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FTIR and Kinetic Studies of the Mechanism of Fe^{3+}-Exchanged TiO_2-Pillared Clay Catalyst for Selective Catalytic Reduction of NO with Ammonia

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A series of FTIR spectroscopic and kinetic studies of the selective catalytic reduction (SCR) of nitric oxide by ammonia were conducted on Fe^{3+}-exchanged TiO_2-pillared clay (Fe-TiO_2-PILC) catalyst. It was found that NO molecules were adsorbed on the fresh Fe-TiO_2-PILC catalyst and then oxidized by O_2 to adsorbed NO_2 and nitrate species. These NO_x adspecies could be reduced by NH_3 at high temperatures. NH_3 molecules could also be adsorbed on the Brønsted acid and Lewis acid sites on the Fe-TiO_2-PILC catalyst to generate, respectively, NH_4^+ ions and coordinated NH_3 species. These NH_3 adspecies were active in reacting with NO, NO + O_2 and NO_2, but the reaction rates of NH_3 + NO + O_2 and NH_3 + NO_2 were much higher than that of NO + NH_3. However, under reaction conditions, the surface of Fe-TiO_2-PILC was mainly covered by NH_4^+ ions and coordinated NH_3, and no NO_x adspecies were detected. This is in agreement with the zero-order for the SCR reaction with respect to NH_3. A possible reaction scheme for the SCR reaction on Fe-TiO_2-PILC was proposed. NO reduction initially involved the reaction between NO_2 and pairs of NH_3 adspecies to form an active intermediate, which finally reacted with gaseous or weakly adsorbed NO to produce N_2 and H_2O. © 2000 Academic Press

Key Words: **selective catalytic reduction; selective catalytic reduction of NO with NH_3; Fe-TiO_2-PILC catalyst;** *in situ* **FTIR; kinetics of NO reduction.**

INTRODUCTION

Selective catalytic reduction (SCR) of NO_x ($x = 1$ or 2) with ammonia is the most efficient technology for its abatement from power plant exhaust gases. SCR has been extensively studied in recent years because of its environmental importance. Great efforts have been focused on searching for good catalysts and understanding the kinetics and mechanism of the SCR reaction. Many catalysts have been reported in the literature to be active, such as vanadia and other transition metal oxides (i.e., Fe, Cr, Mn, Cu), as supported catalysts, pillared clay catalysts, H- and ion-exchanged zeolite catalysts, etc. (1–5).

The commercial catalysts that are used today are V_2O_5 mixed with WO_3 and/or MoO_3 supported on TiO_2 (1, 2). The mechanism of the reaction on vanadia catalysts has been extensively studied and several different mechanisms have been proposed (1, 2, 6–15). Almost all researchers agree that the SCR reaction on vanadia catalysts follows an Eley–Rideal-type mechanism; i.e., a strongly adsorbed ammonia species reacts with a gaseous or weakly adsorbed NO molecule to form molecular N_2. But which ammonia adspecies (Brønsted or Lewis) is involved in the reaction is still under debate (1, 2). However, it was reported that, on zeolite-typed and Fe_2O_3- or CuO-doped catalysts, NO molecules were also adsorbed on the catalysts and then oxidized to NO_2, nitrite, and nitrate species (3, 5, 16–21). Thus, the SCR reaction may also proceed via a Langmuir–Hinshelwood-type mechanism. For instance, Kiovsky *et al.* (3) suggested that NO_2 was the active intermediate in NO reduction by ammonia over H–mordenite. Recently, Komatsu *et al.* (19) and Eng and Bartholomew (20) also studied the SCR reaction mechanism of NO over Cu–ZSM-5 and H–ZSM-5 catalysts, respectively. They suggested that an NO_2-type species reacts with pairs of NH_4^+ ions adsorbed on neighboring acid sites to generate an active intermediate, and then the active intermediate reacts with another NO molecule to generate N_2 and H_2O. In addition, by using IR spectroscopy, Ito *et al.* (21) found that both nitrosonium ion (NO^+) and nitrito ion (NO_2^-) were formed on Ce-exchanged mordenite catalyst. They proposed another NO reduction scheme, in which NO^+ reacts with coordinated NH_3 at low temperatures and NO_2^- reacts with NH_4^+ ions at higher temperatures, producing N_2 and H_2O. Therefore, it seems that the reaction pathways for the SCR reaction of NO by ammonia are different on different catalysts.

In our previous studies, pillared clays (PILCs), metal oxide-doped PILCs, and Fe^{3+}-exchanged PILCs were investigated as catalysts in the SCR reaction (4, 22–25). PILCs are two-dimensional layer materials prepared by exchanging the charge-compensating cations between the clay layers with larger inorganic hydroxyl metal cations and

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then performing dehydration and dehydroxylation at high temperatures. They had strong acidity and good activity in reducing NO to N_2 by NH_3 in the presence of excess oxygen (4). More recently, we have found that Fe^{3+}-exchanged TiO_2-PILCs showed the highest NO conversion in the SCR reaction among the PILC catalysts. Moreover, the catalytic activities were increased by the presence of H_2O and SO_2 at high temperatures, which was attributed to the increase in surface acidity due to sulfation of the catalysts (25). The Fe^{3+}-exchanged TiO_2-pillared clay catalyst was twice as active as the commercial vanadia catalyst, and its Ce-promoted form was more than 3 times more active than the commercial catalyst in the presence of H_2O and SO_2 (25). Also, the Fe-TiO_2-PILC catalysts had higher N_2/N_2O product selectivities and substantially lower activities for SO_2 oxidation to SO_3 under reaction conditions compared to the commercial catalyst (25). It was evident that both Fe^{3+} ions and acidity were important for the SCR reaction on Fe-TiO_2-PILC catalysts. Although much has been investigated on the catalytic performance of the PILC catalysts, little fundamental work has been performed to elucidate the kinetics and mechanism of NO reduction by NH_3 over these catalysts. Therefore, in this paper, we report the results of FTIR and kinetic studies of the SCR reaction over Fe-TiO_2-PILC catalyst. The mechanism of NO reduction was studied by focusing on the surface adspecies and their reaction activity on the catalyst by *in situ* FTIR spectroscopy. The results indicated that NO reduction involved an NO_2 intermediate mechanism on the Fe-TiO_2-PILC catalyst.

EXPERIMENTAL

FTIR study. The preparation of TiO_2-PILC and Fe^{3+}-exchanged TiO_2-PILC has been described elsewhere (25). The iron contents obtained by neutron activation analysis in the TiO_2-PILC and Fe-TiO_2-PILC were 1.53 wt% and 5.93 wt%, respectively. 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 could be pretreated *in situ* in the IR cell. The wafers were first treated at 450°C in a flow of He (99.9998%) for 30 min, and then cooled to desired temperatures, i.e., 350, 300, 250, 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. Thus, the IR absorption features that originated from the structural vibrations of the catalyst were eliminated from the sample spectra. In the experiment, the IR spectra were recorded by accumulating 100 scans at a spectral resolution of 4 cm^{-1}. The gas mixtures (i.e., NO/He, $NO + O_2$/He, NO_2/He, NH_3/He, and $NO + NH_3 + O_2$/He) had the same concentrations as those used in the activity measurements (25), i.e., 1000 ppm NO (when used), 1000 ppm NO_2 (when used), 1000 ppm NH_3 (when used), 2% O_2 (when used), and balance of He. The total gas flow rate was 500 ml/min (ambient conditions). The premixed gases (1.01% NO in He, 0.98% NO_2/He, and 1.00% NH_3 in He) were supplied by Matheson.

