



Title	Formation and Reactions of NH <sub>4</sub> NO <sub>3</sub> during Transient and Steady-State NH <sub>3</sub> -SCR of NO <sub>x</sub> , over H-AFX Zeolites: Spectroscopic and Theoretical Studies
Author(s)	Kubota, Hiroe; Liu, Chong; Toyao, Takashi; Maeno, Zen; Ogura, Masaru; Nakazawa, Naoto; Inagaki, Satoshi; Kubota, Yoshihiro; Shimizu, Ken-ichi
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# Formation and Reactions of $\text{NH}_4\text{NO}_3$ during Transient and Steady-state $\text{NH}_3$ -SCR of $\text{NO}_x$ over H-AFX Zeolites: Spectroscopic and Theoretical Studies

Hiroe Kubota,<sup>†</sup> Chong Liu,<sup>\*,†</sup> Takashi Toyao,<sup>†,‡</sup> Zen Maeno,<sup>†</sup> Masaru Ogura,<sup>§</sup> Naoto Nakazawa,<sup>||</sup> Satoshi Inagaki,<sup>||</sup> Yoshihiro Kubota,<sup>||</sup> Ken-ichi Shimizu<sup>\*,†,‡</sup>

<sup>†</sup>Institute for Catalysis, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan

<sup>‡</sup>Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Katsura, Kyoto 615-8520, Japan

<sup>§</sup>Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

<sup>||</sup>Division of Materials Science and Chemical Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

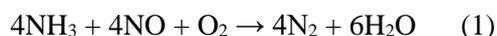
## ABSTRACT

*Operando* infrared (IR) spectroscopy and density functional theory (DFT) calculations were combined to investigate the selective catalytic reduction (SCR) of  $\text{NO}_x$  by  $\text{NH}_3$  over H-AFX zeolites. The steady-state kinetics shows that SCR reactions involving  $\text{NO}_2$  proceed much more rapidly than those of  $\text{NO}$ . Data from *in situ* IR combined with on-line mass spectrometry under transient conditions demonstrate that Brønsted acid sites (BASs) promote the reaction of  $\text{NO}_2$  with  $\text{NH}_3$  to form  $\text{N}_2$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_4\text{NO}_3$  at low temperatures (50–150 °C). Combined with DFT results, these data suggest that  $\text{NO}$  promotes the reduction of  $\text{NH}_4\text{NO}_3$  to  $\text{NH}_4\text{NO}_2$ , which then decomposes into  $\text{N}_2$  and  $\text{H}_2\text{O}$ . Therefore, the accumulation of  $\text{NH}_4\text{NO}_3$  in the zeolite is inhibited by  $\text{NO}$ . Furthermore, when  $\text{NO}$  is absent,  $\text{NH}_4\text{NO}_3$  decomposition into  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$  occurs only at high temperatures (> 200 °C). A comparison of H-AFX and Cu-AFX implies that Cu sites are not active for the reduction of  $\text{NO}_2$  by  $\text{NH}_3$ , and that BASs are responsible for the  $\text{NH}_3$ -SCR reactions involving  $\text{NO}_2$ .

**KEYWORDS:**  $\text{NH}_3$ -SCR, AFX zeolite, kinetics study, *in situ/operando* IR, DFT calculation

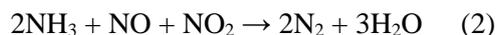
## 1. Introduction

The selective catalytic reduction of nitrogen oxides (NO<sub>x</sub>) by NH<sub>3</sub> (NH<sub>3</sub>-SCR) is widely used to control NO<sub>x</sub> emissions from stationary and mobile sources, including diesel vehicles.<sup>1-4</sup> Transition metal (Fe and Cu) cation-exchanged zeolites are promising for this purpose, and it is generally accepted that the exchanged transition metal cations are the primary catalytically active species promoting the reaction of equimolar amounts of NO and NH<sub>3</sub> in the presence of oxygen in so-called standard SCR.<sup>1,2,5</sup> The associated reaction is



Since the commercialization of Cu-exchanged chabazites (Cu-CHA) for use in NO<sub>x</sub> after-treatment systems,<sup>6,7</sup> attention has been focused on Cu-exchanged zeolites. It has been established that the catalytic cycle during standard SCR consists of the reduction of isolated Cu(II) to Cu(I) and the subsequent reoxidation of Cu(I) to Cu(II).<sup>1-3,5,8</sup> Compared with Cu-CHA, the NO reduction activity of Cu-free H-CHA is negligibly low, and it has been suggested that the Brønsted acid sites (BASs) in zeolites serve as points for the exchange of Cu cations but do not themselves play a significant role in the standard SCR process.<sup>9</sup>

In diesel emission control systems, a diesel oxidation catalyst (DOC) located upstream of the SCR catalyst converts a portion of NO in the exhaust to NO<sub>2</sub>, which has an important effect on the efficiency of the NH<sub>3</sub>-SCR process.<sup>10-21</sup> In the case of both H-<sup>10,11,14</sup> and Fe-exchanged<sup>15-17</sup> zeolites as well as V-based catalysts,<sup>18,19</sup> the SCR activity is significantly enhanced at an NO<sub>2</sub>/NO molar ratio of 1/1 (representing the so-called fast SCR reaction). The associated reaction is



In addition, the catalytic reduction of NO<sub>2</sub> by NH<sub>3</sub> can occur without the presence of NO.<sup>15</sup> In the case that the N<sub>2</sub> selectivity of this reaction is 100%, the process is termed NO<sub>2</sub> SCR or slow SCR<sup>1</sup> and can be summarized as



The SCR activity of H-type zeolites depends significantly on the NO<sub>2</sub> feed. Vartuli et al. reported that the reaction rate of NO<sub>2</sub> SCR is several hundred times faster than that of standard SCR over H-ZSM-5 catalyst.<sup>14</sup> In contrast, NO<sub>2</sub> does not improve the NO reduction activity of Cu-zeolites.<sup>17,22,23</sup> He et al. recently found that the addition of NO<sub>2</sub> can even inhibit NO conversion at low temperatures over Cu-CHA.<sup>24</sup> Moreover, research data have suggested that NO<sub>2</sub> formed in the DOC upstream of the SCR converter can lead to the accumulation of ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) in the zeolite pores, which causes catalyst deactivation<sup>24</sup> and the formation of the undesirable byproduct N<sub>2</sub>O.<sup>25</sup>

The BASs of zeolites play a significant role in NH<sub>3</sub>-SCR reactions involving NO<sub>2</sub> (that is, fast SCR and NO<sub>2</sub> SCR), in which Cu sites are not especially important.<sup>10,11</sup> In fact, because Cu sites can catalyze NO<sub>2</sub> decomposition to NO and O<sub>2</sub>,<sup>26</sup> Cu-zeolites are not ideal model catalysts for studying the role of NO<sub>2</sub> in NH<sub>3</sub>-SCR. Pioneering kinetics and theoretical studies concerning fast or NO<sub>2</sub> SCR utilized H-ZSM-5 zeolites,<sup>10,13</sup> and very little research<sup>20</sup> has focused on the effect of NO<sub>2</sub> on SCR in conjunction with small-pore H-type zeolites.<sup>20</sup> To the best of our knowledge, there is only limited information regarding the relative reaction rates for standard, fast and NO<sub>2</sub> SCR over H-type small-pore zeolites.<sup>27</sup>

AFX zeolite is an 8-membered ring (that is, small pore) material having both *aft* cages (0.55 × 1.35 nm) and smaller *gme* cages (0.33 × 0.74 nm).<sup>28,29</sup> Cu-modified AFX zeolites have recently attracted much

attention as effective catalysts for the  $\text{NH}_3$ -SCR reactions.<sup>4,30-32</sup> The AFX zeolites referred to as SSZ-16 have typically been synthesized using a flexible organic structure-directing agent (OSDA).<sup>33</sup> Recently, Kubota and co-workers developed a highly durable AFX zeolite using a bulky, non-flexible OSDA (TEBOP<sup>2+</sup>).<sup>28</sup> In this study, we employed this H-type AFX (H-AFX) while performing *operando* infrared (IR) spectroscopy, kinetics and density functional theory (DFT) analyses to elucidate the role of  $\text{NO}_2$  in  $\text{NH}_3$ -SCR under both steady-state and transient conditions. Herein, we propose mechanisms for the transformation of  $\text{NO}_2$  to  $\text{N}_2$  or  $\text{N}_2\text{O}$  via  $\text{NH}_4\text{NO}_3$  over H-AFX on the basis of the experimental evidence. Subsequently, we discuss molecular-level insights into the roles of BASs and  $\text{NO}_2$  based on the theoretical results. The mechanism uncovered herein is expected to assist in achieving rational control of  $\text{NH}_4\text{NO}_3$  deposition and  $\text{N}_2\text{O}$  emissions during  $\text{NH}_3$ -SCR in practical systems.

