposure of Fe(95)–ZSM-5 to 1000 ppm NH_3/He at room temperature for 1.5 h.

due to desorption of NO_2 species (majority) and decomposition of nitrate (minority). During the desorption of NO_x, a weak O_2 desorption peak was also detected at 310°C on the Fe–ZSM-5 catalysts, but other N-containing products such as N_2 and N_2O were not observed, indicating that NO decomposition did not occur.

TPSR of Ammonia Adsorbed Species

TPSR experiments were obtained by first saturating Fe(95)–ZSM-5 with ammonia, followed by heating in different flows. Figure 3 shows the results of TPSR between ammonia adsorbed species and gaseous NO/He. NH_3 desorption was significant at low temperatures (i.e., below 100°C). At higher temperatures, the reaction between NO and NH_3 adsorbed species occurred, producing N_2 and H_2O. The maximum NO consumption and N_2 production occurred at about 260°C. O_2 or N_2O was not detected in this experiment.

The TPSR results between ammonia adsorbed species and gaseous O_2 are shown in Fig. 4. Similar to the reaction between NO and ammonia adsorbed species, NH_3 desorption was dominating at low temperatures. Above 250°C, O_2 oxidized ammonia adsorbed species to nitrogen and water. No N_2O or NO_x was observed in the entire process.

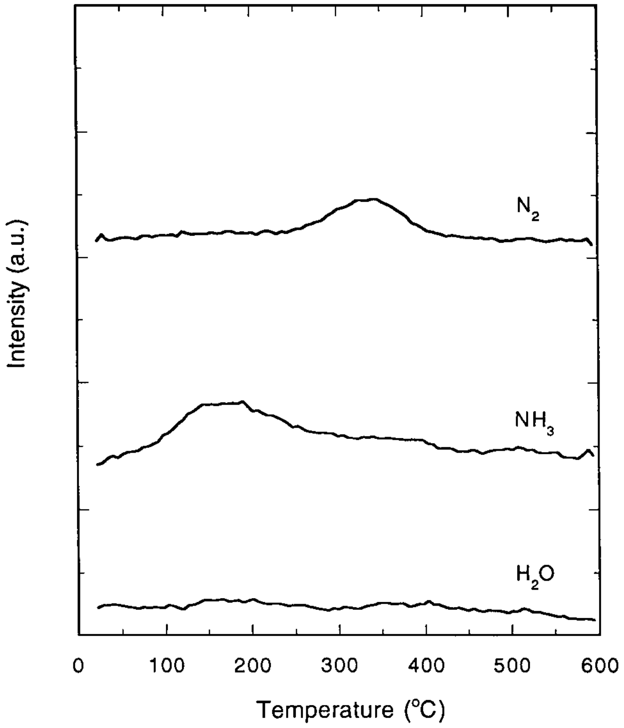

FIG. 4. TPSR profile in 2% O_2/He following exposure of Fe(95)–ZSM-5 to 1000 ppm NH_3/He at room temperature for 1.5 h.

