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Formation and Reactions of NH₄NO₃ during Transient and Steady-state NH₃–SCR of NOₓ over H-AFX Zeolites: Spectroscopic and Theoretical Studies

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ABSTRACT

Operando infrared (IR) spectroscopy and density functional theory (DFT) calculations were combined to investigate the selective catalytic reduction (SCR) of NOₓ by NH₃ over H-AFX zeolites. The steady-state kinetics shows that SCR reactions involving NO₂ proceed much more rapidly than those of 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 NO₂ with NH₃ to form N₂, H₂O and NH₄NO₃ at low temperatures (50–150 °C). Combined with DFT results, these data suggest that NO promotes the reduction of NH₄NO₃ to NH₄NO₂, which then decomposes into N₂ and H₂O. Therefore, the accumulation of NH₄NO₃ in the zeolite is inhibited by NO. Furthermore, when NO is absent, NH₄NO₃ decomposition into N₂O and H₂O 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 NO₂ by NH₃, and that BASs are responsible for the NH₃–SCR reactions involving NO₂.

KEYWORDS: NH₃–SCR, AFX zeolite, kinetics study, in situ/operando IR, DFT calculation
1. Introduction

The selective catalytic reduction of nitrogen oxides (NO\textsubscript{x}) by NH\textsubscript{3} (NH\textsubscript{3}–SCR) is widely used to control NO\textsubscript{x} emissions from stationary and mobile sources, including diesel vehicles\textsuperscript{1–4}. 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\textsubscript{3} in the presence of oxygen in so-called standard SCR\textsuperscript{1,2,5}. The associated reaction is

\[
4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad \text{(1)}
\]

Since the commercialization of Cu-exchanged chabazites (Cu-CHA) for use in NO\textsubscript{x} after-treatment systems\textsuperscript{6,7}, 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).\textsuperscript{1–3,5,8} 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\textsuperscript{9}.

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\textsubscript{2}, which has an important effect on the efficiency of the NH\textsubscript{3}–SCR process\textsuperscript{10–21}. In the case of both H-\textsuperscript{10,11,14} and Fe-exchanged\textsuperscript{15–17} zeolites as well as V-based catalysts\textsuperscript{18,19}, the SCR activity is significantly enhanced at an NO\textsubscript{2}/NO molar ratio of 1/1 (representing the so-called fast SCR reaction). The associated reaction is

\[
2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \quad \text{(2)}
\]

In addition, the catalytic reduction of NO\textsubscript{2} by NH\textsubscript{3} can occur without the presence of NO.\textsuperscript{15} In the case that the N\textsubscript{2} selectivity of this reaction is 100%, the process is termed NO\textsubscript{2} SCR or slow SCR\textsuperscript{1} and can be summarized as

\[
8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \quad \text{(3)}
\]

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

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

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).\textsuperscript{28,29} Cu-modified AFX zeolites have recently attracted much
attention as effective catalysts for the NH$_3$–SCR reactions. The AFX zeolites referred to as SSZ-16 have typically been synthesized using a flexible organic structure-directing agent (OSDA). Recently, Kubota and co-workers developed a highly durable AFX zeolite using a bulky, non-flexible OSDA (TEBOP$^{2+}$). 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 NO$_2$ in NH$_3$–SCR under both steady-state and transient conditions. Herein, we propose mechanisms for the transformation of NO$_2$ to N$_2$ or N$_2$O via NH$_4$NO$_3$ over H-AFX on the basis of the experimental evidence. Subsequently, we discuss molecular-level insights into the roles of BASs and NO$_2$ based on the theoretical results. The mechanism uncovered herein is expected to assist in achieving rational control of NH$_4$NO$_3$ deposition and N$_2$O emissions during NH$_3$–SCR in practical systems.