## 2. Results and Discussion

### 2.1 $\text{NO}_2$ effect on steady-state SCR over H-AFX

To explore the effect of  $\text{NO}_2$  on the SCR reaction rate over the H-AFX catalyst, we carried out steady-state catalytic experiments under standard SCR ( $\text{NO}_2/\text{NO}_x = 0$ ), fast SCR ( $\text{NO}_2/\text{NO}_x = 1/2$ ) and  $\text{NO}_2$  SCR ( $\text{NO}_2/\text{NO}_x = 1$ ) conditions, at temperatures ranging from 150 to 400 °C. An online IR spectrometer was used to determine the concentrations of the feed gas and products during these trials. It was found that the reaction rates of the fast and  $\text{NO}_2$  SCR reactions are significantly higher than those of standard SCR, and that the NO conversions obtained from the standard SCR reaction are negligibly low under the same contact time conditions. As the  $\text{NO}_2/\text{NO}_x$  ratio was increased, the  $\text{NO}_x$  reduction rates at 200 °C increased in the following order: 0.02  $\text{mmol g}^{-1} \text{h}^{-1}$  ( $\text{NO}_2/\text{NO}_x = 0$ ), 2.89  $\text{mmol g}^{-1} \text{h}^{-1}$  ( $\text{NO}_2/\text{NO}_x = 1/2$ ), 27.36  $\text{mmol g}^{-1} \text{h}^{-1}$  ( $\text{NO}_2/\text{NO}_x = 1$ ). It is noteworthy that the  $\text{NO}_x$  reduction rates obtained using the fast SCR and  $\text{NO}_2$  SCR processes are more than two orders of magnitude higher than that for standard SCR. These data are similar to the results in an earlier report by Stevenson et al. regarding  $\text{NH}_3$ -SCR over H-ZSM-5, in which the rate of the  $\text{NO}_2$  SCR process is several hundred times higher than that of the standard SCR rate.<sup>14</sup>

Figure 1 presents Arrhenius plots with estimated apparent activation energies ( $E_a$ ) for the standard, fast and  $\text{NO}_2$  SCR reactions. The reaction rates were determined under conditions using  $\text{NO}_x$  and  $\text{NH}_3$  that gave conversions between 20 and 55%. In the case of standard SCR, the Arrhenius plot is a straight line over the temperature range of 150–400 °C and gives an estimated  $E_a$  of 71  $\text{kJ mol}^{-1}$ , which is larger than the literature value for standard SCR over H-ZSM-5 (56.4  $\text{kJ mol}^{-1}$ ). For fast SCR, there are two kinetic regimes with distinct apparent activation energies. The  $E_a$  is 59  $\text{kJ mol}^{-1}$  in the high-temperature regime (275–350 °C). Unusually low apparent activation energies for fast SCR at 150–225 °C (12  $\text{kJ mol}^{-1}$ ) and  $\text{NO}_2$  SCR (3.8  $\text{kJ mol}^{-1}$ ) suggest that the reaction is limited by diffusion. Similar temperature-dependent kinetic regimes for fast SCR over H-CHA were reported by Schneider et al.,<sup>20</sup> and this phenomenon was explained based on dynamic changes in active sites at certain temperatures. The data obtained for  $\text{NO}_2$  SCR gave the lowest  $E_a$  (3.8  $\text{kJ mol}^{-1}$ ). These results indicate that the presence of  $\text{NO}_2$  in the feed gas decreases the  $E_a$ , thereby increasing the  $\text{NO}_x$  reduction rate. With regard to product selectivity, both the standard and fast SCR selectively converted  $\text{NO}_x$  to  $\text{N}_2$ , whereas half the N was converted to  $\text{N}_2\text{O}$  during the  $\text{NO}_2$  SCR process between 300 and 400 °C. Temperature dependence of  $\text{NO}_x$  conversion and  $\text{N}_2\text{O}$  yields is shown in Figure S1.  $\text{NO}_2$  SCR produces relatively larger amount of  $\text{N}_2\text{O}$  due to

the undesired side reaction of Eqn. (4); N<sub>2</sub>O yields for the NO<sub>2</sub> SCR reaction were around 20%, whereas N<sub>2</sub>O yields for the standard and fast SCR reactions were below 8%. The generation of a significant amount of N<sub>2</sub>O during NO<sub>2</sub> SCR over H-ZSM-5 was previously reported,<sup>14,34</sup> and is possibly a result of the reaction



A separate experiment assessing NO oxidation by H-AFX was also performed. The rate of NO oxidation to NO<sub>2</sub> at 230 °C was found to be 0.12 mmol g<sup>-1</sup> h<sup>-1</sup>, which is close to that obtained from the standard SCR reaction (0.11 mmol g<sup>-1</sup> h<sup>-1</sup>). Because both fast SCR and NO<sub>2</sub> SCR gave higher rates than standard SCR, it is likely that NO<sub>2</sub> is a key intermediate in standard SCR over H-AFX, and that NO oxidation is the rate-limiting step in this process.

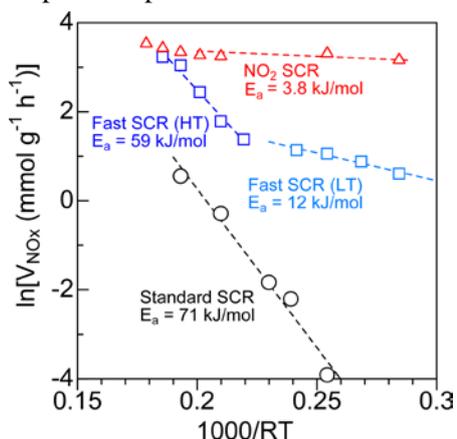


Figure 1. Arrhenius plots for standard SCR, fast SCR at high and low temperature (HT and LT) regimes, and NO<sub>2</sub> SCR over H-AFX zeolites.

## 2.2 Surface species during standard, fast and NO<sub>2</sub> SCR

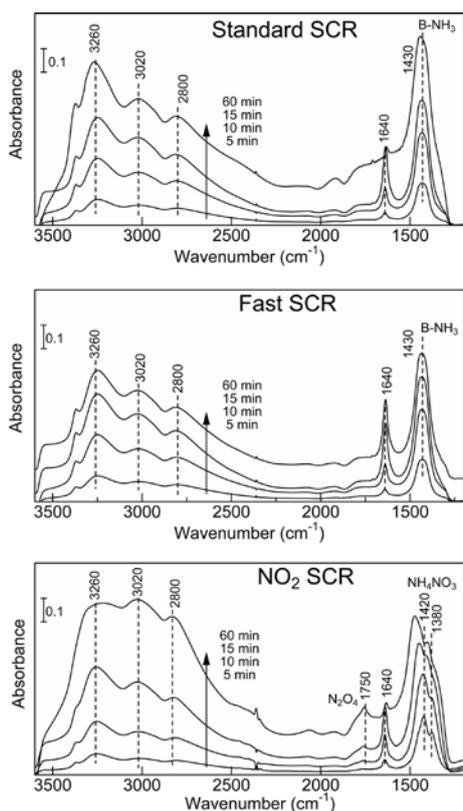


Figure 2. *In situ* IR spectra of adsorbed species on H-AFX (40 mg) during standard, fast and NO<sub>2</sub> SCR at 150 °C.

*In situ* IR spectroscopy was used to characterize the surface species generated during standard, fast and NO<sub>2</sub> SCR. These experiments were conducted at 150 °C using a disc of H-AFX (40 mg). As shown in Figure 2, strong IR bands due to NH<sub>3</sub> adsorbed on the BASs (NH<sub>4</sub><sup>+</sup> on zeolite oxygen, designated as B-NH<sub>3</sub>) were observed at 1430, 2800, 3020 and 3260 cm<sup>-1</sup> during both the standard and fast SCR reactions. In the case of standard SCR, a band most likely attributable to adsorbed NO<sub>2</sub> was initially observed at 1640 cm<sup>-1</sup> but decreased in intensity over time. Under the steady-state standard SCR conditions ( $t = 60$  min), B-NH<sub>3</sub> was evidently the dominant adsorbed species. During fast SCR, the amount of adsorbed NO<sub>2</sub> (associated with a peak at 1640 cm<sup>-1</sup>) increased with reaction time, and both B-NH<sub>3</sub> and adsorbed NO<sub>2</sub> were present on the H-AFX at the steady state ( $t = 60$  min). In contrast to the standard and fast SCR processes, bands at 1420 and 1380 cm<sup>-1</sup> were observed during NO<sub>2</sub> SCR. Based on previous reports,<sup>18,35</sup> these bands are assigned to NH<sub>4</sub>NO<sub>3</sub> accumulated on the catalyst. The bands resulting from the N–H stretching vibrations of NH<sub>4</sub><sup>+</sup> (at 2800, 3020, and 3250 cm<sup>-1</sup>) in the NO<sub>2</sub> SCR spectra are similar to those produced during standard and fast SCR, indicating that B-NH<sub>3</sub> sites are also present in the catalyst under the NO<sub>2</sub> SCR conditions. After 60 min, a band at 1750 cm<sup>-1</sup> was observed, likely due to N<sub>2</sub>O<sub>4</sub> species.<sup>36</sup>