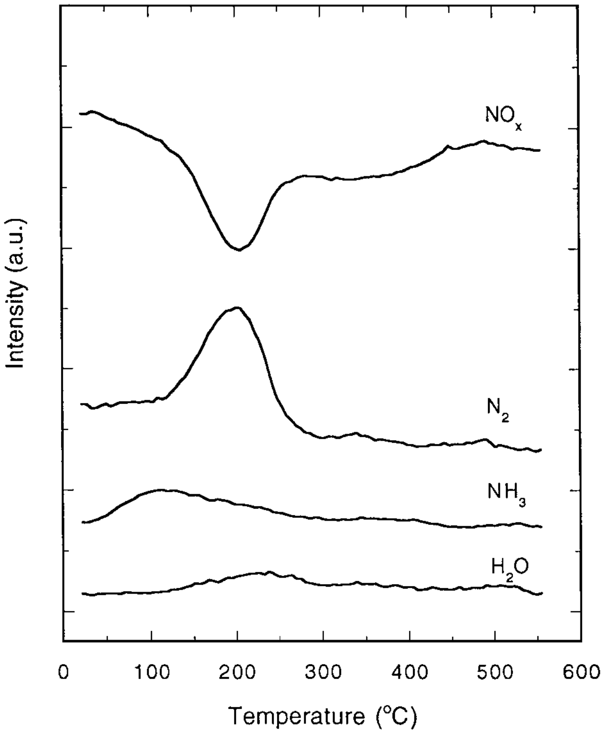

FIG. 5. TPSR profile in 1000 ppm NO + 2% O_2/He following exposure of Fe(95)–ZSM-5 to 1000 ppm NH_3/He at room temperature for 1.5 h.

The TPSR results between 1000 ppm NO + 2% O_2/He mixture and presorbed NH_3 on Fe–ZSM-5 are shown in Fig. 5. In contrast to that with NO only (Fig. 3), NO was consumed significantly at 200°C. Meanwhile, large amounts of N_2 and H_2O were produced (Fig. 5). The reaction temperature was lower than that with either NO or O_2 alone. Again, N_2O was not observed. Since H_2O is more difficult to desorb from ZSM-5 than N_2, the apparent formation temperature for water was slightly higher than that for N_2. As compared with Fig. 3, more N_2 and H_2O were produced and also less ammonia was desorbed at low temperatures. It is clear that oxygen promoted the reaction between NO and ammonia adsorbed species. In this experiment, it was difficult to detect oxygen consumption due to the high oxygen concentration used.

The reaction between NO_2 and ammonia adsorbed species is shown in Fig. 6. After 1000 ppm NO_2/He was introduced into the reactor, the intensity of NO_x decreased immediately and sharply while much N_2 was generated with increasing temperature. This indicates that NO_2 reacted with ammonia adsorbed species and/or adsorbed on the catalyst at low temperatures. Maximum NO_2 consumption occurred at 65 and 200°C. Correspondingly, much N_2 was formed. In addition, N_2O formation was also observed at 200°C. Ammonia desorption was not detected in the entire temperature range, suggesting that the rate of reaction between NO_2 and the NH_3 adsorbed species was faster than the rate of ammonia desorption. At 200°C, the amount of N_2 formation was close to that of N_2O formation. When the temperature was increased to above 250°C, decomposition of NO_2 to NO became significant, as indicated by O_2 formation.

TPSR of NO_x Adsorbed Species with Ammonia

Since the foregoing NO_x TPD profile showed that NO_x could adsorb on Fe(95)–ZSM-5, the TPSR experiment between NO_x adsorbed species and ammonia was investigated. In this experiment, Fe–ZSM-5 was first treated with NO + O_2/He, as indicated in the above TPD experiment. Subsequently, 1000 ppm NH_3/He was passed over the NO_x adsorbed sample and the temperature was increased. As shown in Fig. 7, the intensity of NH_3 decreased sharply at low temperatures, while only a trace amount of N_2 was produced. Ammonia adsorption dominated under this condition. Also, a small amount of NO_x desorbed at low temperatures, possibly being displaced by ammonia. With increasing temperature, the reaction between NH_3 and NO_x adsorbed species occurred, forming N_2 and H_2O. The rate of N_2 formation reached a maximum at 230°C. Only a trace amount of N_2O was detected at 230°C.

TPSR of NO_x Adsorbed Species with Ammonia Adsorbed Species

Since both NO_x and NH_3 could adsorb on Fe–ZSM-5, the TPSR experiments of adsorbed NO_x and adsorbed NH_3