Steady-state kinetic measurement. Steady-state kinetics studies were carried out in a fixed-bed, quartz flow reactor. The reaction temperature was controlled by an Omega (CN-2010) programmable temperature controller. Twenty-five milligrams of catalyst was used in this work. The flue gas was simulated by blending different gaseous reactants. The typical reactant gas composition was as follows: 400–2000 ppm NO, 400–2000 ppm NH_3, 2% O_2, and balance He. The total flow rate was 500 ml/min (ambient conditions). The tubings of the reactor system were wrapped with heating tapes to prevent formation and deposition of ammonium nitrate. The NO and NO_2 concentrations were continually monitored by a chemiluminescent NO/NO_x analyzer (Thermo Electro Corp., Model 10). To avoid errors caused by the oxidation of ammonia in the converter of the NO/NO_x analyzer, an ammonia trap containing phosphoric acid solution was installed before the sample inlet to the chemiluminescent analyzer. The products were also analyzed by a gas chromatograph (Shimadzu, 14A) at 50°C with a 5A molecular sieve column for N_2 and a Porapak Q column for N_2O.

Catalytic activity measurement. The experiments for NO oxidation to NO_2 by O_2 and the reactions of $NO + NH_3$, $NO + NH_3 + O_2$, and $NO_2 + NH_3$ were also performed in the above reaction system. In each experiment, 0.2 g of sample was used. For the NO oxidation experiment, 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 the chemiluminescent NO/NO_x analyzer. The experiments for reactions between NH_3 and NO_x were carried out under stoichiometric ratios of NO_x/NH_3 according to the following reactions:

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \qquad [1]$$

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad [2]$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \qquad [3]$$

i.e., 1500 ppm NO and 1000 ppm NH_3 for reaction [1], 1000 ppm NO, 1000 ppm NH_3, and 2% O_2 for reaction [2], and 750 ppm NO_2 and 1000 ppm NH_3 for reaction [3]. The total flow rate was 500 ml/min (ambient conditions).

RESULTS

IR spectra of nitrogen oxides adsorption on Fe-TiO_2-PILC catalyst. Fe-TiO_2-PILC was first heated at 450°C for 30 min in a flow of He and then cooled to 30°C for

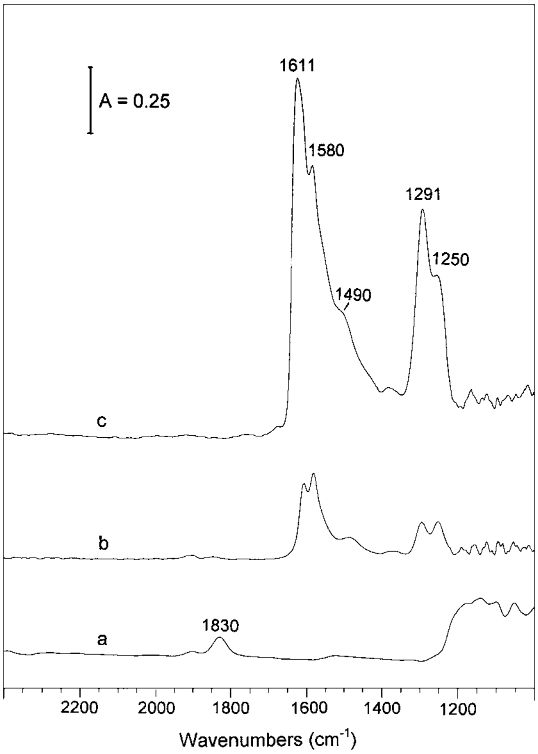

FIG. 1. IR spectra of Fe-TiO_2-PILC treated with (a) 1000 ppm NO, (b) 1000 ppm NO + 2% O_2, and (c) 1000 ppm NO_2 at 30°C for 15 min.

adsorption of NO/He, NO + O_2/He, and NO_2/He. Figure 1 shows the IR spectra after these gases were adsorbed for 15 min. In the spectrum of NO adsorbed on Fe-TiO_2-PILC, only a weak peak was observed at 1830 cm^{-1} (Fig. 1a), which can be assigned to weakly adsorbed NO molecules (26). The peak disappeared after the sample was purged by He for 15 min. After the catalyst was treated in flowing NO + O_2/He for 15 min, four intense bands at 1611, 1580, 1291, and 1250 cm^{-1} as well as a weak band at 1490 cm^{-1} were formed (Fig. 1b). The intensities of these bands increased with time in flowing NO + O_2/He. These IR bands were also observed in the spectrum of NO_2 adsorbed on Fe-TiO_2-PILC (Fig. 1c), but their intensities were much stronger than those of the NO + O_2/He treated sample. The similar IR bands were also detected in the spectrum of NO_2 adsorbed on TiO_2 by Ramis *et al.* (27).

Figure 2 shows a series of IR spectra of NO + O_2 adsorbed on Fe-TiO_2-PILC at different temperatures. After Fe-TiO_2-PILC was treated in flowing NO + O_2/He for 60 min at 30°C and then purged by He for 15 min, strong IR bands were observed at 1611, 1580, 1490, 1291, and 1250 cm^{-1}. With an increase in temperature to 250°C in a flow of He, the bands at 1580, 1490, 1291, and 1250 cm^{-1} decreased sharply, but the 1611 cm^{-1} band was almost unchanged (Figs. 2a–2d), suggesting that the species at 1611 cm^{-1} was more stable than the other species on Fe-TiO_2-PILC catalyst. At 300°C, the 1611 cm^{-1} band also decreased. All of the bands vanished at 350°C.

Several groups have studied NO_x adsorption on ion-exchanged zeolites and metal oxides, and some IR bands due to NO_2, nitro (–NO_2), and nitrate (NO_3^-) species were detected in the 1650–1200 cm^{-1} range (26–30). The bands at 1580, 1490, 1291 and 1250 cm^{-1} showed similar thermal stabilities on the Fe-TiO_2-PILC catalyst. They are most likely attributed to nitrate species (26–31). The band at 1611 cm^{-1} is not easy to assign. Different assignments for the band near 1620 cm^{-1} were present in the literature. Ramis *et al.* (27) assigned the bands at 1630 and 1608 cm^{-1} to nitrate species on NO_2-adsorbed TiO_2. Also, a band at 1633 cm^{-1} on Co–ZSM-5 was attributed to nitrito or nitrate species by Aylor *et al.* (28). However, Li and Armor (29) and Chen *et al.* (30) assigned the band near 1627 cm^{-1} to nitro species when they studied NO_x adsorption on Co–ferrierite and Fe–ZSM-5, respectively. The band near 1630 cm^{-1} was also assigned to NO_2-containing species or to NO_2 by other researchers (20, 31). In fact, the band at 1611 cm^{-1} on Fe-TiO_2-PILC is very close to the asymmetric stretching frequency of gaseous NO_2 molecules (1617 cm^{-1}) (26); we assign it to an NO_2 adspecies (nitro or adsorbed NO_2 molecule) on the catalyst because this species had a thermal stability different from those of other nitrate species (Fig. 2). The above results indicate that NO can be oxidized to NO_2 and nitrate species on Fe-TiO_2-PILC catalyst in the presence of oxygen.