### 2.3 Transient reaction of adsorbed NH<sub>3</sub> with NO<sub>x</sub> + O<sub>2</sub> on H-AFX and Cu-AFX

To monitor the dynamic changes in adsorbed species on the H-AFX as well as in the evolved gas products, we performed time-resolved *in situ* IR experiments at 230 °C while using mass spectrometry (MS) to evaluate the effluent gases (that is, *in situ* IR-MS or *operando* IR). In these trials, a flow type IR cell was connected to the

MS instrumentation and the H-AFX sample disc was exposed to a flow of 0.1% NH<sub>3</sub> in He for 10 min, followed by purging with He for 15 min. Subsequently, *in situ* IR spectra were collected as a function of time in conjunction with a flow of NO + O<sub>2</sub> or NO<sub>2</sub> + O<sub>2</sub> (Figure 3). After purging with He, a peak attributed to B-NH<sub>3</sub> sites at 1430 cm<sup>-1</sup> was observed, while a band due to NH<sub>3</sub> adsorbed on Lewis acid sites (at approximately 1620 cm<sup>-1</sup>) was not. During exposure to the NO + O<sub>2</sub> flow (Figure 3a), the B-NH<sub>3</sub> band was relatively constant for 1000 s, after which the peak intensity decreased with time. Simultaneously, an MS signal corresponding to N<sub>2</sub> (m/e = 28) was observed. It should be noted that the intensity of this MS peak for N<sub>2</sub> corresponded to the relative rate of N<sub>2</sub> formation. The formation of N<sub>2</sub> continued until the adsorbed NH<sub>3</sub> was completely consumed. The evident induction period of 1000 s may have been due to the blocking of active sites (Brønsted acid sites) by NH<sub>3</sub>.<sup>37</sup>

When the NH<sub>3</sub>-exposed H-AFX was treated with a flow of NO<sub>2</sub> + O<sub>2</sub> for 1000 s (Figure 3b), IR peaks assignable to NH<sub>4</sub>NO<sub>3</sub> (NH<sub>4</sub><sup>+</sup> at 1420 cm<sup>-1</sup> and NO<sub>3</sub><sup>-</sup> at 1380 cm<sup>-1</sup>) appeared. Based on reference spectra for NH<sub>3</sub> on BASs (B-NH<sub>3</sub>) and NH<sub>4</sub>NO<sub>3</sub>, the peaks in the range of 1365-1560 cm<sup>-1</sup> were deconvoluted into two components (Figure S2). The areas of each peak are plotted as functions of time in Figure 3b (right). After an induction period of 500 s, the intensity of the B-NH<sub>3</sub> band decreased in conjunction with N<sub>2</sub> formation and the accumulation of NH<sub>4</sub>NO<sub>3</sub>. The maximum intensity of the N<sub>2</sub> signal, which reflects the initial rate of N<sub>2</sub> formation, is higher under the NO<sub>2</sub> + O<sub>2</sub> mixture compared to the NO + O<sub>2</sub> trial, indicating that the reduction of NO<sub>x</sub> by adsorbed NH<sub>3</sub> is faster under NO<sub>2</sub> + O<sub>2</sub>. Taking into account the fact that NO<sub>2</sub> is produced by NO + O<sub>2</sub> on the BASs of zeolites,<sup>16</sup> the formation of N<sub>2</sub> over H-AFX is interpreted as the reduction of NO<sub>2</sub> by adsorbed NH<sub>3</sub> to yield N<sub>2</sub>. As noted above, the rate of the oxidation of NO to NO<sub>2</sub> on H-AFX is relatively slow, such that the transient rate of N<sub>2</sub> formation under NO + O<sub>2</sub> is slower than under NO<sub>2</sub> + O<sub>2</sub>.

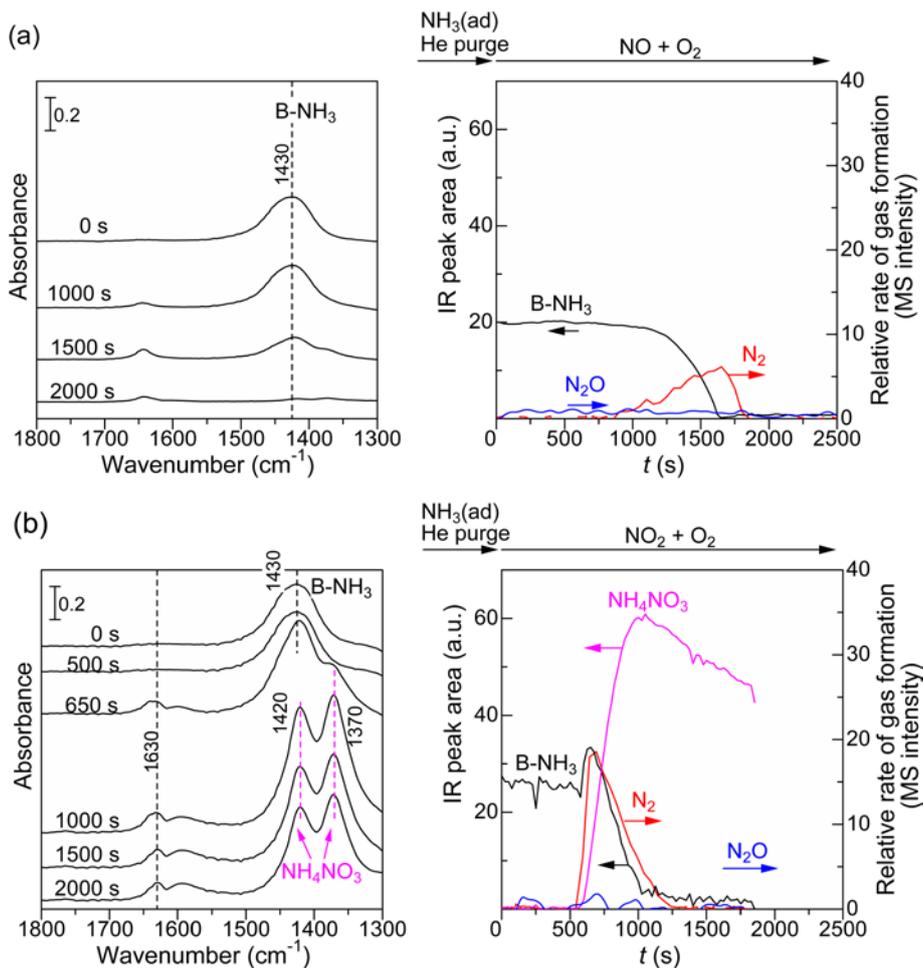


Figure 3. *In situ* IR spectra (left) of adsorbed species on H-AFX during the reaction of adsorbed  $\text{NH}_3$  with  $\text{NO}_x$  at  $230^\circ\text{C}$  (a) under 500 ppm  $\text{NO} + 10\% \text{O}_2$  and (b) under 500 ppm  $\text{NO}_2 + 10\% \text{O}_2$ . The right figures show the time dependence of the IR peak area for surface species and the intensity of the MS signal for  $\text{N}_2$ .

The same experiments were then performed using  $\text{NH}_3$ -exposed Cu-AFX, and the IR-MS results under  $\text{NO} + \text{O}_2$  and  $\text{NO}_2 + \text{O}_2$  are shown in Figures 4a and 4b, respectively. After the He purge, the IR spectra show a peak at  $1620\text{ cm}^{-1}$  due to  $\text{NH}_3$  adsorbed on Cu(II) sites (designated as Cu- $\text{NH}_3$ ) together with a strong band due to the B- $\text{NH}_3$  ( $1430\text{ cm}^{-1}$ ). When the catalyst was exposed to a flow of  $\text{NO} + \text{O}_2$  (Figure 4a), the intensity of these bands decreased, while  $\text{N}_2$  formation was simultaneously observed by MS analysis. Within 800 s, these  $\text{NH}_3$  species were completely consumed to give  $\text{N}_2$ .