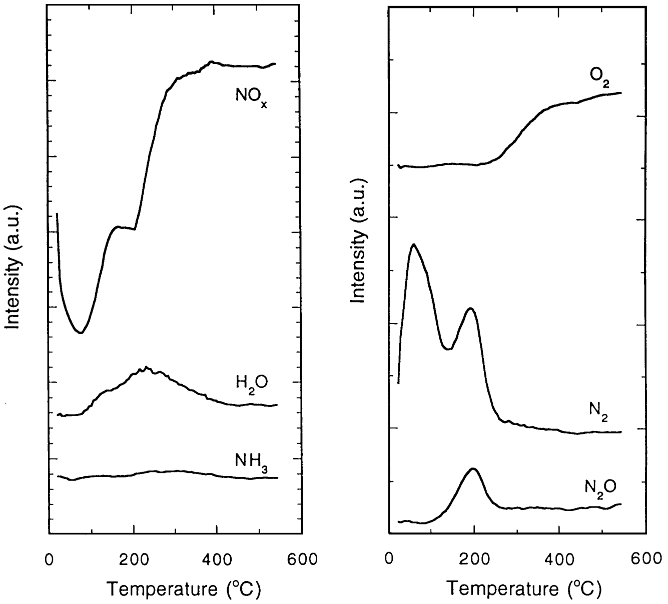

FIG. 6. TPSR profile in 1000 ppm NO_2/He following exposure of Fe(95)–ZSM-5 to 1000 ppm NH_3/He at room temperature for 1.5 h.

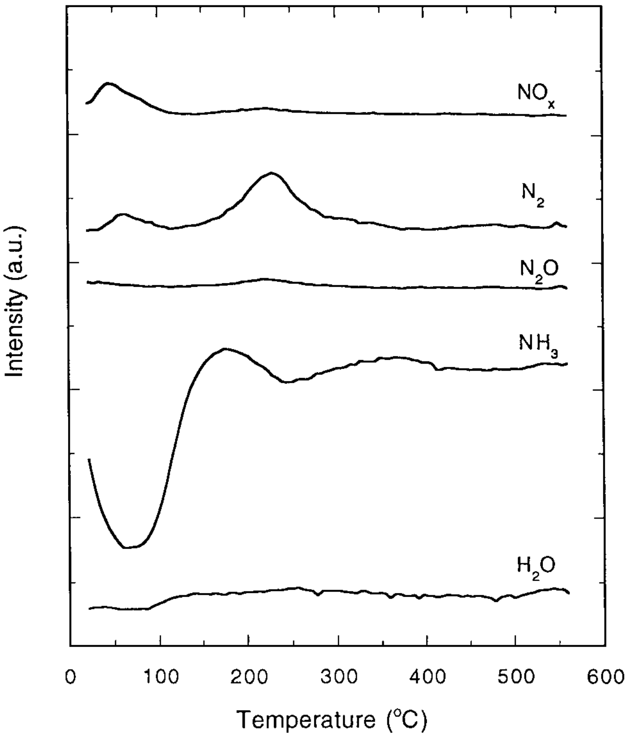

FIG. 7. TPSR profile in 1000 ppm NH_3/He following exposure of Fe(95)–ZSM-5 to 1000 ppm NO + 2% O_2/He at 500°C.