2. Results and Discussion

2.1 NO$_2$ effect on steady-state SCR over H-AFX

To explore the effect of NO$_2$ on the SCR reaction rate over the H-AFX catalyst, we carried out steady-state catalytic experiments under standard SCR (NO$_2$/NO$_x$ = 0), fast SCR (NO$_2$/NO$_x$ = 1/2) and NO$_2$ SCR (NO$_2$/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 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 NO$_2$/NO$_x$ ratio was increased, the NO$_x$ reduction rates at 200 °C increased in the following order: 0.02 mmol g$^{-1}$ h$^{-1}$ (NO$_2$/NO$_x$ = 0), 2.89 mmol g$^{-1}$ h$^{-1}$ (NO$_2$/NO$_x$ = 1/2), 27.36 mmol g$^{-1}$ h$^{-1}$ (NO$_2$/NO$_x$ = 1). It is noteworthy that the NO$_x$ reduction rates obtained using the fast SCR and 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 NH$_3$–SCR over H-ZSM-5, in which the rate of the NO$_2$ SCR process is several hundred times higher than that of the standard SCR rate.

Figure 1 presents Arrhenius plots with estimated apparent activation energies ($E_a$) for the standard, fast and NO$_2$ SCR reactions. The reaction rates were determined under conditions using NO$_x$ and 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 kJ mol$^{-1}$, which is larger than the literature value for standard SCR over H-ZSM-5 (56.4 kJ mol$^{-1}$). For fast SCR, there are two kinetic regimes with distinct apparent activation energies. The $E_a$ is 59 kJ mol$^{-1}$ in the high-temperature regime (275–350 °C). Unusually low apparent activation energies for fast SCR at 150–225 °C (12 kJ mol$^{-1}$) and NO$_2$ SCR (3.8 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., and this phenomenon was explained based on dynamic changes in active sites at certain temperatures. The data obtained for NO$_2$ SCR gave the lowest $E_a$ (3.8 kJ mol$^{-1}$). These results indicate that the presence of NO$_2$ in the feed gas decreases the $E_a$, thereby increasing the NO$_x$ reduction rate. With regard to product selectivity, both the standard and fast SCR selectively converted NO$_x$ to N$_2$, whereas half the N was converted to N$_2$O during the NO$_2$ SCR process between 300 and 400 °C. Temperature dependence of NO$_x$ conversion and N$_2$O yields is shown in Figure S1. NO$_2$ SCR produces relatively larger amount of N$_2$O due to
the undesired side reaction of Eqn. (4); N₂O yields for the NO₂ SCR reaction were around 20%, whereas N₂O yields for the standard and fast SCR reactions were below 8%. The generation of a significant amount of N₂O during NO₂ SCR over H-ZSM-5 was previously reported, and is possibly a result of the reaction

\[ 2\text{NO}_2 + 2\text{NH}_3 + \text{O}_2 \rightarrow 2\text{N}_2\text{O} + 3\text{H}_2\text{O}. \] (4)

A separate experiment assessing NO oxidation by H-AFX was also performed. The rate of NO oxidation to NO₂ at 230 °C was found to be 0.12 mmol g⁻¹ h⁻¹, which is close to that obtained from the standard SCR reaction (0.11 mmol g⁻¹ h⁻¹). Because both fast SCR and NO₂ SCR gave higher rates than standard SCR, it is likely that NO₂ 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 NO₂ SCR over H-AFX zeolites.

2.2 Surface species during standard, fast and NO₂ SCR
**Figure 2. In situ** IR spectra of adsorbed species on H-AFX (40 mg) during standard, fast and NO₂ SCR at 150 °C.

In situ IR spectroscopy was used to characterize the surface species generated during standard, fast and NO₂ 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 NH₃ adsorbed on the BASs (NH₄⁺ on zeolite oxygen, designated as B-NH₃) were observed at 1430, 2800, 3020 and 3260 cm⁻¹ during both the standard and fast SCR reactions. In the case of standard SCR, a band most likely attributable to adsorbed NO₂ was initially observed at 1640 cm⁻¹ but decreased in intensity over time. Under the steady-state standard SCR conditions (t = 60 min), B-NH₃ was evidently the dominant adsorbed species. During fast SCR, the amount of adsorbed NO₂ (associated with a peak at 1640 cm⁻¹) increased with reaction time, and both B-NH₃ and adsorbed NO₂ 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⁻¹ were observed during NO₂ SCR. Based on previous reports, these bands are assigned to NH₄NO₃ accumulated on the catalyst. The bands resulting from the N–H stretching vibrations of NH₄⁺ (at 2800, 3020, and 3250 cm⁻¹) in the NO₂ SCR spectra are similar to those produced during standard and fast SCR, indicating that B-NH₃ sites are also present in the catalyst under the NO₂ SCR conditions. After 60 min, a band at 1750 cm⁻¹ was observed, likely due to N₂O₄ species.