In contrast to the results for H-AFX (Figure 3), the transient reaction of B- $\text{NH}_3$  under  $\text{NO}_2 + \text{O}_2$  over the Cu-AFX was much slower than the reaction under  $\text{NO} + \text{O}_2$  (Figure 4). In the case of the Cu-AFX, lower rates of both B- $\text{NH}_3$  consumption and  $\text{N}_2$  formation were observed under  $\text{NO}_2 + \text{O}_2$  compared to under  $\text{NO} + \text{O}_2$ . The completion of  $\text{N}_2$  formation under  $\text{NO}_2 + \text{O}_2$  required more than 2000 s, while  $\text{N}_2$  formation was complete within 800 s under  $\text{NO} + \text{O}_2$ . A comparison of the results for the SCR reactions over H-AFX and Cu-AFX in the presence of  $\text{NO}_2$  (Figure 3b vs. Figure 4b) indicates that the Cu sites show a negative effect on the transient reaction of adsorbed  $\text{NH}_3$  under  $\text{NO}_2 + \text{O}_2$ . This implies that the BASs serve as active sites for the reduction of  $\text{NO}_2$  by adsorbed  $\text{NH}_3$ , while Cu sites do not play an active role in this transient reaction. Comparing

the data for H-AFX and Cu-AFX under NO + O<sub>2</sub> (Figure 3a vs. Figure 4a) indicates that the Cu-AFX provides a higher N<sub>2</sub> formation rate and more rapid B-NH<sub>3</sub> consumption than the H-AFX, possibly due to a higher rate of NO oxidation to NO<sub>2</sub> on Cu sites than on H<sup>+</sup> sites. The N<sub>2</sub> formation for the NH<sub>3</sub>-adsorbed Cu-AFX under NO + O<sub>2</sub> (Figure 4b) can be explained by the following two pathways. One is the H<sup>+</sup>-catalyzed reduction of NO<sub>2</sub> by adsorbed NH<sub>3</sub>. Taking into account that Cu sites can catalyze NO<sub>2</sub> decomposition to O<sub>2</sub> and NO,<sup>26</sup> another possibility is the Cu-catalyzed NO<sub>2</sub> decomposition to give NO which is then reduced by adsorbed NH<sub>3</sub> over Cu sites.

Additionally, IR bands due to nitrate species on Cu<sup>II</sup> sites were observed at 1570, 1596, and 1620 cm<sup>-1</sup> in the spectrum obtained from the Cu-AFX under the NO<sub>2</sub> + O<sub>2</sub> mixture (Figures 4b and S3). The accumulation of these nitrates on the Cu-AFX catalyst suggests that the reaction of B-NH<sub>3</sub> with nitrate species on Cu sites is relatively slow. The role of such Cu nitrates in the SCR reaction is not yet fully understood, especially the question as to whether these are involved in the reaction cycle.<sup>39,40</sup> Nevertheless, recent time-resolved IR<sup>40</sup> and X-ray absorption spectroscopy (XAS)<sup>41</sup> studies of Cu-CHA show that the Cu nitrates are kinetically insignificant under typical low-temperature SCR conditions, indicative of their less important role in the SCR cycle.

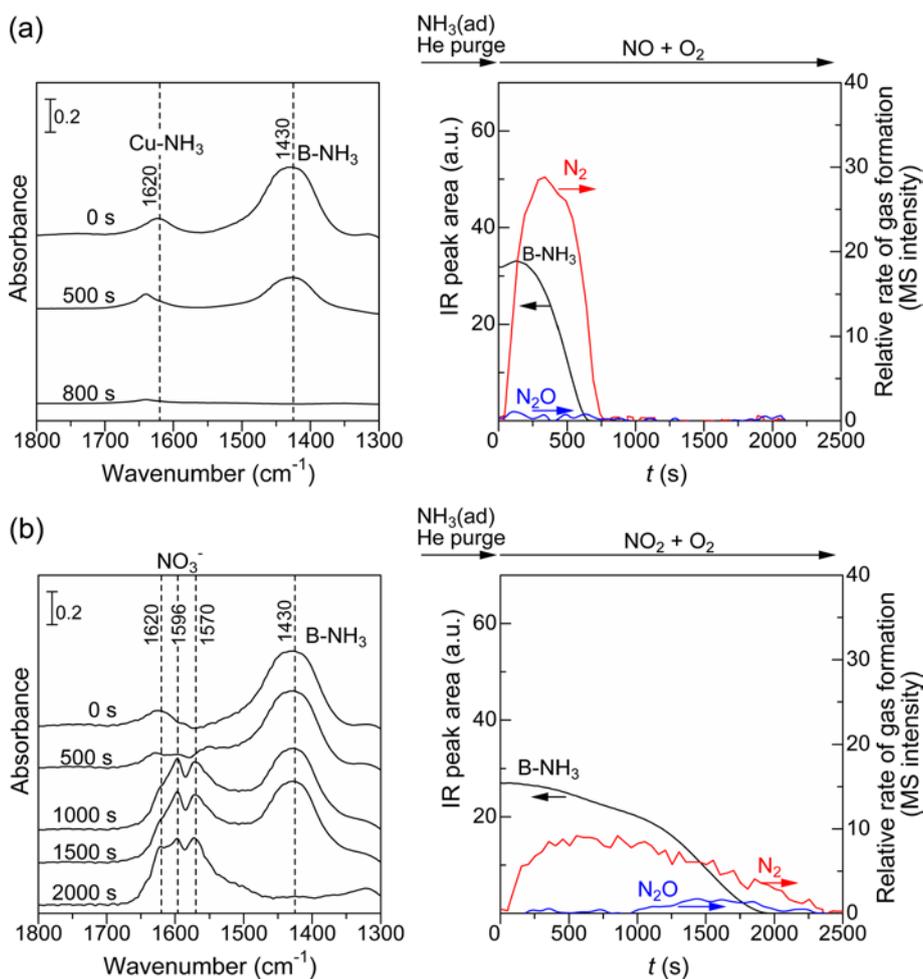


Figure 4. *In situ* IR spectra (left) of adsorbed species on Cu-AFX during the reaction of adsorbed NH<sub>3</sub> with NO<sub>x</sub> at 230 °C (a) under 500 ppm NO + 10% O<sub>2</sub> and (b) under 500 ppm NO<sub>2</sub> + 10% O<sub>2</sub>. The right figures show the

time dependence of the IR peak areas for surface species and the MS signal intensity for N<sub>2</sub>.

#### 2.4 Transient reaction of adsorbed NH<sub>3</sub> with NO<sub>x</sub> on H-AFX

We subsequently studied the H-AFX catalyzed reaction of B-NH<sub>3</sub> with NO<sub>x</sub> in the absence of O<sub>2</sub>. Transient experiments were performed at 150 °C using NH<sub>3</sub>-exposed H-AFX with a flow of NO + NO<sub>2</sub> or NO<sub>2</sub> (Figure 5). Under NO + NO<sub>2</sub>, B-NH<sub>3</sub> was consumed by NO + NO<sub>2</sub> to yield N<sub>2</sub> after an induction period of 500 s. In contrast, the reaction under NO<sub>2</sub> shows a higher rate of N<sub>2</sub> production such that significant amounts of NH<sub>4</sub>NO<sub>3</sub> were accumulated on H-AFX. The absence of NH<sub>4</sub>NO<sub>3</sub> accumulation under the NO + NO<sub>2</sub> flow suggests that NO promoted the decomposition of NH<sub>4</sub>NO<sub>3</sub><sup>42,43</sup> or inhibited the formation of NH<sub>4</sub>NO<sub>3</sub>.<sup>35,42,43</sup> The experimental observations suggest that NH<sub>3</sub> adsorbed on H<sup>+</sup> sites reacted with NO<sub>2</sub> to produce N<sub>2</sub> and NH<sub>4</sub>NO<sub>3</sub> (Eqn. (5)). The resulting NH<sub>4</sub>NO<sub>3</sub> was further able to react with NO to yield N<sub>2</sub>, NO<sub>2</sub> and H<sub>2</sub>O (Eqn. (6)).