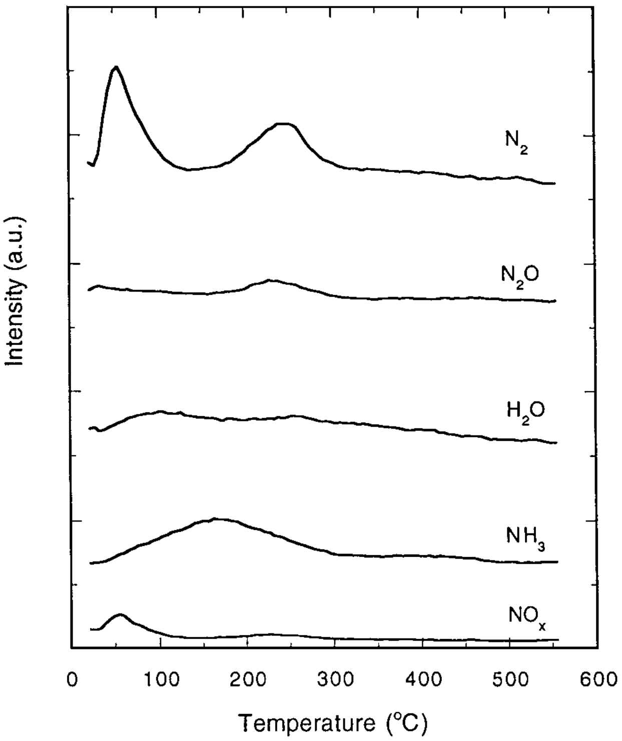

FIG. 8. TPSR profile in He following exposure of Fe(95)–ZSM-5 to 1000 ppm NO + 1000 ppm NH_3 + 2% O_2/He at room temperature for 1.5 h.

were also studied. In this case, the mixture gas containing 1000 ppm NO + 1000 ppm NH_3 + 2% O_2/He was passed through Fe(95)–ZSM-5 at room temperature for 1.5 h. As indicated above, both NO_x and NH_3 adsorbed species were present on the catalyst. The sample obtained was purged with He for 1 h and then ramped to 600°C. The peaks for N_2 formation were observed at 55 and 245°C (Fig. 8), indicating that two different reactions between NO_x and NH_3 adsorbed species had taken place. A small amount of N_2O was observed at 245°C. The desorption of NO_x and NH_3 was detected at low temperatures.

After Fe–ZSM-5 was treated with NO + NH_3 + O_2/He and then purged with He, the sample was heated in flowing 1000 ppm NO/He. As shown in Fig. 9, nitrogen formation occurred at 50 and 170°C when NO was consumed at 170°C. N_2O formation was not observed. A small amount of NH_3 was desorbed at low temperatures.

Figure 10 shows the TPSR experiment of NO_2 with adsorbed NO_x + ammonia. After 1000 ppm NO_2/He was passed through the catalyst that was preadsorbed with NO_x and ammonia and the temperature was increased, NO_2 adsorption and/or the reaction between NO_2 and adsorbed NO_x + NH_3 were observed. Similar to the TPSR experiment of NO_2 with NH_3 adsorbed species (Fig. 6), N_2 formation occurred at 50 and 200°C by consuming NO_2. Also, N_2O formation was observed at 200°C and NO_2 decomposition occurred at high temperatures.

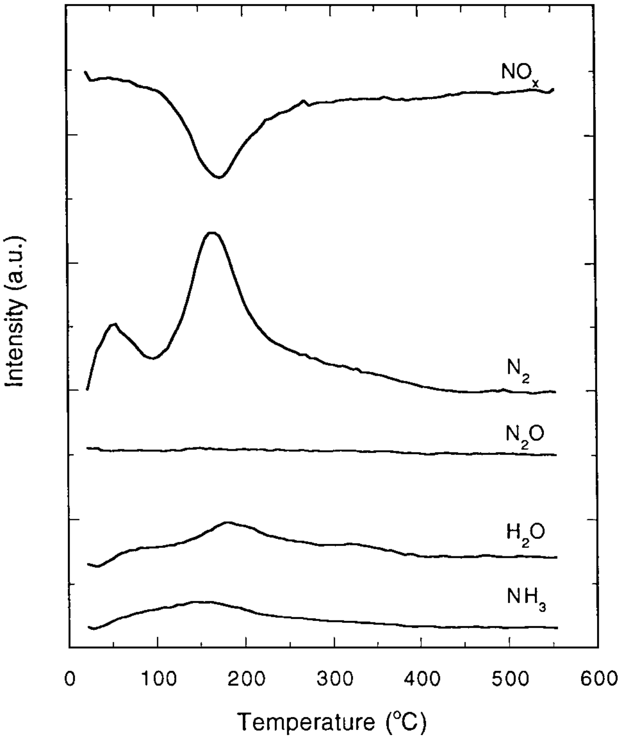

FIG. 9. TPSR profile in 1000 ppm NO/He following exposure of Fe(95)–ZSM-5 to 1000 ppm NO + 1000 ppm NH_3 + 2% O_2/He at room temperature for 1.5 h.

