Investigation of the common intermediates over Fe-ZSM-5 in NH₃-SCR reaction at low temperature by *in situ* DRIFTS

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ABSTRACT

The surface species formed in the reaction of NO and NO₂ with pre-adsorbed NH₃ over a Fe-ZSM-5 catalyst (1.27 wt.% Fe, $SiO_2/Al_2O_3 = 25$) at low temperature (140°C) were studied by *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Through using a background spectrum of NH₃-saturated Fe-ZSM-5, we clearly observed the formation of common intermediates resulting from the reaction of NO₂ or NO + O₂ with pre-adsorbed NH₃. This presents strong evidence that the oxidation of NO to form surface nitrates and nitrites is the key step for standard SCR at low temperature. In addition, the results suggest that in the SCR reaction at low temperature, the NH_4^+ ions absorbed on Brønsted acid sites are less active than NH₃ adsorbed on Lewis acid sites related to Fe species.

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Introduction

The selective catalytic reduction of NO$_x$ by ammonia (NH₃-SCR) is an efficient technology for NO$_x$ control in lean-burn vehicles (Johnson and Joshi, 2018). Cu- and Fe-exchanged zeolite catalysts have been studied as NH₃-SCR catalysts for decades. Currently, Cu-SSZ-13 (Cu-exchanged small-pore zeolite) catalysts are the state-of-the-art commercial SCR catalysts for diesel vehicles and have been extensively studied in recent years (Beale et al., 2015). In spite of their outstanding hydrothermal stability and SCR activity, Cu-SSZ-13 catalysts exhibit decreased N₂ selectivity at high temperature above 350°C after hydrothermal aging (Kim et al., 2014). Compared to Cu-exchanged zeolites, Fe-exchanged zeolites (such as Fe-ZSM-5 and Fe-BEA) exhibited outstanding activity and N₂ selectivity at temperatures above 300°C in the standard SCR reaction as indicated in reaction (1) (Devadas et al., 2006).
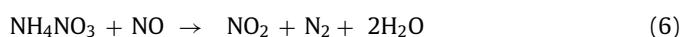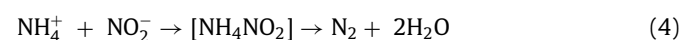
$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{1}$$
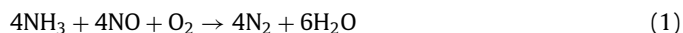
In fact, high activity at low temperatures (≤300°C) is important for application of SCR catalysts in lean-burn vehicle NO$_x$ control. The relatively low activity in the standard SCR reaction at temperatures below 300°C is the main shortcoming of Fe-exchanged zeolites. Increasing the NO₂/NO$_x$ molar ratio to 0.5 is an efficient

way to enhance the low temperature activity of Fe-ZSM-5, due to the occurrence of the fast SCR reaction, as shown in reaction (2) (Devadas et al., 2006; Grossale et al., 2008, 2009; Iwasaki et al., 2009, Iwasaki and Shinjoh, 2010a).

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \tag{2}$$
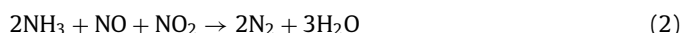
Since the fast SCR reaction is important for enhancing the deNO$_x$ efficiency of Fe-ZSM-5, the mechanism and kinetics of the fast SCR reaction over Fe-ZSM-5 have been extensively studied (Devadas et al., 2006; Grossale et al., 2008, 2009; Iwasaki et al., 2009; Iwasaki and Shinjoh, 2010a; Ruggeri et al., 2012). According to the previous literature, the basic reaction steps over Fe-ZSM-5 in the fast SCR reaction at low temperatures can be summarized as: the disproportion of NO₂ is the first step (reaction (3)), then ammonium nitrite forms and decomposes to N₂ and water as shown in reaction (4). Simultaneously, nitrates react with adsorbed NH₃ to form NH₄NO₃ as indicated in reaction (5). Furthermore, the reduction of NH₄NO₃ by NO as in reaction (6) is considered to be the rate-determining step in the fast SCR reaction over Fe-ZSM-5.

$$2\,NO_2 + O^{2-} \rightarrow NO_3^- + NO_2^- \tag{3}$$

$$NH_4^+ + NO_2^- \rightarrow [NH_4NO_2] \rightarrow N_2 + 2H_2O \tag{4}$$

$$NH_4^+ + NO_3^- \rightarrow NH_4NO_3 \tag{5}$$

$$NH_4NO_3 + NO \rightarrow NO_2 + N_2 + 2H_2O \tag{6}$$

As the SCR mechanisms studies over Fe-ZSM-5 mentioned above show, the ammonium nitrates/nitrites that are formed through the interaction of nitrates/ nitrites with NH_4^+ ions are considered the key intermediates in the SCR reaction (Long and Yang, 2002; Devadas et al., 2006; Grossale et al., 2008, 2009; Iwasaki et al., 2009; Iwasaki and Shinjoh, 2010a; Ruggeri et al., 2012).