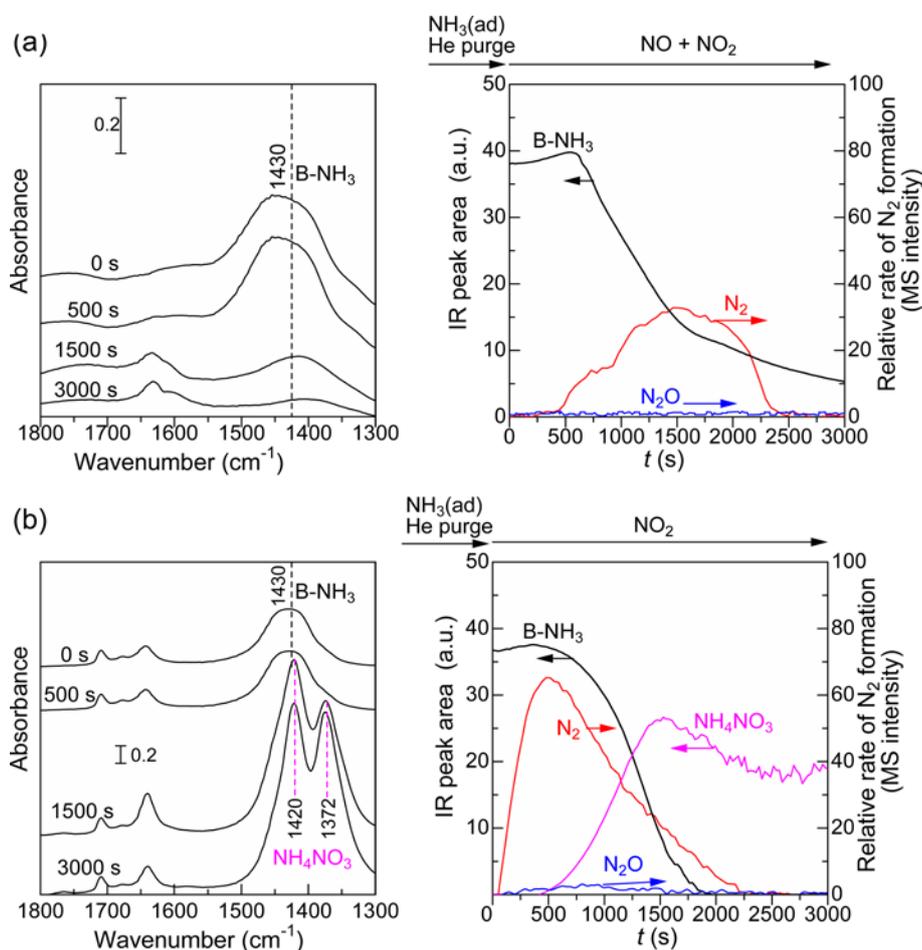


Figure 5. *In situ* IR spectra (left) of adsorbed species on H-AFX during the reaction of adsorbed NH<sub>3</sub> at 150 °C (a) under 250 ppm NO + 250 ppm NO<sub>2</sub> and (b) under 500 ppm NO<sub>2</sub>. The right figures show the time dependence of the IR peak area for surface species and the intensity of the MS signal for N<sub>2</sub>.

To understand the effect of temperature on reaction (5), we studied the temperature-programmed surface reaction (TPSR) of adsorbed  $\text{NH}_3$  on H-AFX under a flow of  $\text{NO}_2$  (Figure 6). In these trials, an IR H-AFX disc was first exposed to 0.1%  $\text{NH}_3$  for 0.5 h at 30 °C, followed by purging with He. The catalyst was subsequently heated to 500 °C at 10 °C  $\text{min}^{-1}$  under 500 ppm  $\text{NO}_2$ . The adsorbed species and effluent gases were monitored by IR and MS, respectively. Above 50 °C, B- $\text{NH}_3$  consumption,  $\text{N}_2$  formation, and  $\text{NH}_4\text{NO}_3$  accumulation on the H-AFX were observed simultaneously. At 280 °C,  $\text{NH}_4\text{NO}_3$  consumption and  $\text{N}_2\text{O}$  formation occurred simultaneously. These results show that reaction (5) occurs at temperature range of 50–150 °C. The reaction pathways for  $\text{NH}_4\text{NO}_3$  conversion to  $\text{N}_2\text{O}$  and for the decomposition of  $\text{NH}_4\text{NO}_3$  with  $\text{NO}$  to yield  $\text{N}_2$  (Eqn. (6)) are discussed in the following section.

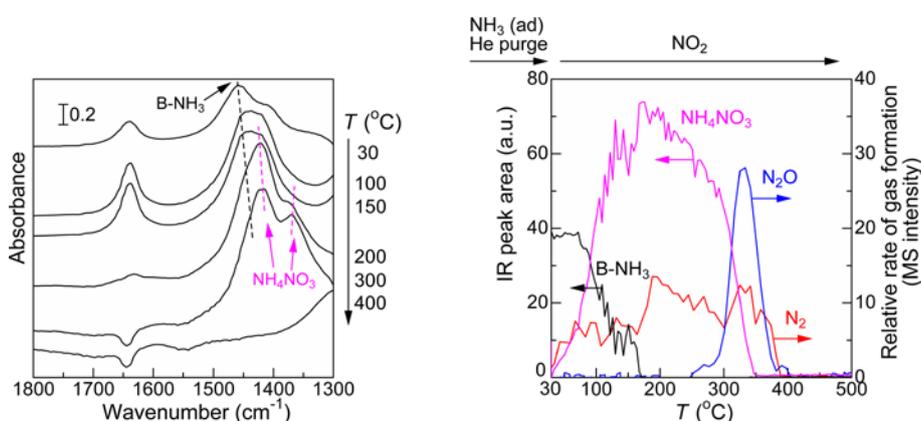


Figure 6. *In situ* IR spectra (left) acquired during the temperature-programmed surface reaction (TPSR) of adsorbed  $\text{NH}_3$  under 500 ppm  $\text{NO}_2$  over H-AFX, pre-exposed to 500 ppm  $\text{NH}_3$  at 30 °C for 0.5 h. The right figure shows the time dependence of the IR peak area for surface species and the MS intensity for  $\text{N}_2$

### 2.5 Conversion of $\text{NH}_4\text{NO}_3$ to $\text{N}_2$ or $\text{N}_2\text{O}$

To provide direct evidence for reaction (6), we carried out *in situ* IR analyses of  $\text{NH}_4\text{NO}_3$ -loaded H-AFX under a flow of  $\text{NO}$  at elevated temperatures. Based on a literature method,<sup>23,44,45</sup>  $\text{NH}_4\text{NO}_3$ -loaded H-AFX ( $\text{NH}_4\text{NO}_3$  loading of 1  $\text{mmol g}^{-1}$ ) was prepared by the impregnation method, via adding 200  $\mu\text{L}$  of a 0.2 M  $\text{NH}_4\text{NO}_3$  solution dropwise to 40 mg of H-AFX, followed by drying in an oven at 80 °C for 5 h. After obtaining the background IR spectrum of the  $\text{NH}_4\text{NO}_3$ -impregnated H-AFX at 30 °C under He, the IR cell was heated (10 °C  $\text{min}^{-1}$ ) under a flow of 500 ppm  $\text{NO}/\text{He}$ . Figure 7 shows the IR difference spectra of the  $\text{NH}_4\text{NO}_3$ -impregnated H-AFX at various temperatures. The negative peaks appearing at 1420, 1380, 3020 and 3260  $\text{cm}^{-1}$  as the temperature increases indicate the consumption of adsorbed  $\text{NH}_4\text{NO}_3$ . Above 200 °C, the intensity of the negative peaks leveled off. The  $\text{NO}$ -assisted decomposition of  $\text{NH}_4\text{NO}_3$  on SCR catalysts has also been observed in previous studies.<sup>43,46</sup>

In the case of the  $\text{NH}_4\text{NO}_3$ -impregnated H-AFX, the shapes of the negative peaks are close to those of the positive bands that appear when  $\text{NH}_3$ -exposed H-AFX is treated with a flow of  $\text{NO}_2$  (Figure S4). This result suggests that the  $\text{NH}_4\text{NO}_3$  impregnated into the H-AFX is essentially the same as the  $\text{NH}_4\text{NO}_3$  formed by the reaction of  $\text{NO}_2$  with  $\text{NH}_3$ . We also compared the IR spectra of physical mixtures of  $\text{NH}_4\text{NO}_3$  and H-AFX, in

which the  $\text{NH}_4\text{NO}_3$  particles primarily present at the external surfaces of the H-AFX. A comparison of the IR spectra (Figure S4) suggests that the physically mixed  $\text{NH}_4\text{NO}_3$  affords different spectroscopic features to the material obtained from an  $\text{NH}_3 + \text{NO}_2$  flow or the impregnated  $\text{NH}_4\text{NO}_3$ , indicative of the different adsorption states in these specimens. The  $\text{NH}_4\text{NO}_3$  species generated from the reaction of  $\text{NH}_3$  and  $\text{NO}_2$  or impregnated from an  $\text{NH}_4\text{NO}_3$  solution are more likely to be adsorbed on the BASs rather than at the external surfaces of the zeolite. The above comparisons demonstrate that the  $\text{NH}_4\text{NO}_3$  sample prepared via impregnation is a better representation of the state of accumulated  $\text{NH}_4\text{NO}_3$  during  $\text{NH}_3$ -SCR over H-AFX. Thus, we used such a sample in further TPSR trials as a model of the reaction of  $\text{NH}_4\text{NO}_3$  inside the H-AFX zeolite. For these experiments, the amount of impregnated  $\text{NH}_4\text{NO}_3$  ( $1.0 \text{ mmol g}^{-1}$ ) is less than the concentration of Al atoms in the H-AFX catalyst ( $2.7 \text{ mmol g}^{-1}$ ), so as to avoid over-loading of  $\text{NH}_4\text{NO}_3$  at the external surfaces of the zeolite.