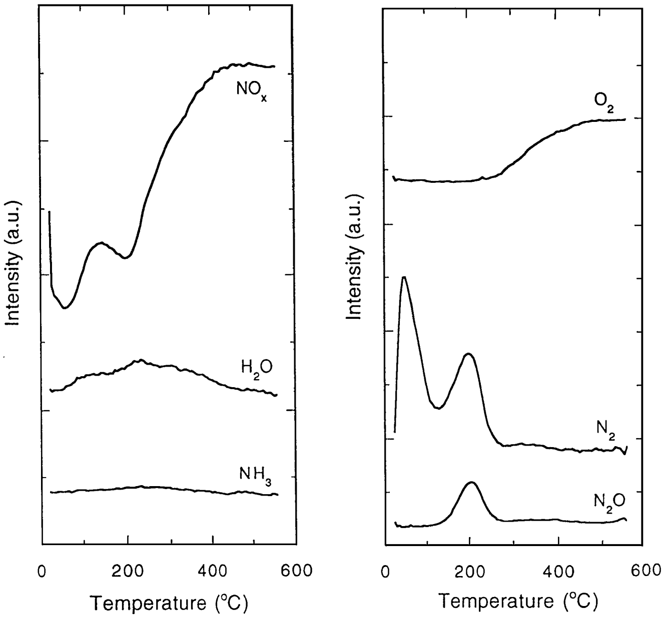

FIG. 10. TPSR profile in 1000 ppm NO_2/He following exposure of Fe(95)–ZSM-5 to 1000 ppm NO + 1000 ppm NH_3 + 2% O_2/He at room temperature for 1.5 h.

DISCUSSION

The above TPD experiments indicated that both NO_x and NH_3 adsorbed on the Fe–ZSM-5 catalysts, which was in agreement with our previous FTIR results (14, 25). Physisorbed and chemisorbed NO_x and NH_3 species were formed (Figs. 1 and 2). The addition of iron to ZSM-5 did not influence significantly physisorbed NO_x and NH_3 species. They were related to the structure of ZSM-5 and were not stable at high temperatures. In contrast, chemisorbed NH_3 (mainly NH_4^+) and NO_x (mainly NO_2) were strongly affected by Fe. As expected, the replacement of H^+ by Fe^{2+} or Fe^{3+} resulted in a decrease in the number of Brønsted acid sites and thus decreased the formation of NH_4^+ ions. Lobree *et al.* (21) also reported a decrease in Brønsted acidity when increasing Fe content in Fe–ZSM-5. However, even when the protons in ZSM-5 were completely substituted by $FeCl_3$, quite an amount of Brønsted acid sites remained on Fe(300)–ZSM-5 after hydrolysis (27). This catalyst is still very active for the SCR reaction (15). A careful analysis using 1.00% NH_3/He as standard gas indicated that the amount of NH_4^+ ions was approximately 50 μmol on Fe(95)–ZSM-5. By comparison, the chemisorbed NO_x were bonded directly to iron sites and increased with Fe content. The amount of chemisorbed NO_x species (mainly NO_2) was approximately 20 μmol on Fe(95)–ZSM-5.