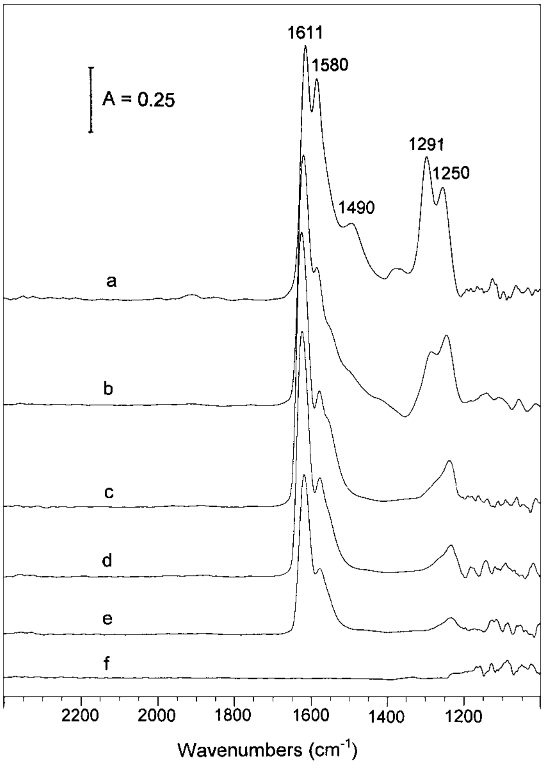

FIG. 2. IR spectra of Fe-TiO_2-PILC treated in flowing 1000 ppm NO + 2% O_2 at 30°C for 60 min and then purged by He at (a) 30, (b) 100, (c) 200, (d) 250, (e) 300, and (f) 350°C.

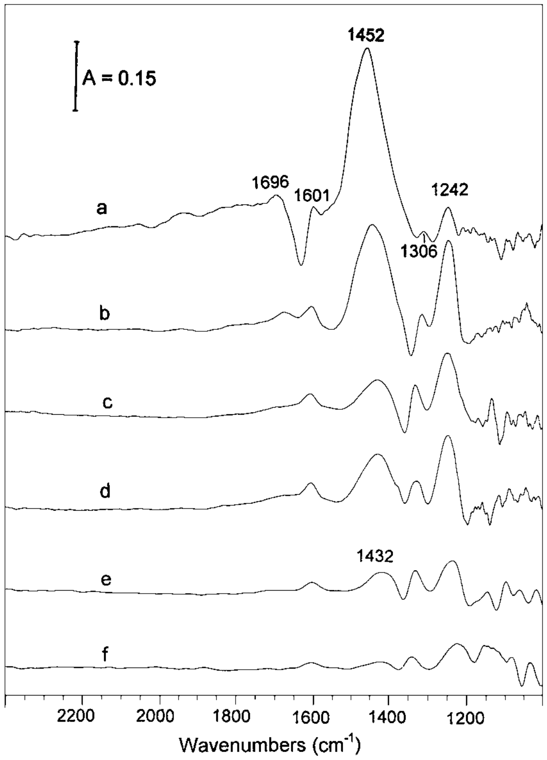

FIG. 3. IR spectra of Fe-TiO$_2$-PILC treated in flowing 1000 ppm NH$_3$ at 30°C for 30 min and then purged by He at (a) 30, (b) 100, (c) 200, (d) 250, (e) 300, and (f) 350°C.

IR spectra of NH$_3$ adsorption on Fe-TiO$_2$-PILC. The IR spectra of adsorbed ammonia on Fe-TiO$_2$-PILC at different temperatures are shown in Fig. 3. After the sample was treated in flowing NH$_3$/He for 30 min and then purged with He for 15 min at 30°C, a strong band at 1452 cm^{-1} and four weaker bands at 1696, 1601, 1306, and 1242 cm^{-1} were observed. The bands at 1696 and 1452 cm^{-1} are due to the symmetric and asymmetric bending vibrations of NH_4^+ that was chemisorbed on the Brønsted acid sites, while the bands at 1601 and 1242 cm^{-1} can be assigned to asymmetric and symmetric bending vibrations of the N–H bonds in NH$_3$ coordinately linked to Lewis acid sites (32, 33). The band at 1306 cm^{-1} was also observed on the spectrum of NH$_3$ adsorbed on pure TiO$_2$-PILC, with a stronger intensity (25). It was also found that the intensity of this band decreased with an increase of Fe content in the Fe-TiO$_2$-PILC catalysts (25). Hence, the band at 1306 cm^{-1} is probably due to NH$_3$ adsorbed on different Lewis sites, e.g., TiO$_2$ or Al$_2$O$_3$, and these sites could be partially covered by iron on the catalysts. The present results indicate that there were more Brønsted acid sites than Lewis acid sites in Fe-TiO$_2$-PILC at 30°C. With an increase in temperature, the intensity of 1242 cm^{-1} increased first (at the expense of the 1452 cm^{-1} band), passing through a maximum at 100°C, and then decreased at higher temperatures. The increase in 1242 cm^{-1} band suggests a transformation from Brønsted acid sites to Lewis acid sites on Fe-TiO$_2$-PILC at higher temperatures. The intensities of the other bands decreased with increasing temperature, as shown in Fig. 3, indicating desorption of NH$_3$. The above IR bands also shifted slightly at higher temperatures. For instance, the 1452 cm^{-1} band shifted to 1432 cm^{-1}, and the 1306 cm^{-1} band shifted to 1331 cm^{-1} at 300°C. Upon heating of the sample to 350°C, only a trace amount of the bands due to NH_4^+ or coordinated NH$_3$ were detected on the surface of Fe-TiO$_2$-PILC catalyst (Fig. 3f).

IR spectra of the reaction between nitrogen oxides and ammonia adspecies. Fe-TiO$_2$-PILC was first treated with NH$_3$/He for 30 min followed by a He purge at 250°C. NO/He was then introduced into the cell and IR spectra were recorded as a function of time (Fig. 4). As noted above, NH_4^+ ions (1432 cm^{-1}) and coordinated NH$_3$ (1608, 1331, and 1249 cm^{-1}) were generated after Fe-TiO$_2$-PILC was treated with NH$_3$/He and their IR bands did not decrease in flowing He for 15 min. After NO/He was passed over the sample for 0.25–2 min, the bands attributed to ammonia adspecies decreased. At the same time, two new weak bands were observed at 1827 and 1618 cm^{-1} (Figs. 4b and 4c). As mentioned above, the band at 1827 cm^{-1} was due to weakly adsorbed NO species, while the band at 1618 cm^{-1} might come from adsorbed H$_2$O or NO$_2$ or both (26). These