2.3 Transient reaction of adsorbed NH₃ with NOₓ + O₂ 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% NH3 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 + O2 or NO2 + O2 (Figure 3). After purging with He, a peak attributed to B-NH3 sites at 1430 cm\(^{-1}\) was observed, while a band due to NH3 adsorbed on Lewis acid sites (at approximately 1620 cm\(^{-1}\)) was not. During exposure to the NO + O2 flow (Figure 3a), the B-NH3 band was relatively constant for 1000 s, after which the peak intensity decreased with time. Simultaneously, an MS signal corresponding to N2 (m/e = 28) was observed. It should be noted that the intensity of this MS peak for N2 corresponded to the relative rate of N2 formation. The formation of N2 continued until the adsorbed NH3 was completely consumed. The evident induction period of 1000 s may have been due to the blocking of active sites (Brønsted acid sites) by NH3.37

When the NH3-exposed H-AFX was treated with a flow of NO2 + O2 for 1000 s (Figure 3b), IR peaks assignable to NH4NO3 (NH4+ at 1420 cm\(^{-1}\) and NO3- at 1380 cm\(^{-1}\)) appeared. Based on reference spectra for NH3 on BASs (B-NH3) and NH4NO3, the peaks in the range of 1365-1560 cm\(^{-1}\) 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-NH3 band decreased in conjunction with N2 formation and the accumulation of NH2NO3. The maximum intensity of the N2 signal, which reflects the initial rate of N2 formation, is higher under the NO2 + O2 mixture compared to the NO + O2 trial, indicating that the reduction of NOx by adsorbed NH3 is faster under NO2 + O2. Taking into account the fact that NO2 is produced by NO + O2 on the BASs of zeolites,16 the formation of N2 over H-AFX is interpreted as the reduction of NOx by adsorbed NH3 to yield N2. As noted above, the rate of the oxidation of NO to NO2 on H-AFX is relatively slow, such that the transient rate of N2 formation under NO + O2 is slower than under NO2 + O2.
Figure 3. *In situ* IR spectra (left) of adsorbed species on H-AFX during the reaction of adsorbed NH$_3$ with NO$_x$ at 230 °C (a) under 500 ppm NO + 10% O$_2$ and (b) under 500 ppm NO$_2$ + 10% 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 N$_2$.

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

In contrast to the results for H-AFX (Figure 3), the transient reaction of B-NH$_3$ under NO$_2$ + O$_2$ over the Cu-AFX was much slower than the reaction under NO + O$_2$ (Figure 4). In the case of the Cu-AFX, lower rates of both B-NH$_3$ consumption and N$_2$ formation were observed under NO$_2$ + O$_2$ compared to under NO + O$_2$. The completion of N$_2$ formation under NO$_2$ + O$_2$ required more than 2000 s, while N$_2$ formation was complete within 800 s under NO + O$_2$. A comparison of the results for the SCR reactions over H-AFX and Cu-AFX in the presence of NO$_2$ (Figure 3b vs. Figure 4b) indicates that the Cu sites show a negative effect on the transient reaction of adsorbed NH$_3$ under NO$_2$ + O$_2$. This implies that the BASs serve as active sites for the reduction of NO$_2$ by adsorbed 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 + O₂ (Figure 3a vs. Figure 4a) indicates that the Cu-AFX provides a higher N₂ formation rate and more rapid B-NH₃ consumption than the H-AFX, possibly due to a higher rate of NO oxidation to NO₂ on Cu sites than on H⁺ sites. The N₂ formation for the NH₃-adsorbed Cu-AFX under NO + O₂ (Figure 4b) can be explained by the following two pathways. One is the H⁺-catalyzed reduction of NO₂ by adsorbed NH₃. Taking into account that Cu sites can catalyze NO₂ decomposition to O₂ and NO,²⁶ another possibility is the Cu-catalyzed NO₂ decomposition to give NO which is then reduced by adsorbed NH₃ over Cu sites.