The TPSR results indicated that NH_3 adsorbed species was reactive with NO, O_2, NO + O_2, and NO_2, producing H_2O, N_2, and/or N_2O. Among them, O_2 and NO were less reactive with NH_3 adsorbed species. The temperatures for maximum N_2 formation were 330 and 260°C, respectively (Figs. 3 and 4). Also, with O_2 or NO, more NH_3 desorbed at low temperatures and less N_2 formation was observed. By comparison, NO + O_2 and NO_2 were more active in reacting with NH_3 adsorbed species, as indicated by the results that the reactions occurred at lower temperatures ($\leq$200°C) and less NH_3 desorption was detected (Figs. 5 and 6). With different gases, the amount of N_2 product increased in the order O_2 ($\approx$28 μmol) < NO ($\approx$66 μmol) < NO + O_2 ($\approx$150 μmol) < NO_2 ($\approx$170 μmol + 53 μmol N_2O). In contrast, the amount of desorbed NH_3 decreased in the sequence O_2 ($\approx$120 μmol) > NO ($\approx$100 μmol) > NO + O_2 ($\approx$30 μmol) > NO_2 ($\approx$0 μmol). NO consumption and N_2 formation increased significantly in the presence of O_2. Because O_2 could oxidize NO to NO_2 and the reactivity of NH_3 adsorbed species with NO_2 was much higher than that with NO, NO_2 was probably an intermediate for the SCR reaction. As shown in Fig. 7, NO_x adsorbed species was also reactive to NH_3. Since NH_3 was strongly and abundantly adsorbed on Fe–ZSM-5, it was possible that the reaction occurred between adsorbed NH_3 (rather than gaseous NH_3) and NO_x adsorbed species.

When NH_3 and NO_x were coadsorbed on Fe–ZSM-5 at room temperature, TPSR of the coadsorbed species with He, NO/He, and NO_2/He showed N_2 formation near 55 and 170–245°C (Figs. 8–10). The N_2 formation at two peaks suggests two types of reaction occurred. To study the reactions, two separate experiments were performed. One was the TPSR between NO_x adsorbed species and NH_4^+ ions. After saturation with NH_3 at room temperature, Fe(95)–ZSM-5 was heated at 150°C in He for 30 min. NH_3 TPD profile showed only one broad peak at 390°C, indicating no physisorbed or coordinated NH_3 on the sample. Fe–ZSM-5 was then exposed to 1000 ppm NO + 2% O_2/He at room temperature for 1.5 h followed by purging with He for another 1 h. Subsequently, the temperature was increased linearly. As shown in Fig. 11, only one peak for N_2 and N_2O formation was observed at 280°C. The other experiment was the TPSR between ammonia adsorbed species and chemisorbed NO_x species (mainly NO_2). In this case, the NO_x adsorbed Fe–ZSM-5 was treated at 70°C for 30 min and then cooled to room temperature in He. The NO_x TPD experiment showed that only one desorption peak appeared at 310°C, indicating that N_2O_3 or physisorbed NO_x was not present. Fe–ZSM-5 was then exposed to 1000 ppm NH_3/He at room temperature for 1.5 h. TPSR in He showed that the reaction between NH_3 adsorbed species and chemisorbed NO_2 took place at 245°C, forming N_2 and H_2O (Fig. 12). The above two experiments suggest that N_2 formation near 55°C resulted from the reactions of physisorbed NH_3 with N_2O_3 and/or physisorbed NO_x. It might not be related to the iron ions of Fe–ZSM-5. This conclusion was further supported by the TPSR result that the N_2 formation near 55°C was also observed on H–ZSM-5 that was treated with NH_3 + NO + O_2 at room