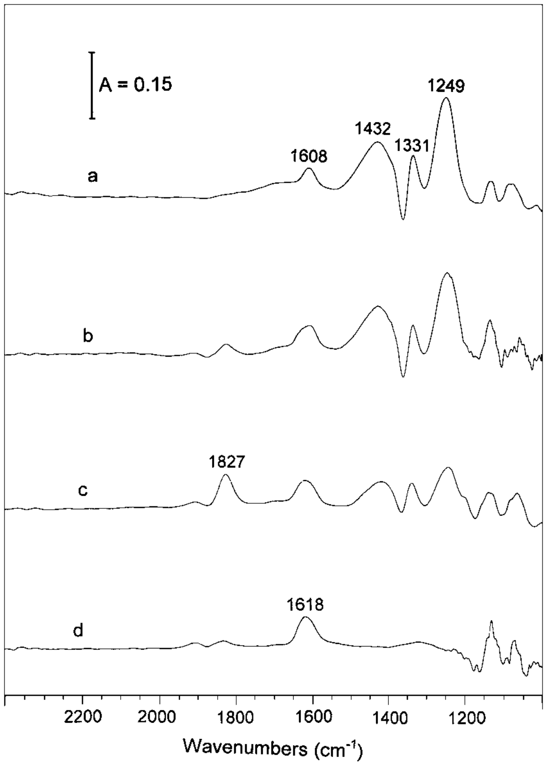

FIG. 4. IR spectra taken at 250°C upon passing 1000 ppm NO over the NH$_3$ presorbed on Fe-TiO$_2$-PILC for (a) 0, (b) 0.25, (c) 2, and (d) 5 min.

results indicate that the reaction between ammonia adspecies (both NH_4^+ ions and coordinated NH_3) and NO occurred because the bands due to ammonia adspecies did not decrease in flowing He. After 5 min, all of the ammonia adspecies bands diminished. Only an IR band at 1618 cm^{-1} and a very weak band at 1827 cm^{-1} were detected (Fig. 4d). The decrease of the 1827 cm^{-1} band due to weakly adsorbed NO may be due to oxidation of NO to NO_2 by residual oxygen.

The IR spectra of the reaction between ammonia adspecies and $NO + O_2$/He at 250°C are shown in Fig. 5. By comparison, after $NO + O_2$/He was passed over the ammonia-adsorbed Fe-TiO_2-PILC catalyst for 15 s, the bands attributed to ammonia adspecies decreased. All of the ammonia adspecies bands vanished in 2 min. At the same time, a new peak was observed at 1618 cm^{-1}, suggesting formation of adsorbed H_2O or NO_2 species. This indicates that oxygen increased the reaction rate between NO and ammonia adspecies.

The reaction between ammonia adspecies and NO_2/He at 250°C also took place faster than the reaction with NO. After NO_2/He was introduced into the ammonia-adsorbed Fe-TiO_2-PILC for 2 min, all of the bands due to NH_4^+ ions and coordinated NH_3 vanished. Meanwhile, NO_2 (1612 cm^{-1}) and nitrate species (1582 and 1235 cm^{-1}) were formed (Fig. 6).

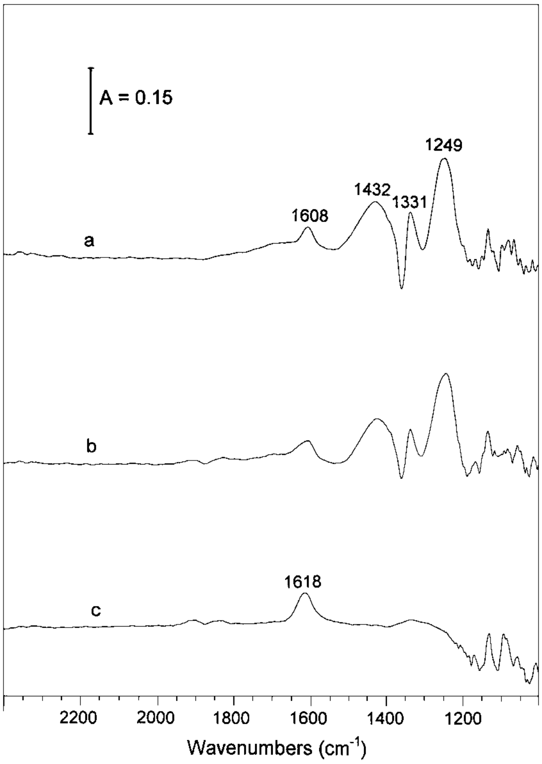

FIG. 5. IR spectra taken at 250°C upon passing 1000 ppm $NO + 2\%$ O_2 over the NH_3 presorbed on Fe-TiO_2-PILC for (a) 0, (b) 0.25, and (c) 2 min.

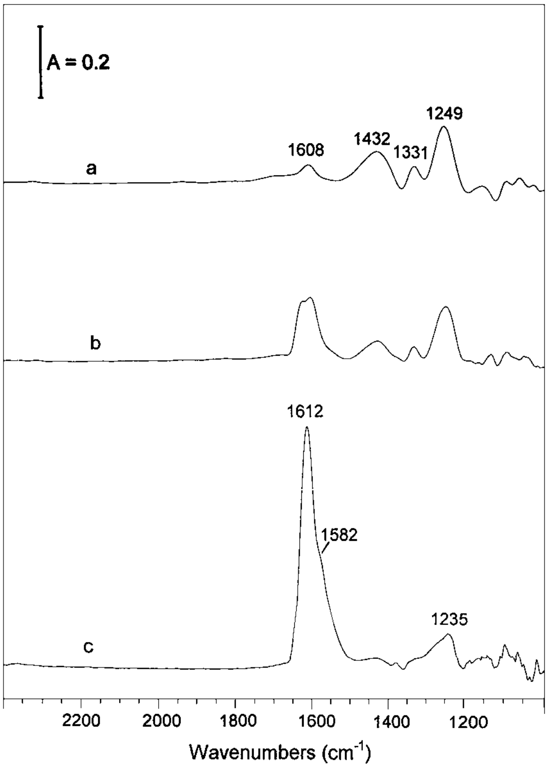

FIG. 6. IR spectra taken at 250°C upon passing 1000 ppm NO_2 over the NH_3 presorbed on Fe-TiO_2-PILC for (a) 0, (b) 0.25, and (c) 2 min.

IR spectra of the reaction between NH_3 and NO_x adspecies. In this experiment, the reactants were introduced into Fe-TiO_2-PILC catalyst in reversed order. The sample was first treated with $NO + O_2$/He at 250°C for 30 min and then purged with He for 15 min. As indicated above, NO_2 (1614 cm^{-1}) and nitrate species (1572 and 1235 cm^{-1}) were formed (Fig. 7a). After that, NH_3/He was passed over the NO_x-adsorbed catalyst and the IR spectra recorded as a function of time are shown in Figs. 7b–7e. After NH_3/He was introduced into the cell for 1 min, IR bands due to NO_2 adspecies at 1614 cm^{-1} and nitrate species at 1235 cm^{-1} decreased quickly but that due to nitrate species at 1572 cm^{-1} hardly changed. Meanwhile, IR bands attributed to NH_4^+ ions (1432 cm^{-1}) and coordinated NH_3 (1324 and 1246 cm^{-1}) were formed (Fig. 7b). This indicated that NO_x adspecies had reacted with NH_3. After 15 min, all of the NO_x adspecies bands disappeared and only ammonia adspecies were detected on the Fe-TiO_2-PILC catalyst (Fig. 7e).