Additionally, IR bands due to nitrate species on Cu²⁺ sites were observed at 1570, 1596, and 1620 cm⁻¹ in the spectrum obtained from the Cu-AFX under the NO₂ + O₂ mixture (Figures 4b and S3). The accumulation of these nitrates on the Cu-AFX catalyst suggests that the reaction of B-NH₃ 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.²⁹,⁴⁰ Nevertheless, recent time-resolved IR⁴⁰ and X-ray absorption spectroscopy (XAS)⁴¹ 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 NH₃ with NOₓ at 230 °C (a) under 500 ppm NO + 10% O₂ and (b) under 500 ppm NO₂ + 10% O₂. The right figures show the
time dependence of the IR peak areas for surface species and the MS signal intensity for N₂.

2.4 Transient reaction of adsorbed NH₃ with NOₓ on H-AFX

We subsequently studied the H-AFX catalyzed reaction of B-NH₃ with NOₓ in the absence of O₂. Transient experiments were performed at 150 °C using NH₃-exposed H-AFX with a flow of NO + NO₂ or NO₂ (Figure 5). Under NO + NO₂, B-NH₃ was consumed by NO + NO₂ to yield N₂ after an induction period of 500 s. In contrast, the reaction under NO₂ shows a higher rate of N₂ production such that significant amounts of NH₄NO₃ were accumulated on H-AFX. The absence of NH₄NO₃ accumulation under the NO + NO₂ flow suggests that NO promoted the decomposition of NH₄NO₃ or inhibited the formation of NH₄NO₃. The experimental observations suggest that NH₃ adsorbed on H⁺ sites reacted with NO₂ to produce N₂ and NH₄NO₃ (Eqn. (5)). The resulting NH₄NO₃ was further able to react with NO to yield N₂, NO₂ and H₂O (Eqn. (6)).

\[
\begin{align*}
2\text{NH}_3\text{ad} + 2\text{NO}_2 & \rightarrow \text{N}_2 + \text{NH}_4\text{NO}_3 + \text{H}_2\text{O} \\
\text{NH}_4\text{NO}_3 + \text{NO} & \rightarrow \text{N}_2 + \text{NO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

Figure 5. In situ IR spectra (left) of adsorbed species on H-AFX during the reaction of adsorbed NH₃ at 150 °C (a) under 250 ppm NO + 250 ppm NO₂ and (b) under 500 ppm NO₂. The right figures show the time dependence of the IR peak area for surface species and the intensity of the MS signal for N₂.
To understand the effect of temperature on reaction (5), we studied the temperature-programmed surface reaction (TPSR) of adsorbed NH₃ on H-AFX under a flow of NO₂ (Figure 6). In these trials, an IR H-AFX disc was first exposed to 0.1% NH₃ for 0.5 h at 30 °C, followed by purging with He. The catalyst was subsequently heated to 500 °C at 10 °C min⁻¹ under 500 ppm NO₂. The adsorbed species and effluent gases were monitored by IR and MS, respectively. Above 50 °C, B-NH₃ consumption, N₂ formation, and NH₄NO₃ accumulation on the H-AFX were observed simultaneously. At 280 °C, NH₄NO₃ consumption and N₂O formation occurred simultaneously. These results show that reaction (5) occurs at temperature range of 50–150 °C. The reaction pathways for NH₄NO₃ conversion to N₂O and for the decomposition of NH₄NO₃ with NO to yield N₂ (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 NH₃ under 500 ppm NO₂ over H-AFX, pre-exposed to 500 ppm NH₃ 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 N₂.**

2.5 Conversion of NH₄NO₃ to N₂ or N₂O

To provide direct evidence for reaction (6), we carried out *in situ* IR analyses of NH₄NO₃-loaded H-AFX under a flow of NO at elevated temperatures. Based on a literature method,²³,₄₄,₄₅ NH₄NO₃-loaded H-AFX (NH₄NO₃ loading of 1 mmol g⁻¹) was prepared by the impregnation method, via adding 200 μL of a 0.2 M NH₄NO₃ 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 NH₄NO₃-impregnated H-AFX at 30 °C under He, the IR cell was heated (10 °C min⁻¹) under a flow of 500 ppm NO/He. Figure 7 shows the IR difference spectra of the NH₄NO₃-impregnated H-AFX at various temperatures. The negative peaks appearing at 1420, 1380, 3020 and 3260 cm⁻¹ as the temperature increases indicate the consumption of adsorbed NH₄NO₃. Above 200 °C, the intensity of the negative peaks leveled off. The NO-assisted decomposition of NH₄NO₃ on SCR catalysts has also been observed in previous studies.⁴³,⁴₆