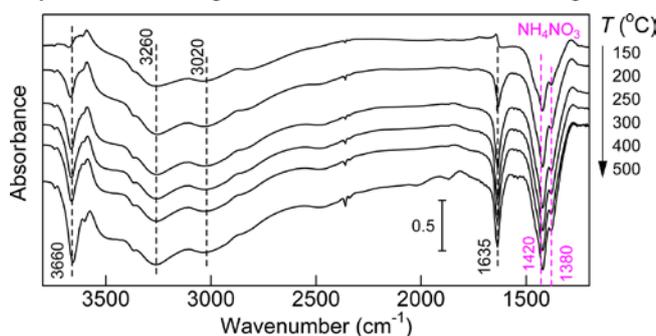


Figure 7. *In situ* IR spectra of  $1 \text{ mmol g}^{-1}$   $\text{NH}_4\text{NO}_3$ -loaded H-AFX (40 mg) during heating from 30 to 500 °C at  $10 \text{ °C min}^{-1}$  under 500 ppm NO.

In a separate flow reactor, TPSR experiments involving  $\text{NH}_4\text{NO}_3$  ( $1 \text{ mmol g}^{-1}$ )-impregnated H-AFX (in powder form) were carried out under flows of various gas mixtures (Figure 8). The concentrations of both  $\text{N}_2$  and  $\text{N}_2\text{O}$  in the effluent gas were quantified using MS. Because  $\text{NO}_2$  was quantified by IR using a long pathlength (8 m) gas cell, the time response for  $\text{NO}_2$  data was slower than those for the other gases. The results obtained under a flow of NO (Figure 8a) confirm the formation of  $\text{N}_2$  and  $\text{NO}_2$  over the temperature range of 50-200 °C. Note that the slow decay of the signal associated with the  $\text{NO}_2$  concentration above 200 °C can be ascribed to the slower response of the IR detector compared to the MS instrument. The formation of  $\text{NO}_2$  indicates that  $\text{NH}_4\text{NO}_3$  is reduced by NO to yield  $\text{NO}_2$  and ammonium nitrite ( $\text{NH}_4\text{NO}_2$ ), which is consistent with the pathway proposed by Weitz et al.<sup>43,47,48</sup> It is also well known that  $\text{NH}_4\text{NO}_2$  readily decomposes to  $\text{N}_2$  and  $\text{H}_2\text{O}$  at low temperatures ( $< 100 \text{ °C}$ ).<sup>47,48</sup> Combined with the corresponding IR results in Figure 7, these data indicate that reaction (6) is actually the combination of the following two reactions.



In the absence of NO, the decomposition of  $\text{NH}_4\text{NO}_3$  can afford  $\text{N}_2\text{O}$ ,<sup>42,49</sup> and the TPSR profile (Figure 8b) obtained under a He flow in the absence of NO shows  $\text{N}_2\text{O}$  formation between 200 and 350 °C with only a trace amount of  $\text{N}_2$ . This indicates that  $\text{N}_2\text{O}$  was produced via the decomposition of  $\text{NH}_4\text{NO}_3$  in the absence of NO, as in the following reaction (Eqn. (9)).<sup>42</sup>



The TPSR profile acquired under NO<sub>2</sub> flow (Figure 8c) shows that N<sub>2</sub>O was the main product. This can be explained by considering that NO<sub>2</sub> decomposition to NO and O<sub>2</sub> is slow over H-AFX, such that reaction (9) proceeds more rapidly than reaction (7).

Under NH<sub>3</sub>-SCR conditions, NH<sub>3</sub> co-exists in the gas mixture, and so we also studied the effect of NH<sub>3</sub> on the reactivity of NH<sub>4</sub>NO<sub>3</sub> under NO (Figure 8d). The TPSR profile of NH<sub>4</sub>NO<sub>3</sub>-loaded H-AFX under a flow of an NO + NH<sub>3</sub> mixture shows reduced N<sub>2</sub> formation compared to the amount generated under NO. Additionally, N<sub>2</sub>O formation was accelerated by the addition of NH<sub>3</sub>. It is therefore obvious that NH<sub>3</sub> inhibits reaction (6) and most likely reaction (7), such that reaction (9) is accelerated. Previously, Weitz et al.<sup>43</sup> studied the role of BASs of zeolites in the reduction of NH<sub>4</sub>NO<sub>3</sub> by NO, and reported that these sites catalyze reaction (8). Under a flow of an NO + NH<sub>3</sub> mixture at low temperatures, NH<sub>3</sub> can be readily adsorbed on the BASs of H-AFX, reducing the number of such sites available for reaction (8) and lowering the amount of N<sub>2</sub> formed during TPSR analyses. The TPSR experiments using NH<sub>4</sub>NO<sub>3</sub>-SiO<sub>2</sub> under NO provided no evidence for the formation of N<sub>2</sub> or N<sub>2</sub>O (results not shown), indicating that the BASs are active sites for the key reactions for the formation of N<sub>2</sub> and N<sub>2</sub>O (that is, reactions (7) and (9)).

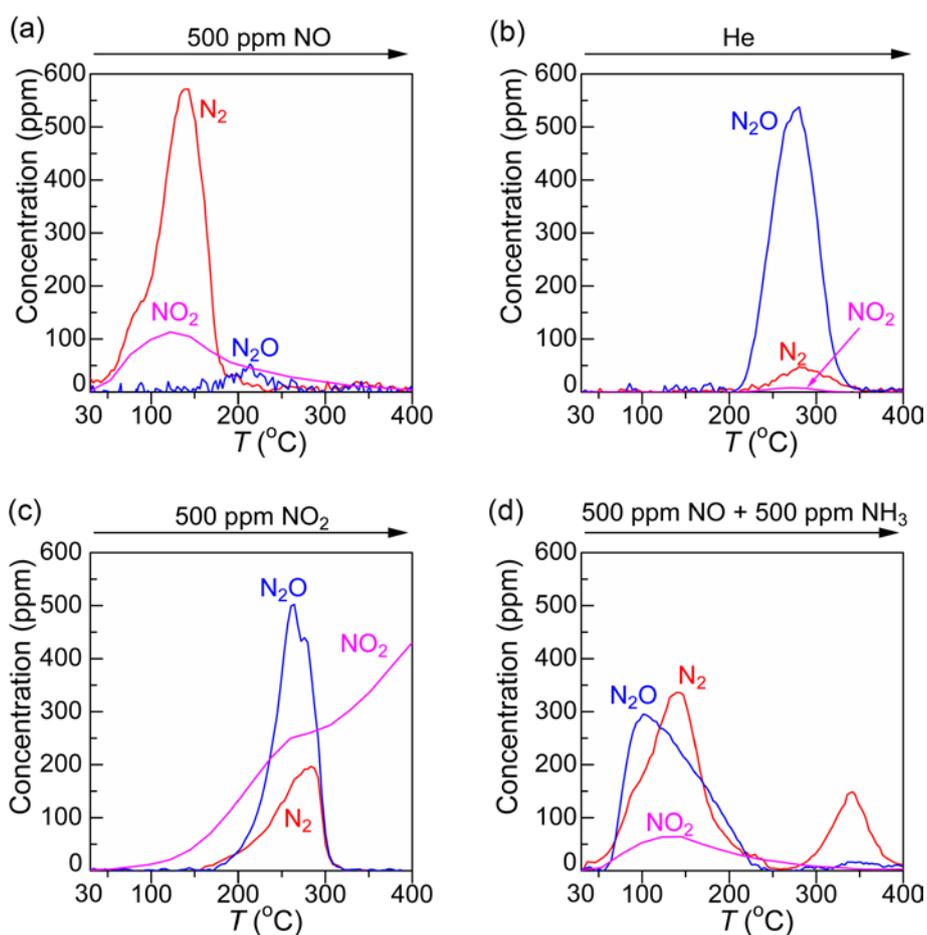


Figure 8. The TPSR profiles obtained using 1 mmol g<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub>-loaded H-AFX (40 mg) during heating from 30 to 400 °C at 10 °C min<sup>-1</sup> under (a) 500 ppm NO, (b) He, (c) 500 ppm NO<sub>2</sub> and (d) 500 ppm NO + 500 ppm NH<sub>3</sub>.