IR spectra of Fe-TiO_2-PILC in a flow of $NO + NH_3 + O_2$/He. To identify the species present on the catalyst under reaction conditions, IR spectra were recorded when Fe-TiO_2-PILC was heated from 30°C to 350°C in a flow of $NO + NH_3 + O_2$/He. As shown in Fig. 8, the bands due to NH_4^+ ions and coordinated NH_3 species were observed at 1697, 1601, 1452, and 1248 cm^{-1}. Raising the temperature resulted in a decrease in the intensity of NH_4^+ ions. For

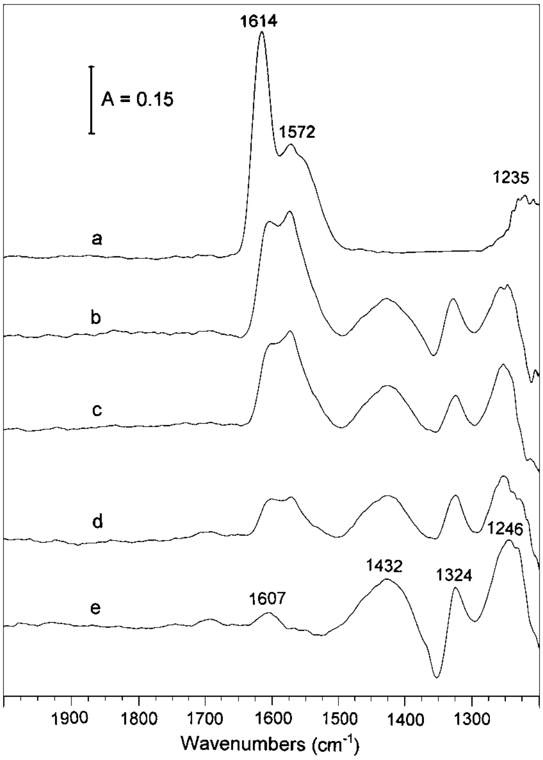

FIG. 7. IR spectra taken at 250°C upon passing 1000 ppm NH_3 over the NO + O_2 presorbed on Fe-TiO_2-PILC for (a) 0, (b) 1, (c) 2, (d) 5, and (e) 15 min.

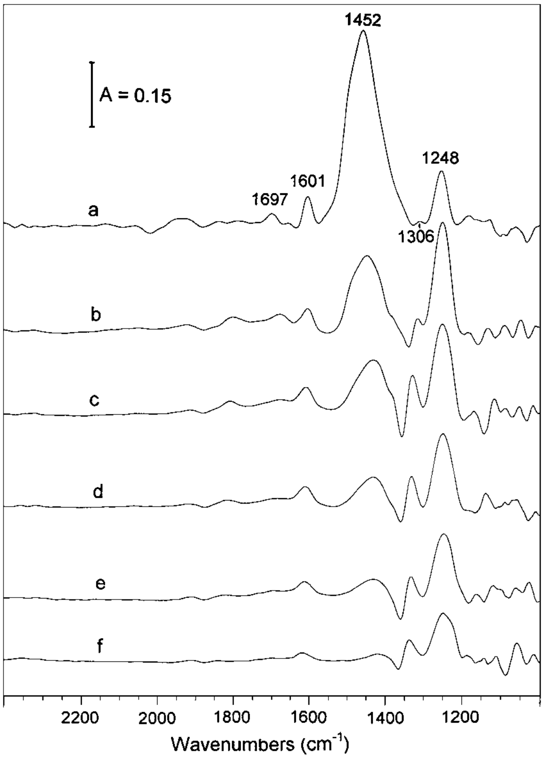

FIG. 8. IR spectra of Fe-TiO_2-PILC in a flow of 1000 ppm NO + 1000 ppm NH_3 + 2% O_2/He at (a) 30, (b) 100, (c) 200, (d) 250, (e) 300, and (f) 350°C.

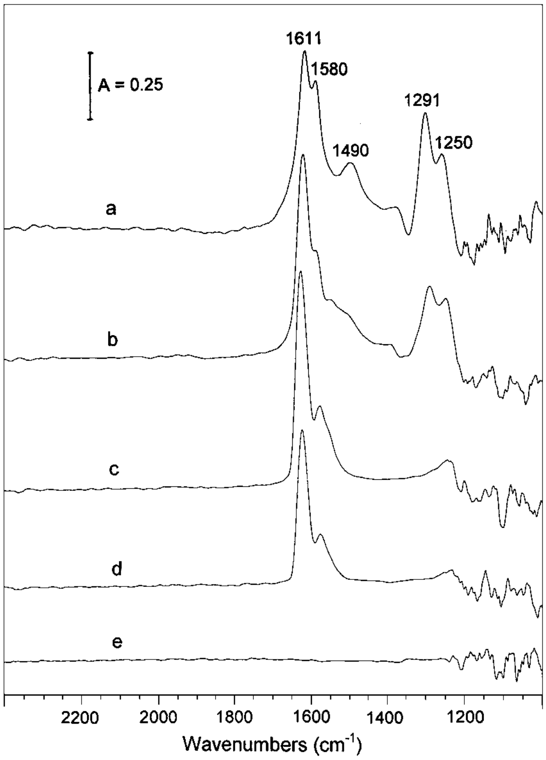

FIG. 9. IR spectra of TiO_2-PILC treated in flowing 1000 ppm NO + 2% O_2 at 30°C for 60 min and then purged by He at (a) 30, (b) 100, (c) 250, (d) 300, and (e) 350°C.

coordinated NH_3 species, the IR bands increased first and then decreased with increasing temperature. The ammonia adspecies were still observed at 350°C on Fe-TiO_2-PILC catalyst (Fig. 8f). In the whole temperature range, the IR bands due to NO_x adspecies were not detected on the catalyst under reaction conditions, suggesting the adsorption of NH_3 was much stronger than that of NO_x.

IR spectra of NO + O_2 and NH_3 adsorption on TiO_2-PILC. The IR spectra of NO + O_2 adsorbed on pure TiO_2-PILC are shown in Fig. 9. After TiO_2-PILC was treated at 30°C in flowing NO + O_2/He for 60 min and then purged by He for 15 min, IR bands due to adsorbed NO_2 (1611 cm^{-1}) and nitrate species (1580, 1490, 1291, and 1250 cm^{-1}) were observed (Fig. 9). This is similar to the observations on Fe-TiO_2-PILC catalyst, but the intensity of the band due to NO_2 adspecies on the TiO_2-PILC was slightly weaker compared to that on Fe-TiO_2-PILC (Fig. 2). Increasing the temperature resulted in decreases in the intensities of the above IR bands. All of the bands vanished at 350°C. The adsorption of NH_3 on TiO_2-PILC was also similar to that on Fe-TiO_2-PILC; i.e., both NH_4^+ ions (1670 and 1451 cm^{-1}) and coordinated NH_3 (1596, 1313, and 1242 cm^{-1}) were formed, as described in our previous study (25).