In the case of the NH₄NO₃-impregnated H-AFX, the shapes of the negative peaks are close to those of the positive bands that appear when NH₃-exposed H-AFX is treated with a flow of NO₂ (Figure S4). This result suggests that the NH₄NO₃ impregnated into the H-AFX is essentially the same as the NH₄NO₃ formed by the reaction of NO₂ with NH₃. We also compared the IR spectra of physical mixtures of NH₄NO₃ and H-AFX, in
which the NH₄NO₃ particles primarily present at the external surfaces of the H-AFX. A comparison of the IR spectra (Figure S4) suggests that the physically mixed NH₄NO₃ affords different spectroscopic features to the material obtained from an NH₃ + NO₂ flow or the impregnated NH₄NO₃, indicative of the different adsorption states in these specimens. The NH₄NO₃ species generated from the reaction of NH₃ and NO₂ or impregnated from an NH₄NO₃ 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 NH₄NO₃ sample prepared via impregnation is a better representation of the state of accumulated NH₄NO₃ during NH₃–SCR over H-AFX. Thus, we used such a sample in further TPSR trials as a model of the reaction of NH₄NO₃ inside the H-AFX zeolite. For these experiments, the amount of impregnated NH₄NO₃ (1.0 mmol g⁻¹) is less than the concentration of Al atoms in the H-AFX catalyst (2.7 mmol g⁻¹), so as to avoid over-loading of NH₄NO₃ at the external surfaces of the zeolite.

Figure 7. In situ IR spectra of 1 mmol g⁻¹ NH₄NO₃-loaded H-AFX (40 mg) during heating from 30 to 500 °C at 10 °C min⁻¹ under 500 ppm NO.

In a separate flow reactor, TPSR experiments involving NH₄NO₃(1 mmol g⁻¹)-impregnated H-AFX (in powder form) were carried out under flows of various gas mixtures (Figure 8). The concentrations of both N₂ and N₂O in the effluent gas were quantified using MS. Because NO₂ was quantified by IR using a long pathlength (8 m) gas cell, the time response for NO₂ data was slower than those for the other gases. The results obtained under a flow of NO (Figure 8a) confirm the formation of N₂ and NO₂ over the temperature range of 50-200 °C. Note that the slow decay of the signal associated with the NO₂ concentration above 200 °C can be ascribed to the slower response of the IR detector compared to the MS instrument. The formation of NO₂ indicates that NH₄NO₃ is reduced by NO to yield NO₂ and ammonium nitrite (NH₄NO₂), which is consistent with the pathway proposed by Weitz et al.⁴³,⁴⁷,⁴⁸ It is also well known that NH₄NO₂ readily decomposes to N₂ and H₂O at low temperatures (≤ 100 °C).⁴⁷,⁴⁸ Combined with the corresponding IR results in Figure 7, these data indicate that reaction (6) is actually the combination of the following two reactions.

\[
\text{NH}_4\text{NO}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{NH}_4\text{NO}_2 \quad (7)
\]

\[
\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \quad (8)
\]

In the absence of NO, the decomposition of NH₄NO₃ can afford N₂O⁴²,⁴⁹ and the TPSR profile (Figure 8b) obtained under a He flow in the absence of NO shows N₂O formation between 200 and 350 °C with only a trace amount of N₂. This indicates that N₂O was produced via the decomposition of NH₄NO₃ in the absence of NO, as in the following reaction (Eqn. (9)).⁴²

\[
\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O} \quad (9)
\]
The TPSR profile acquired under NO\textsubscript{2} flow (Figure 8c) shows that N\textsubscript{2}O was the main product. This can be explained by considering that NO\textsubscript{2} decomposition to NO and O\textsubscript{2} is slow over H-AFX, such that reaction (9) proceeds more rapidly than reaction (7).