## 2.6 DFT study on $\text{NH}_4\text{NO}_3$ decomposition

To provide molecular-level insights into the elementary steps of  $\text{NH}_4\text{NO}_3$  conversion over H-AFX, we further performed DFT calculations using a 48T hexagonal unit cell (Figure S5). The formation of  $\text{N}_2\text{O}$  from  $\text{NH}_4\text{NO}_3$  was initially investigated (Figure 9a). The adsorption of  $\text{NH}_4\text{NO}_3$  on the protonic H-AFX zeolite was found to result in the proton transfer from the BAS to the nitrate moiety, giving  $\text{HNO}_3$  and  $\text{NH}_4^+$ . These species in turn are stabilized by hydrogen-bonding interactions at the negative oxygen sites of the zeolite framework. The decomposition of  $\text{NH}_4\text{NO}_3$  into  $\text{N}_2\text{O}$  proceeds via two sequential dehydration reactions. The first dehydration occurs via a proton transfer from  $\text{NH}_4^+$  to the OH moiety of the protonated nitrate group, which produces the  $\text{H}_2\text{NNO}_2$  intermediate with simultaneous proton back-donation to the zeolite framework oxygen (Int\_ $\text{H}_2\text{NNO}_2$ ). This reaction is endothermic by 84 kJ/mol with an activation energy barrier of 138 kJ/mol. In the corresponding transition state (TS1), a water molecule is already generated, and the  $\text{NO}_2$  moiety interacts with the  $\text{NH}_3$  fragment at an N–N distance ( $d_{\text{N-N}}$ ) of 2.67 Å. The production of the  $\text{H}_2\text{NNO}_2$  intermediate is accompanied by N–N bond formation ( $d_{\text{N-N}} = 1.48$  Å) and the regeneration of a BAS. The reorientation of the  $\text{H}_2\text{NNO}_2$  intermediate (Int\_ $\text{H}_2\text{NNO}_2(\text{reo})$ ) decreases the system energy by -38 kJ/mol and initiated the second dehydration reaction. With the participation of both the BAS and the water generated from the first dehydration, the conversion of  $\text{H}_2\text{NNO}_2$  via TS2 proceeds with an activation barrier of 52 kJ/mol, and the production of  $\text{N}_2\text{O}$  significantly stabilizes the system by -91 kJ/mol. During the BAS-catalyzed decomposition of  $\text{NH}_4\text{NO}_3$  into  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$ , the first dehydration producing the  $\text{H}_2\text{NNO}_2$  intermediate is the rate-determining step, with an activation barrier of 138 kJ/mol. When H-AFX is absent, the non-catalytic decomposition of  $\text{NH}_4\text{NO}_3$  requires a much higher energy barrier of 181 kJ/mol for the first dehydration (Figure S6), indicative of the essential catalytic role of BASs during the conversion of  $\text{NH}_4\text{NO}_3$  into  $\text{N}_2\text{O}$ .

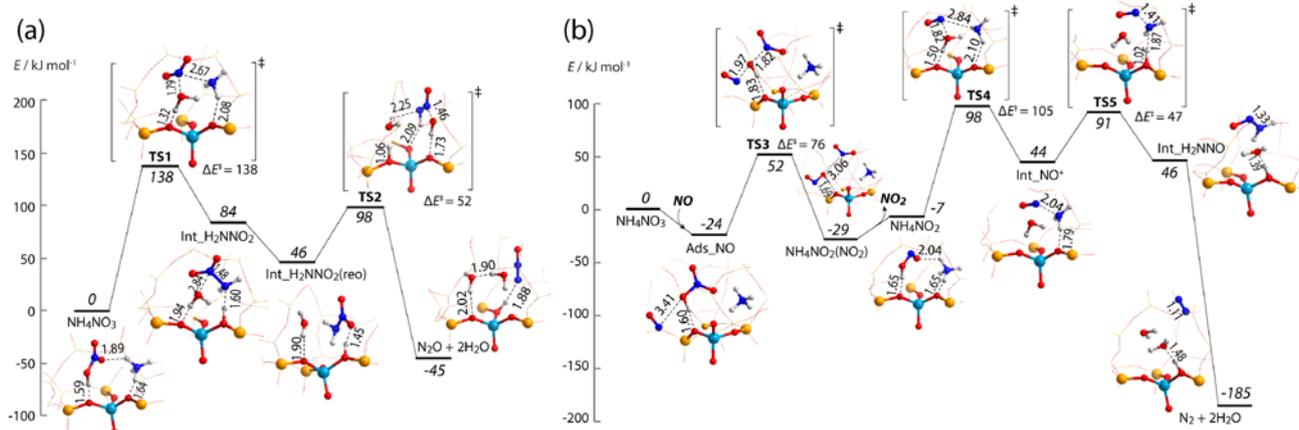
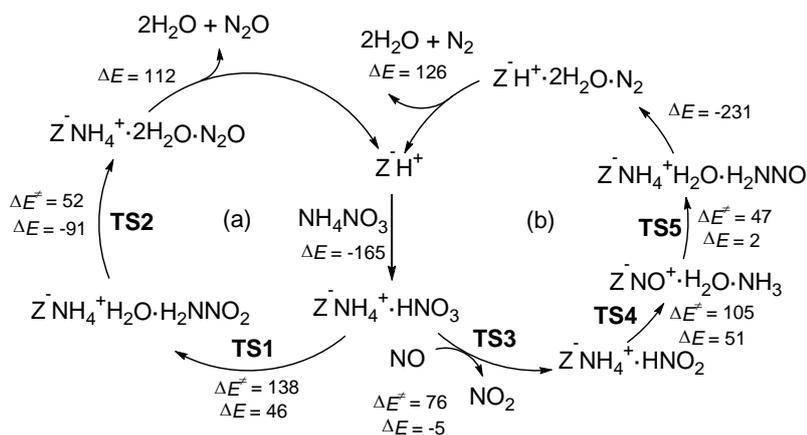


Figure 9. Energy profiles for the decomposition of  $\text{NH}_4\text{NO}_3$  on the protonic H-AFX zeolite: (a) direct decomposition of  $\text{NH}_4\text{NO}_3$  and (b) NO-assisted  $\text{NH}_4\text{NO}_3$  decomposition via an  $\text{NH}_4\text{NO}_2$  intermediate. Atomic distances are in Å.

The NO-assisted  $\text{NH}_4\text{NO}_3$  decomposition was subsequently investigated and compared (Figure 9b). Based on our experimental evidence, it was assumed that NO first reacts with  $\text{NH}_4\text{NO}_3$  to generate  $\text{NO}_2$  and  $\text{NH}_4\text{NO}_2$ , which then decomposes into  $\text{N}_2$  and  $\text{H}_2\text{O}$ . The DFT results suggest that the production of  $\text{NH}_4\text{NO}_2$  is

realized by the hydroxyl group transfer from the protonated nitrate group ( $\text{HNO}_3$ ) to the adsorbed NO, which generates nitrous acid ( $\text{HNO}_2$ ) and free  $\text{NO}_2$  ( $\text{HNO}_3 + \text{NO} \rightarrow \text{HNO}_2 + \text{NO}_2$ ). This reaction passes through TS3 with an activation barrier of 76 kJ/mol. The release of  $\text{NO}_2$  leads to the formation of  $\text{HNO}_2$  and  $\text{NH}_4^+$  stabilized at the negative oxygen sites of zeolite, which can be considered as equivalent to adsorbed  $\text{NH}_4\text{NO}_2$  with its nitrite group protonated by the BAS. During the conversion from ammonium nitrate to nitrite, the  $\text{NH}_4^+$  moiety is not directly involved but rather acts as a spectator. The following decomposition reaction of the  $\text{NH}_4\text{NO}_2$  is similar to that of  $\text{NH}_4\text{NO}_3$ , although the activation barrier for the first dehydration is much lower (TS4,  $\Delta E^\ddagger = 105$  kJ/mol) than for  $\text{NH}_4\text{NO}_3$  (TS1,  $\Delta E^\ddagger = 138$  kJ/mol). In contrast to  $\text{NH}_4\text{NO}_3$  decomposition, in which  $\text{H}_2\text{NNO}_2$  is produced in a single elementary step, the decomposition of  $\text{NH}_4\text{NO}_2$  to  $\text{H}_2\text{NNO}$  occurs via a stepwise mechanism, in which  $\text{NO}^+$  intermediate is formed (Int\_  $\text{NO}^+$  in Figure 9b). The cationic nature of this  $\text{NO}^+$  intermediate was confirmed by Bader charge analysis (Figure S7). Compared with free gaseous NO ( $Q_{\text{N}} = +0.52$  e) or adsorbed NO in a siliceous AFX framework ( $Q_{\text{N}} = +0.50$  e), this  $\text{NO}^+$  possesses a much higher positive charge on the terminal N ( $Q_{\text{N}} = +0.80$  e, Int\_  $\text{NO}^+$  in Figure S7), which is similar to the case ( $Q_{\text{N}} = +0.86$  e) when surrounding adsorbed  $\text{NH}_3$  and  $\text{H}_2\text{O}$  were removed and only  $\text{NO}^+$  was present at the negative site of  $1\text{Al}^{3+}$  substituted AFX as charge-compensation cation. Such a  $\text{NO}^+$  intermediate shows a high reactivity towards further reaction with  $\text{NH}_3$ , which requires an activation barrier of only 47 kJ/mol (TS5) to afford an  $\text{H}_2\text{NNO}$  intermediate and a Brønsted proton connected back to the zeolite framework oxygen. The decomposition of  $\text{H}_2\text{NNO}$  subsequently occurs via proton transfers,<sup>50,51</sup> which affords the final products of  $\text{N}_2$  and  $\text{H}_2\text{O}$  with a strong exothermicity. The various reactions of  $\text{NH}_4\text{NO}_3$  over H-AFX are summarized in Scheme 1.