Steady-state kinetics studies. For determining the order of reaction with respect to NO, the concentration of NH_3 was kept constant at 1000 ppm, while the concentration of

NO was varied from 400 to 2000 ppm. Similarly, in determining the order with respect to NH_3, the concentration of NO was kept at 1000 ppm, while the concentration of NH_3 was varied between 400 and 2000 ppm. Since only 25 mg of catalyst was used, less than 15% NO conversion was obtained at 300°C in these experiments. Therefore, the reactor may be treated as a differential reactor. Because N_2O was not detected at 300°C on the Fe- TiO_2-PILC catalyst in the SCR reaction (25), the reaction rate can be expressed as either NO conversion or N_2 formation. The experimental results on the rate of N_2 formation as a function of nitric oxide and ammonia concentration are presented in Figs. 10 and 11, respectively. The rate of N_2 formation increased linearly with NO concentration, but it was almost unchanged with an increase in NH_3 concentration. The intrinsic reaction rate of N_2 formation as a function of reactant concentrations can be expressed as

$$r_{N2} = k[NO]^x[NH_3]^y \qquad [4]$$

The reaction order x with respect to NO was calculated to be 0.93, while the reaction order y with respect to NH_3 was zero at 300°C. The value of x is unity for vanadia and a number of other catalysts (1).

Catalytic behavior of Fe-TiO$_2$-PILC. Catalytic activities were obtained on Fe-TiO_2-PILC in a temperature range from 250 to 450°C for the reactions of $NO + NH_3$, $NO + NH_3 + O_2$ and $NO_2 + NH_3$. The experiments were carried out under stoichiometric ratios of NO_x/NH_3 according to reactions [1–3]. The results are summarized in Fig. 12. Less than 30% NO was reduced by NH_3 in the absence of O_2 on the Fe-TiO_2-PILC catalysts. By comparison, more than 95% NO_2 conversion was obtained at high temperatures in the absence of O_2. In the presence of O_2, NO conversion was increased sharply to 89–92% at 375–450°C. These results clearly indicate that the reaction rates of the reactions of $NO_2 + NH_3$ and $NO + NH_3 + O_2$ were much higher than that of $NO + NH_3$ in the entire temperature range. This was consistent with the above IR results that NO_2 and $NO + O_2$ were more active than NO in reacting with NH_3 adspecies. The product selectivity for N_2O was less than 1.4% in these reactions.

The oxidation activities of NO to NO_2 by O_2 on Fe-TiO_2-PILC and TiO_2-PILC were also measured in this work. The oxidation activity of NO to NO_2 on TiO_2-PILC was very low, and less than 2% NO was oxidized to NO_2 at 250–450°C (Fig. 13). After Fe ions were exchanged to TiO_2-PILC, the oxidation activity of NO increased significantly under the same conditions. This suggests that the Fe ions increased the rate of the oxidation of NO to NO_2.

A further series of empty-tube experiments was performed to determine the rates of the homogeneous

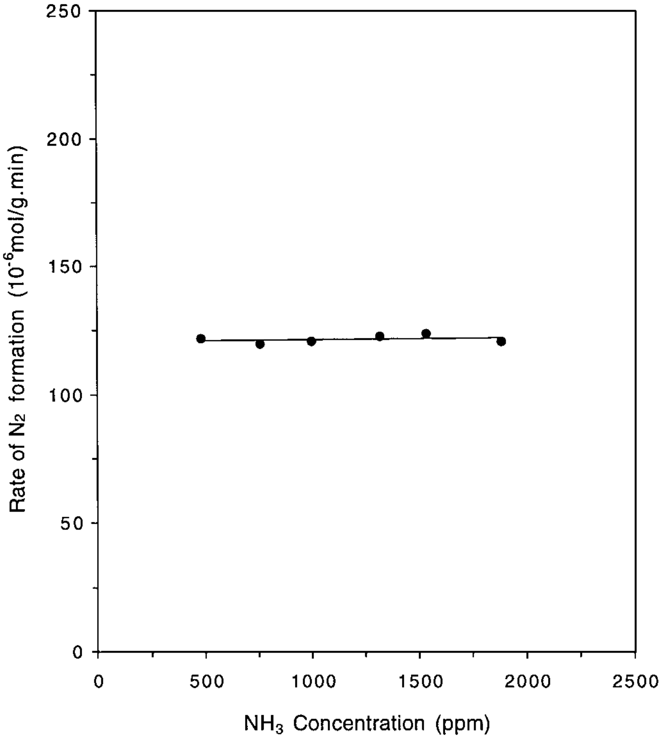

FIG. 11. Dependence of N_2 formation rate on NH_3 concentration on Fe-TiO_2-PILC at 300°C under the conditions of 25 mg of sample, 1000 ppm NO, 400–2000 ppm NH_3, 2% O_2, and 500 ml/min total flow rate.

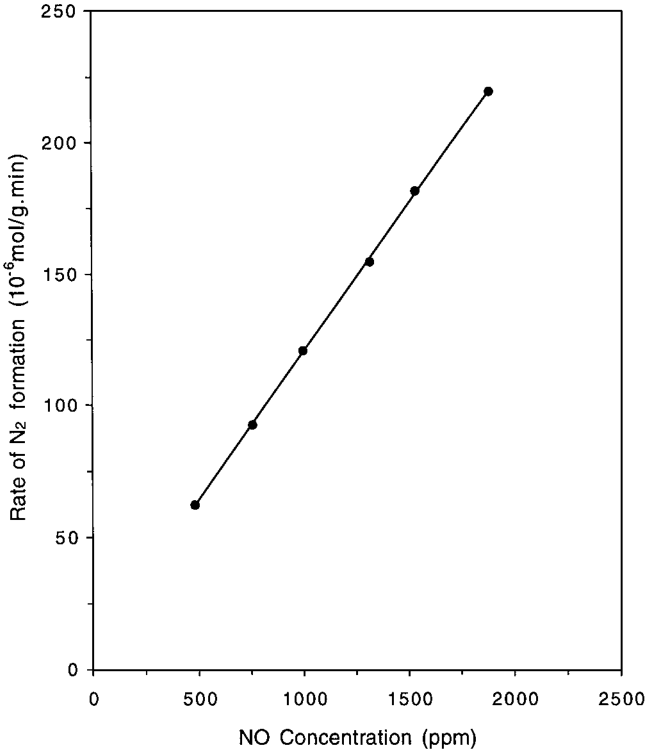

FIG. 10. Dependence of N_2 formation rate on NO concentration on Fe-TiO_2-PILC at 300°C under the conditions of 25 mg of sample, 1000 ppm NH_3, 400–2000 ppm NO, 2% O_2, and 500 ml/min total flow rate.