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

Figure 8. The TPSR profiles obtained using 1 mmol g\textsuperscript{-1} NH\textsubscript{4}NO\textsubscript{3}-loaded H-AFX (40 mg) during heating from 30 to 400 °C at 10 °C min\textsuperscript{-1} under (a) 500 ppm NO, (b) He, (c) 500 ppm NO\textsubscript{2} and (d) 500 ppm NO + 500 ppm NH\textsubscript{3}.
2.6 DFT study on NH₄NO₃ decomposition

To provide molecular-level insights into the elementary steps of NH₄NO₃ conversion over H-AFX, we further performed DFT calculations using a 48T hexagonal unit cell (Figure S5). The formation of N₂O from NH₄NO₃ was initially investigated (Figure 9a). The adsorption of NH₄NO₃ on the protonic H-AFX zeolite was found to result in the proton transfer from the BAS to the nitrate moiety, giving HNO₃ and NH₄⁺. These species in turn are stabilized by hydrogen-bonding interactions at the negative oxygen sites of the zeolite framework. The decomposition of NH₄NO₃ into N₂O proceeds via two sequential dehydration reactions. The first dehydration occurs via a proton transfer from NH₄⁺ to the OH moiety of the protonated nitrate group, which produces the H₂NNO₂ intermediate with simultaneous proton back-donation to the zeolite framework oxygen (Int_H₂NNO₂). 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 NO₂ moiety interacts with the NH₃ fragment at an N–N distance (d_{N–N}) of 2.67 Å. The production of the H₂NNO₂ intermediate is accompanied by N–N bond formation (d_{N–N} = 1.48 Å) and the regeneration of a BAS. The reorientation of the H₂NNO₂ intermediate (Int_H₂NNO₂(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 H₂NNO₂ via TS2 proceeds with an activation barrier of 52 kJ/mol, and the production of N₂O significantly stabilizes the system by -91 kJ/mol. During the BAS-catalyzed decomposition of NH₄NO₃ into N₂O and H₂O, the first dehydration producing the H₂NNO₂ intermediate is the rate-determining step, with an activation barrier of 138 kJ/mol. When H-AFX is absent, the non-catalytic decomposition of NH₄NO₃ 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 NH₄NO₃ into N₂O.

![Figure 9. Energy profiles for the decomposition of NH₄NO₃ on the protonic H-AFX zeolite: (a) direct decomposition of NH₄NO₃ and (b) NO-assisted NH₄NO₃ decomposition via an NH₂NNO₂ intermediate. Atomic distances are in Å.](image)

The NO-assisted NH₄NO₃ decomposition was subsequently investigated and compared (Figure 9b). Based on our experimental evidence, it was assumed that NO first reacts with NH₄NO₃ to generate NO₂ and NH₂NNO₂, which then decomposes into N₂ and H₂O. The DFT results suggest that the production of NH₂NNO₂ is
realized by the hydroxyl group transfer from the protonated nitrate group (HNO$_3$) to the adsorbed NO, which generates nitrous acid (HNO$_2$) and free NO$_2$ (HNO$_3$ + NO → HNO$_2$ + NO$_2$). This reaction passes through TS3 with an activation barrier of 76 kJ/mol. The release of NO$_2$ leads to the formation of HNO$_2$ and NH$_4^+$ stabilized at the negative oxygen sites of zeolite, which can be considered as equivalent to adsorbed NH$_4$NO$_2$ with its nitrite group protonated by the BAS. During the conversion from ammonium nitrate to nitrite, the NH$_4^+$ moiety is not directly involved but rather acts as a spectator. The following decomposition reaction of the NH$_4$NO$_2$ is similar to that of NH$_4$NO$_3$, although the activation barrier for the first dehydration is much lower (TS4, $\Delta E^\neq = 105$ kJ/mol) than for NH$_4$NO$_3$ (TS1, $\Delta E^\neq = 138$ kJ/mol). In contrast to NH$_4$NO$_3$ decomposition, in which H$_2$NNO$_2$ is produced in a single elementary step, the decomposition of NH$_4$NO$_2$ to H$_2$NNO occurs via a stepwise mechanism, in which NO$^-$ intermediate is formed (Int$_{\text{NO}^-}$ in Figure 9b). The cationic nature of this NO$^+$ intermediate was confirmed by Bader charge analysis (Figure S7). Compared with free gaseous NO ($Q_N = +0.52$ e) or adsorbed NO in a siliceous AFX framework ($Q_N = +0.50$ e), this NO$^+$ possesses a much higher positive charge on the terminal N ($Q_N = +0.80$ e, Int$_{\text{NO}^+}$ in Figure S7), which is similar to the case ($Q_N = +0.86$ e) when surrounding adsorbed NH$_3$ and H$_2$O were removed and only NO$^+$ was present at the negative site of 1Al$^{3+}$ substituted AFX as charge-compensation cation. Such a NO$^+$ intermediate shows a high reactivity towards further reaction with NH$_3$, which requires an activation barrier of only 47 kJ/mol (TS5) to afford an H$_2$NNO intermediate and a Brønsted proton connected back to the zeolite framework oxygen. The decomposition of H$_2$NNO subsequently occurs via proton transfers,$^{50,51}$ which affords the final products of N$_2$ and H$_2$O with a strong exothermicity. The various reactions of NH$_4$NO$_3$ over H-AFX are summarized in Scheme 1.