**Scheme 1. DFT-calculated reaction pathways for  $\text{NH}_4\text{NO}_3$  decomposition under (a) non-NO-assisted and (b) NO-assisted conditions during  $\text{NH}_3$ -SCR reaction over H-AFX**



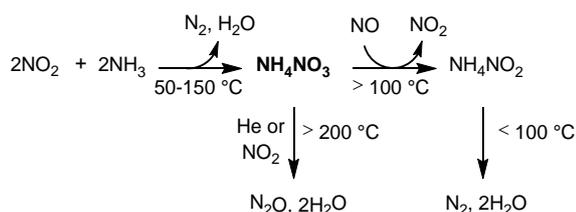
A comparison of the reaction profiles (Figure 9 and Scheme 1) indicates that direct  $\text{NH}_4\text{NO}_3$  decomposition requires a much higher reaction energy barrier than NO-assisted  $\text{NH}_4\text{NO}_3$  decomposition. To further assess temperature and entropy effects, we considered the Gibbs free energies of the key elementary steps (Table S1). These thermodynamic values were calculated using the results of frequency analysis. At a reaction temperature of 150 °C, the computed Gibbs free activation energies are 113 and 96 kJ/mol (TS1 and TS4) for the first dehydration reactions of  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{NO}_2$ , respectively. For the reaction of NO with

NH<sub>4</sub>NO<sub>3</sub>, the Gibbs free energy activation barrier to TS3 was calculated using the reference states of NH<sub>4</sub>NO<sub>3</sub> and gaseous NO. The resulting value of 99 kJ/mol contains significant translational and rotational entropic contributions of free-state NO, as the adsorption process involves a strong negative entropy effect. The Gibbs free energy calculations show that the reaction of NO and NH<sub>4</sub>NO<sub>3</sub> to afford NO<sub>2</sub> and NH<sub>4</sub>NO<sub>2</sub> has a similar energy barrier (99 kJ/mol) to the further dehydration of NH<sub>4</sub>NO<sub>2</sub> (96 kJ/mol). In addition, these free energy barriers are lower than that of the first dehydration reaction of NH<sub>4</sub>NO<sub>3</sub> (113 kJ/mol), which is the rate-determining step in direct NH<sub>4</sub>NO<sub>3</sub> decomposition. These data confirm that NO-assisted NH<sub>4</sub>NO<sub>3</sub> decomposition to produce N<sub>2</sub> is more favorable than direct NH<sub>4</sub>NO<sub>3</sub> decomposition to N<sub>2</sub>O, which is consistent with our experimental observations.

## 2.7 Reaction pathways of NH<sub>3</sub>-SCR over H-AFX zeolite via NH<sub>4</sub>NO<sub>3</sub>

Summarizing the above experimental and theoretical results, the reaction pathways for NH<sub>3</sub>-SCR via NH<sub>4</sub>NO<sub>3</sub> over H-AFX are shown in Scheme 2. The initial important role of the BASs is to store NH<sub>3</sub> by forming NH<sub>4</sub><sup>+</sup>. Following this, the BASs catalytically promote the reaction of the adsorbed NH<sub>3</sub> with NO<sub>2</sub> to yield N<sub>2</sub>, H<sub>2</sub>O, and adsorbed NH<sub>4</sub>NO<sub>3</sub> in the temperature range of 50–150 °C (Figure 6). The rate of NO reduction under the NO<sub>2</sub>-free (standard) SCR conditions is two orders of magnitude lower than the NO<sub>x</sub> reduction rates under fast SCR and NO<sub>2</sub> SCR conditions (Figure 1), possibly because NO<sub>2</sub> formation from BAS-catalyzed NO oxidation is too slow. Hence, the addition of NO<sub>2</sub> significantly enhances the NO<sub>x</sub> reduction rate. When NO is present (in the case of fast SCR conditions), the reduction of NH<sub>4</sub>NO<sub>3</sub> by NO yields gas-phase NO<sub>2</sub> (Figure 8a) and NH<sub>4</sub>NO<sub>2</sub>, which then decompose into N<sub>2</sub> (Figure 8a) and H<sub>2</sub>O at low temperatures. Hence, NH<sub>4</sub>NO<sub>3</sub> accumulation in the zeolite is retarded by NO (Figures 2, 5a, and 9a). NH<sub>3</sub> inhibits this process by blocking the BASs that otherwise serve as active sites for NH<sub>4</sub>NO<sub>3</sub> reduction with NO (Figure 8d). In the absence of NO, NH<sub>4</sub>NO<sub>3</sub> decomposition into N<sub>2</sub>O and H<sub>2</sub>O is catalyzed by BASs above 200 °C (Figures 6, 8b, and 9b). During steady-state fast SCR, the NH<sub>4</sub>NO<sub>3</sub> formed on the catalyst is quickly consumed by reaction with NO, so that NH<sub>4</sub>NO<sub>3</sub> does not accumulate on the catalyst (Figure 2). In the case of NO<sub>2</sub> SCR, the NH<sub>4</sub>NO<sub>3</sub> intermediate cannot react with NO and instead decomposes into N<sub>2</sub>O and H<sub>2</sub>O above 200 °C. Consequently, nearly half the reduced product of steady-state NO<sub>2</sub> SCR is N<sub>2</sub>O. It should be noted that NH<sub>4</sub>NO<sub>3</sub> may be continuously accumulated on the catalyst below 200 °C, which makes it difficult to measure the steady-state reaction rates of the NO<sub>2</sub> SCR in this temperature range. In the case of the metal-exchanged SCR catalyst, Cu (or Fe) sites catalyze the oxidation of NO to NO<sub>2</sub>, which results in higher rates of NH<sub>4</sub><sup>+</sup> consumption under NO + O<sub>2</sub> (Figure 4a). This pathway may contribute to the removal of NO during transient operation of the SCR system.

### Scheme 2. Proposed mechanism for the NH<sub>3</sub>-SCR reaction over H-AFX



### 3. Conclusion

This study investigated the formation and reactions of  $\text{NH}_4\text{NO}_3$  during the transient and steady-state  $\text{NH}_3$ -SCR of  $\text{NO}_x$  over H-AFX zeolites using *operando* IR spectroscopy, kinetics analysis and DFT calculations. Steady-state kinetics demonstrates that the SCR of  $\text{NO}_2$  or  $\text{NO}/\text{NO}_2$  mixture is more than two orders of magnitude faster than the SCR of  $\text{NO}$ . In the case of SCR involving  $\text{NO}_2$  over H-AFX, BASs play an essential role by promoting the reaction of the adsorbed  $\text{NH}_3$  with  $\text{NO}_2$  to yield  $\text{N}_2$ ,  $\text{H}_2\text{O}$ , and adsorbed  $\text{NH}_4\text{NO}_3$  at low temperatures (50–150 °C). Transient *operando* IR and DFT studies suggest that, when  $\text{NO}$  is present,  $\text{NH}_4\text{NO}_3$  is reduced by  $\text{NO}$  to yield  $\text{NO}_2$  and  $\text{NH}_4\text{NO}_2$ , after which  $\text{NH}_4\text{NO}_2$  decomposes into  $\text{N}_2$  and  $\text{H}_2\text{O}$ . Thus,  $\text{NH}_4\text{NO}_3$  accumulation in the zeolite is retarded by the presence of  $\text{NO}$ . In the absence of  $\text{NO}$ , the decomposition of  $\text{NH}_4\text{NO}_3$  into  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$  is more difficult, which only occurs at high temperatures (> 200 °C) with the assistance of BASs. A comparison of the SCR performance between H-AFX and Cu-AFX suggests that Cu sites only promote  $\text{NH}_3$ -SCR under  $\text{NO} + \text{O}_2$  but show a negative effect under  $\text{NO}_2 + \text{O}_2$ , indicating that BASs rather than Cu sites are active for the reduction of  $\text{NO}_2$  by adsorbed  $\text{NH}_3$ . The presented results emphasize the essential roles of BASs and  $\text{NO}_2$  in the SCR over zeolite catalysts.

### Author Information

Corresponding authors

\*E-mail for K.S.: [kshimizu@cat.hokudai.ac.jp](mailto:kshimizu@cat.hokudai.ac.jp).

\*E-mail for C.L.: [chongliu@cat.hokudai.ac.jp](mailto:chongliu@cat.hokudai.ac.jp).

### Associated Content

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at <http://pubs.acs.org>.

Experimental details for sample preparation,  $\text{NH}_3$ -SCR reactions, *in situ* IR and on-line MS, and temperature-programmed surface reaction (TPSR) experiments; details regarding DFT calculations; additional theoretical results.

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