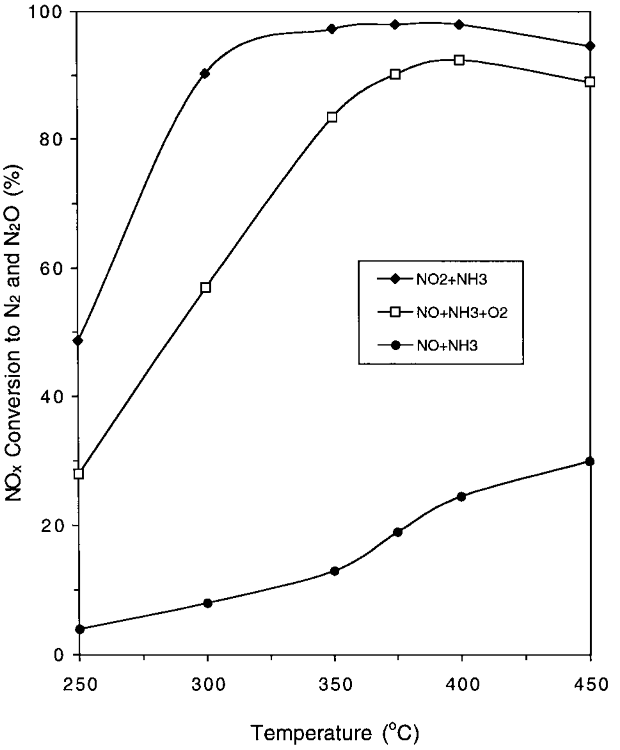

FIG. 12. Catalytic activities on Fe-TiO_2-PILC for the reactions of $NO + NH_3$ (1500 ppm NO and 1000 ppm NH_3), $NO + NH_3 + O_2$ (1000 ppm NO, 1000 ppm NH_3, and 2% O_2), and $NO_2 + NH_3$ (750 ppm NO_2 and 1000 ppm NH_3) under the conditions of 0.2 g of sample and 500 ml/min total flow rate.

oxidation of NO to NO_2. The same reaction conditions were used, i.e., 1000 ppm NO, 2% O_2, 500 ml/min flow rate, with the same quartz reactor. Less than 1.5% NO conversion to NO_2 was observed in the temperature range of 250–450°C.

DISCUSSION

Adsorption of NO_x and reaction between NO_x adspecies and NH_3. The FTIR spectra presented above indicate that NO, NO_2, and nitrate species were adsorbed on Fe-TiO_2-PILC catalyst after the sample was treated, respectively, with NO/He, $NO + O_2$/He, and NO_2/He (Figs. 1 and 2). The NO adsorption was very weak and its IR band at 1830 cm^{-1} disappeared when the catalyst was purged by He. The presence of O_2 increased NO adsorption due to the formation of NO_2 and nitrate adspecies. NO_2 adsorption was much stronger than NO adsorption for Fe-TiO_2-PILC catalyst. The NO_2 adspecies was the dominant species on the surface of Fe-TiO_2-PILC at high temperatures. NO_2 and nitrate species were also formed on TiO_2-PILC after it was treated in flowing $NO + O_2$/He, but the intensity of the NO_2 band was weaker than that on Fe-TiO_2-PILC (Fig. 9). This result suggests that the formation rate of NO_2 was lower on TiO_2-PILC, which was further proven by the result that the oxidation activity of NO to NO_2 on Fe-TiO_2-PILC was much higher than that on TiO_2-PILC (Fig. 13). The above results indicated that NO could be adsorbed and then oxidized to NO_2 and nitrates in the presence of O_2 on both TiO_2-PILC and Fe-TiO_2-PILC. This is similar to the results obtained on CuO/Al_2O_3 and zeolite catalysts (16–20), but different from that obtained on vanadia-based catalysts (1, 2). Most researchers reported that no nitrogen oxide adspecies were formed on the vanadia catalysts under conditions of low NO concentrations (500–2000 ppm). TiO_2-PILC is a two-dimensional layer material which consists of TiO_2 pillars and clay layers. The pillars keep the silicate layers separated and create interlayer spacing (gallery) of molecular dimensions (34–36). After TiO_2-PILC was exchanged with iron nitrate solution, Fe^{3+} ions substituted some cations in clay layers, i.e., mainly H^+, and also residual Na^+, K^+, and Mg^{2+}, and the isolated Fe^{3+} ions were probably bound to titania pillars in Fe-TiO_2-PILC (25). The Fe^{3+} ions on Fe-TiO_2-PILC enhanced significantly the formation of NO_2. Since NO_2 and nitrate species were also observed when $NO + O_2$ was passed over TiO_2 in our previous work (37), the NO_x adspecies on Fe-TiO_2-PILC may be bound to both Fe^{3+} sites and TiO_2 pillars. After NH_3/He was passed over the NO_x-adsorbed Fe-TiO_2-PILC catalyst at 250°C, NO_2 and nitrate species disappeared (Fig. 7), indicating that these NO_x adspecies were reduced by NH_3 at high temperatures.

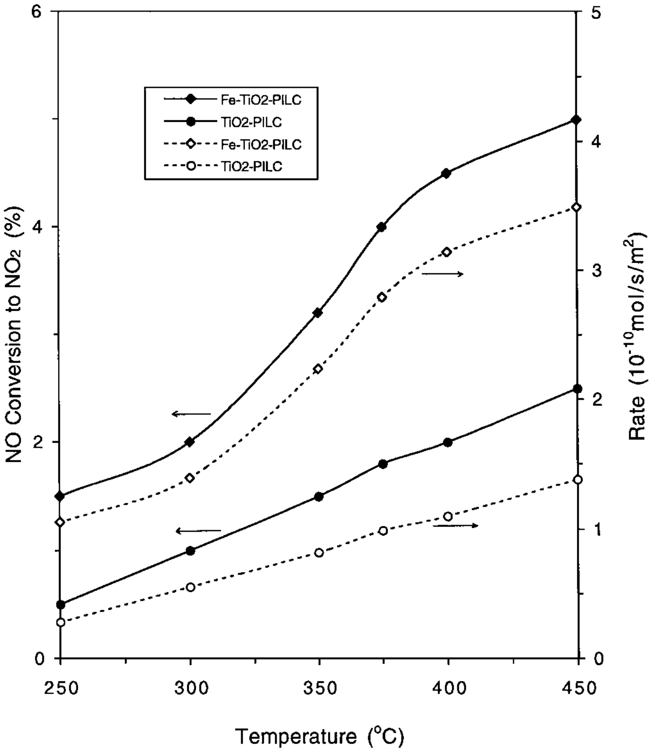

FIG. 13. Oxidation activity of NO to NO_2 by O_2 on Fe-TiO_2-PILC and TiO_2-PILC under the conditions of 0.2 g of sample, 1000 ppm NO, 2% O_2, and 500 ml/min total flow rate.

Adsorption of NH_3 and reactions between NH_3 adspecies and NO_x. It is known that both Lewis and Brønsted acid sites exist on pillared clays. Pillars (e.g., TiO_2) serve as the major source for Lewis acidity. On Fe-TiO_2-PILC, Fe^{3+} ions may also be Lewis acid sites. Two sources for Brønsted acidity in pillared clays have been discussed in the literature. One derives from the structural hydroxyl groups in the clay layers. The most likely proton site for montmorillonite is located at the Al(VI)–O–MgO linkage, where Al(VI) is the octahedrally coordinated Al, and Mg is one that has substituted an Al in the octahedral layer. Another source of proton derives from the cationic oligomers which upon heating decompose into metal oxide pillars and liberate protons (34–36). There was a larger proportion of Brønsted acid sites than Lewis acid sites at room temperature. After ammonia was adsorbed on TiO_2-PILC and Fe-TiO_2-PILC, NH_4^+ ions and coordinated NH_3 were formed (Fig. 3 and Ref. 25). They were also detected on Fe-TiO_2-PILC catalyst at high temperatures (but below 350°C). Both of them were active in reacting with NO, $NO + O_2$, and NO_2. After these gases were passed over the ammonia that was adsorbed on Fe-TiO_2-PILC at 250°C, the NH_3 adspecies vanished (Figs. 4–6). Moreover, the reaction rates of $NO + O_2 + NH_3$ and $NO_2 + NH_3$ were much higher than that of $NO + NH_3$, as identified by the *in situ* FTIR spectra (Figs. 6–8) and the catalytic activity measurements (Fig. 12). The presence of O_2 improved significantly the reactivity between NO and NH_3. This may be related to the formation of NO_2 on the surface of the Fe-TiO_2-PILC catalyst.