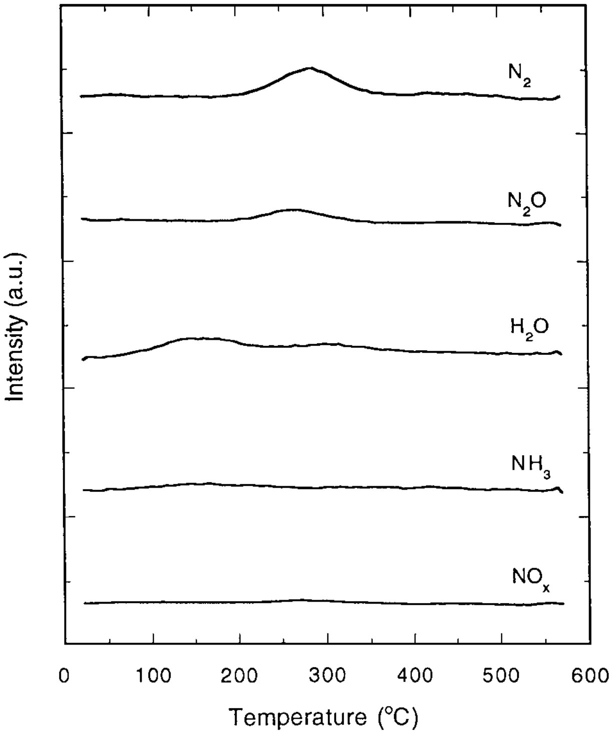

FIG. 11. TPSR profile in He of Fe(95)–ZSM-5 that was treated with 1000 ppm NH_3/He at room temperature for 1.5 h, heated in He at 150°C for 0.5 h, and then exposed to 1000 ppm NO + 2% O_2/He at room temperature for 1.5 h.

temperature. On the Fe–ZSM-5 surface, N_2O_3 and physisorbed NO_x ($NO + NO_2$) could react with physisorbed NH_3 to form ammonium nitrite in the presence of trace H_2O impurity (which was present in our experiments and probably in all experiments by others as well) according to the following reactions:

$$N_2O_3 + 2NH_3 + H_2O \rightarrow 2NH_4NO_2, \qquad [1]$$

$$NO_2 + NO + 2NH_3 + H_2O \rightarrow 2NH_4NO_2, \qquad [2]$$

$$2NO_2 + 2NH_3 + H_2O \rightarrow NH_4NO_3 + NH_4NO_2. \qquad [3]$$

It is known that ammonium nitrite is not stable and decomposes at 60–70°C (28). Hence N_2 formation near 55°C may be due to decomposition of ammonium nitrite:

$$NH_4NO_2 \rightarrow N_2 + 2H_2O. \qquad [4]$$

During the TPSR experiment between $NO + O_2$ and NH_3 adsorbed species, ammonium nitrite formation was rather slow at low temperatures due to slow NO_x formation. Hence, the reaction near 55°C was not observed (Fig. 5).

The reactions at 170–245°C are more important for the SCR mechanism because high SCR activity was usually obtained at high temperatures for Fe–ZSM-5 (14, 15). At high temperatures, the catalyst surface was dominated by NO_2 and NH_4^+ ions (25). TPD experiments showed that NO_2 desorbed at a lower temperature than NH_4^+ ions (310°C vs 390°C, Figs. 1 and 2), hence it was more mobile at high temperatures. On Fe–ZSM-5 coadsorbed with NO_2 and NH_4^+, some $[NH_4^+]_x[NO_2]_y$-type species could form, e.g., $[NH_4^+]_2[NO_2]$, as suggested by Eng and Bartholomew on H–ZSM-5 (10). The foregoing TPD results also indicated that the ratio of NH_4^+/NO_2 was approximately 2.5 for Fe(95)–ZSM-5. $[NH_4^+]_2[NO_2]$ could be formed from the diffusion of one molecular NO_2 to two neighboring NH_4^+ ions. Alternatively, the small pore sizes in ZSM-5 facilitated the formation of this complex without the need for surface mobility. In the presence of NO and NO_2, $[NH_4^+]_2[NO_2]$ reacted with them to produce N_2 and/or N_2O at high temperatures according to two reactions:

$$[NH_4^+]_2NO_2\,(s) + NO(g) \rightarrow 2N_2 + 3H_2O + 2H^+, \qquad [5]$$

$$[NH_4^+]_2NO_2\,(s) + NO_2(g) \rightarrow N_2 + N_2O + 3H_2O + 2H^+. \qquad [6]$$

This was identified by the above TPSR experiments. TPSR between NO and $NO_x + NH_3$ adsorbed species showed that a large amount of N_2 (≈145 μmol) formed at 170°C and no N_2O formation was observed (Fig. 9). By comparison,