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

A comparison of the reaction profiles (Figure 9 and Scheme 1) indicates that direct NH$_4$NO$_3$ decomposition requires a much higher reaction energy barrier than NO-assisted NH$_4$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 NH$_4$NO$_3$ and NH$_4$NO$_2$, respectively. For the reaction of NO with
NH₄NO₃, the Gibbs free energy activation barrier to TS3 was calculated using the reference states of NH₄NO₃ 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 NH₄NO₃ to afford NO₂ and NH₄NO₂ has a similar energy barrier (99 kJ/mol) to the further dehydration of NH₂NO₂ (96 kJ/mol). In addition, these free energy barriers are lower than that of the first dehydration reaction of NH₄NO₃ (113 kJ/mol), which is the rate-determining step in direct NH₄NO₃ decomposition. These data confirm that NO-assisted NH₄NO₃ decomposition to produce N₂ is more favorable than direct NH₄NO₃ decomposition to N₂O, which is consistent with our experimental observations.

2.7 Reaction pathways of NH₃–SCR over H-AFX zeolite via NH₄NO₃

Summarizing the above experimental and theoretical results, the reaction pathways for NH₃–SCR via NH₄NO₃ over H-AFX are shown in Scheme 2. The initial important role of the BASs is to store NH₃ by forming NH₄⁺. Following this, the BASs catalytically promote the reaction of the adsorbed NH₃ with NO₂ to yield N₂, H₂O, and adsorbed NH₂NO₃ in the temperature range of 50–150 °C (Figure 6). The rate of NO reduction under the NO₂-free (standard) SCR conditions is two orders of magnitude lower than the NO₃ reduction rates under fast SCR and NO₂ SCR conditions (Figure 1), possibly because NO₂ formation from BAS-catalyzed NO oxidation is too slow. Hence, the addition of NO₂ significantly enhances the NO₃ reduction rate. When NO is present (in the case of fast SCR conditions), the reduction of NH₄NO₃ by NO yields gas-phase NO₂ (Figure 8a) and NH₄NO₂, which then decompose into N₂ (Figure 8a) and H₂O at low temperatures. Hence, NH₄NO₃ accumulation in the zeolite is retarded by NO (Figures 2, 5a, and 9a). NH₃ inhibits this process by blocking the BASs that otherwise serve as active sites for NH₄NO₃ reduction with NO (Figure 8d). In the absence of NO, NH₂NO₃ decomposition into N₂O and H₂O is catalyzed by BASs above 200 °C (Figures 6, 8b, and 9b). During steady-state fast SCR, the NH₄NO₃ formed on the catalyst is quickly consumed by reaction with NO, so that NH₂NO₃ does not accumulate on the catalyst (Figure 2). In the case of NO₂ SCR, the NH₄NO₃ intermediate cannot react with NO and instead decomposes into N₂O and H₂O above 200 °C. Consequently, nearly half the reduced product of steady-state NO₂ SCR is N₂O. It should be noted that NH₄NO₃ may be continuously accumulated on the catalyst below 200 °C, which makes it difficult to measure the steady-state reaction rates of the NO₂ SCR in this temperature range. In the case of the metal-exchanged SCR catalyst, Cu (or Fe) sites catalyze the oxidation of NO to NO₂, which results in higher rates of NH₄⁺ consumption under NO + O₂ (Figure 4a). This pathway may contribute to the removal of NO during transient operation of the SCR system.

Scheme 2. Proposed mechanism for the NH₃–SCR reaction over H-AFX
3. Conclusion

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

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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, NH$_3$–SCR reactions, \textit{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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