Mechanism of the SCR reaction on Fe-TiO_2-PILC. The foregoing results indicated that both NO_2 (resulting from oxidation of NO by O_2) and NH_3 could be separately adsorbed on Fe-TiO_2-PILC at high temperatures. However, under the SCR reaction conditions, the surface of Fe-TiO_2-PILC was found to be covered mainly by NH_4^+ ions and coordinated NH_3 (Fig. 8). No NO_x adspecies was detected. The IR spectra were very similar to the spectrum of NH_3 adsorption on Fe-TiO_2-PILC (Fig. 3). The strong adsorption of ammonia on Fe-TiO_2-PILC was consistent with the zero-order of the reaction with respect to NH_3. Since the reaction rates of $NO + NH_3 + O_2$ and $NO_2 + NH_3$ were much higher than that of $NO + NH_3$, and NO_2 adspecies was detected on the Fe-TiO_2-PILC catalyst, it seems that NO_2 is an intermediate in the SCR reaction, as suggested by some researchers (3, 16–20). But under the reaction conditions, the reaction between NO_2 and ammonia adspecies was faster than that between NO and O_2 so that the steady-state concentration of NO_x adspecies was below the detection limits of our IR spectroscopy. In addition, considering that the catalytic $NO + NH_3 + O_2$ reaction was carried out with a 1/1 ratio of NO/NH_3, and more than 90% NO conversion was obtained at high temperatures (Fig. 12), gaseous or weakly adsorbed NO molecules must also have taken part in the reaction for producing N_2. Otherwise, the maximum NO conversion should be less than 75% on Fe-TiO_2-PILC catalyst according to reaction [3] if only NO_2 was involved in the reaction with NH_3 adspecies. Hence, the SCR reaction of NO by NH_3 on the Fe-TiO_2-PILC catalyst most probably takes place according to the following steps:

$$2NH_3 + 2H^+ \rightarrow 2NH_4^+ \qquad [5]$$

$$2NH_3 \rightarrow 2NH_{3(a)} \qquad [6]$$

$$NO + 1/2O_2 \rightarrow NO_2 \qquad [7]$$

$$NO_2 + 2NH_4^+ \rightarrow NO_2[NH_4^+]_2 \qquad [8]$$

$$NO_2 + 2NH_{3(a)} \rightarrow NO_2[NH_3]_2 \qquad [9]$$

$$NO_2[NH_4^+]_2 + NO \rightarrow \cdots \rightarrow 2N_2 + 3H_2O + 2H^+ \qquad [10]$$

$$NO_2[NH_3]_2 + NO \rightarrow \cdots \rightarrow 2N_2 + 3H_2O \qquad [11]$$

The above reaction scheme was similar to those on Cu-ZSM-5 and H-ZSM-5 catalysts, reported, respectively, by Komatsu *et al.* (19) and Eng and Bartholomew (20). In the SCR reaction, gaseous NH_3 molecules are first adsorbed on the Brønsted acid and Lewis acid sites to form, respectively, NH_4^+ ions and coordinated NH_3 species. NO molecules are also adsorbed on the Fe-TiO_2-PILC catalyst and then oxidized to NO_2 adspecies. Then one molecule of NO_2 reacts with two adjacent NH_4^+ ions or coordinated NH_3 species to form active complexes $NO_2[NH_4^+]_2$ and $NO_2[NH_3]_2$. These active complexes finally react with one molecule of NO to produce N_2 and H_2O and thus complete the catalytic cycle. In addition, the ammonia adspecies could be oxidized by O_2 to form N_2, N_2O, and NO at high temperatures, but this may be negligible because very high NO conversion was still obtained at 450°C on the Fe-TiO_2-PILC catalyst (Fig. 12). Because of the slow homogeneous NO oxidation reaction and the results shown in Figs. 12 and 13, reaction [7] is probably the rate-determining step for the SCR reaction. At low surface NO coverages, reaction [7] should be near first-order with respect to NO. It follows that the overall reaction should also be near first-order, which is indeed the case. During the SCR reaction, nitrate species may also take part in the reaction with ammonia adspecies. However, since their concentrations were much lower than those of NO_2 adspecies at high temperatures (Fig. 2), we did not include reactions with nitrate in the above scheme. TiO_2-PILC showed strong surface acidity but very low activity in the oxidation of NO to NO_2; its SCR activity was therefore moderate (25). After it was exchanged with Fe^{3+} ions, Fe^{3+} ions on Fe-TiO_2-PILC increased the oxidation reaction rate of NO to NO_2 by O_2 significantly, as compared with TiO_2-PILC (Fig. 13). Hence, a high SCR activity was expected on the Fe-TiO_2-PILC catalyst (25). In addition, the improvement of surface acidity will increase the concentration of ammonia adsorption and thus enhance the amount of NH_3 and NH_4^+ pairs, which will also increase the catalytic activity for the SCR reaction. This point has been elucidated in our previous studies. The presence of H_2O and SO_2 in the reaction gases improved the SCR activity on the $Fe\text{-}TiO_2$-PILC catalyst due to an increase in surface acidity (25).

CONCLUSIONS

1. FTIR spectra showed that NO molecules were oxidized by O_2 to form adsorbed NO_2 and nitrate species on the $Fe\text{-}TiO_2$-PILC catalyst. NO_2 adspecies was the dominant species and was more stable than nitrate species at high temperatures (i.e., $>250°C$). It could be reduced by ammonia at high temperatures.

2. Ammonia molecules were adsorbed on the Brønsted acid sites and Lewis acid sites of the catalyst to generate, respectively, NH_4^+ ions and coordinated NH_3 species. Both of them could react with NO, $NO + O_2$, and NO_2 at high temperature, but the reactions with $NH_3 + NO + O_2$ and $NH_3 + NO_2$ were much faster than the reaction with $NO + NH_3$.

3. *In situ* FTIR experiments revealed that the surface of $Fe\text{-}TiO_2$-PILC was covered mainly by NH_4^+ ions and coordinated NH_3, and no NO_x adspecies was detected under the reaction conditions.

4. Steady-state kinetics experiments showed that the reaction order for NO was near one and that for NH_3 was zero, which was in good agreement with the above FTIR results.

5. A possible reaction scheme for the SCR reaction on $Fe\text{-}TiO_2$-PILC was proposed. The initial step was adsorption of NH_3 on neighboring acid sites. The adsorbed NH_3 then reacted with NO_2 to generate an active intermediate which finally reacted with NO to produce N_2 and H_2O.

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