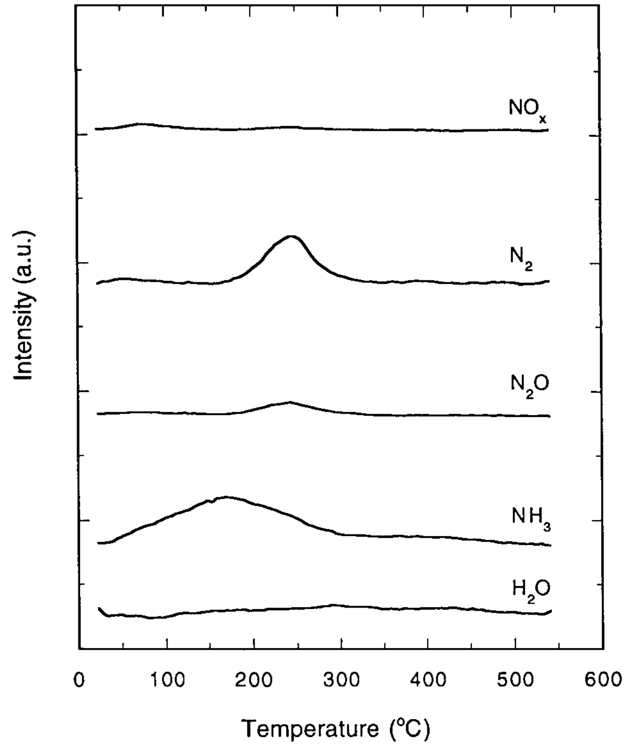

FIG. 12. TPSR profile in He of Fe(95)–ZSM-5 that was treated with 1000 ppm NO + 2% O_2/He for 1 h, heated in He at 70°C for 0.5 h, and then exposed to 1000 ppm NH_3/He at room temperature for 1.5 h.

almost the same amounts of N_2 ($\approx$71 μmol) and N_2O ($\approx$63 μmol) were obtained at 200°C during TPSR of NO_2 with adsorbed $NO_x + NH_3$ (Fig. 10). It is noted that reaction [6] ocurred between equimolar NO_2 and NH_4^+. When the amount of NO_2 was less than that of NH_4^+, as in the case of TPSR of adsorbed $NO_x + NH_3$ in He (Fig. 8), the N_2O formed might be further reduced by NH_4^+ according to the reaction

$$3N_2O + 2NH_4^+ \rightarrow 4N_2 + 3H_2O + 2H^+. \qquad [7]$$

It was reported that Fe–ZSM-5 was a good catalyst for N_2O reduction by ammonia (29). This would result in more N_2 but less N_2O formation (Fig. 8). In addition, it is interesting to note that the reaction between $NO_x + NH_3$ adsorbed species with NO occurred at a lower temperature than that with NO_2 (170°C vs 200°C, as shown in Figs. 9 and 10). This means that $[NH_4^+]_2NO_2$ would prefer to react with NO, rather than NO_2, in the presence of NO and NO_2, which is the situation during the SCR reaction on Fe–ZSM-5. In the SCR reaction, some of the NO molecules are oxidized to NO_2 species by O_2 on Fe^{3+} sites (22, 25). Near-equilibrium between NO and NO_2 could be established at high temperatures (25). NH_3 molecules are adsorbed on the Brønsted acid sites to form NH_4^+ ions. NO_2 first reacts with a pair of NH_4^+ ions to form a complex, $[NH_4^+]_2NO_2$. Subsequently, the active complex reacts with another NO to produce N_2 and H_2O and thus completes the catalytic cycle. This is a somewhat simplified reaction scheme which is similar to that on Fe–TiO_2–PILC (20) and H–ZSM-5 (10). Because the reactivity of $[NH_4^+]_2NO_2$ to NO (producing N_2) was higher than that to NO_2 (producing N_2 and N_2O), N_2O formation could not be observed during the SCR reaction. In addition, N_2O formation was also not observed during the TPSR experiment between O_2 and ammonia adsorbed species (Fig. 4). Another possible path for N_2O formation due to ammonia oxidation by oxygen (1, 2) was eliminated. Therefore, N_2 would be the only N-containing product during the SCR reaction on Fe–ZSM-5, as indicated by our previous studies on SCR performance at 250–600°C (14–16).

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