On the other hand, it is generally considered that Brønsted acid sites (Si-(OH)-Al) in Fe-ZSM-5 are important to the formation of intermediates through interaction of NH_4^+ ions on Brønsted acid sites with surface nitrates or nitrites. For instance, Long and Yang (2002) observed a marked decrease of NH_4^+ ions on the Brønsted acid sites after passing a flow of NO over NH_3 pre-adsorbed Fe-ZSM-5 in Fourier transform infrared spectrometer (FTIR) experiments. However, besides adsorption on Brønsted acid sites to form NH_4^+, NH_3 can also absorb on Lewis acid sites coordinated with Fe^{3+} and extra-framework Al^{3+} in Fe-zeolites (Schwidder et al., 2008a; Brandenberger et al., 2009). Moreover, Brandenberger et al. (2009) proved that Brønsted acidity is not required for adsorbing or activating ammonia in the standard SCR reaction. The results of Schwidder et al. (2008b) also showed that high reaction rates in standard SCR could be achieved with non-acidic Fe-ZSM-5 (s-Fe-silicalite) in the temperature range of 250-650°C. They considered that the role of Brønsted acid sites could be attributed to the acid-catalyzed decomposition of intermediate NH_4NO_2 to N_2 and H_2O, as proposed by Li et al. (2006). Recently, advances in the study of V_2O_5/TiO_2 SCR catalysts showed that nitric oxide reacts predominantly with NH_3 coordinated to Lewis sites of vanadia, and Brønsted sites are not involved in the catalytic cycle but mainly serve as an NH_3 pool to replenish the Lewis sites (Marberger et al., 2016). Our group proposed a new reaction pathway for V_2O_5/TiO_2 in the standard SCR reaction, whereby the NH_3 coordinates to the vanadyl species and subsequently reacts with NO in the gas phase, resulting in the formation of the intermediate nitrosamide (NH_2NO) (He et al., 2018). Furthermore, Chen et al. (2016) showed evidence for the participation of NH_3 species adsorbed on Lewis sites in SCR reactions over Fe-ZSM-5, where the proton generated by reduction of Fe(III) to Fe(II) can interact with NH_3 on Lewis sites to form the intermediate NH_4^+. Additionally, in the SCR reaction over Fe-ZSM-5, Fe species are considered as redox active sites for NO oxidation to form nitrates/nitrites (a crucial step) and the ion-exchanged Fe^{3+} or monomeric iron species are commonly considered as the most active species (Delahay et al., 2005; Iwasaki et al., 2008; Schwidder et al., 2008b; Brandenberger et al., 2010; You et al., 2020). Delahay et al. (2005) proposed that a Fe^{2+} / Fe^{3+} species redox cycle in the SCR reaction and the re-oxidation of Fe^{2+} species should be the slow step for Fe-ZSM-5 in standard SCR. Thus, the enhancement of NO_x reduction in fast SCR can be attributed to the presence of NO_2, skipping the step of NO oxidation. However, the results of Schwidder et al. (2008b) showed that isolated Fe sites also contributed to the good activity of Fe-ZSM-5 even under fast SCR conditions. Those results inspire us to further study the role of Fe species in the NH_3-SCR reaction over Fe-ZSM-5.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is a useful tool for investigating the surface species on catalysts and is widely used to study reaction intermediates in the NH_3-SCR reaction on Fe-ZSM-5 catalysts. Ruggeri et al. (2012) investigated surface intermediates during NO_2 adsorption on Fe-ZSM-5 with pre-adsorbed NH_3 by *in situ* DRIFTS, and they confirmed the key role of ferric nitrites/nitrates in the reaction pathway, and Fe redox sites involved in the critical reduction of surface nitrates by NO. However, the formation of nitrite intermediates and changes in the Lewis acid sites correlated to Fe sites were not detected in their study.

In this work, a novel approach to the identifying the reaction intermediates on Fe-ZSM-5 in the standard and fast SCR reactions was pursued using *in situ* DRIFTS. By using the spectrum collected on an NH_3-saturated Fe-ZSM-5 sample as background, the surface species dynamics for NH_3 pre-adsorbed Fe-ZSM-5 exposed to NO_2 and NO + O_2 were clearly observed. The possible reaction pathways related to Fe sites as Lewis acid sites and nitrate species adsorption sites were discussed.

1. Materials and methods

1.1. Catalyst preparation

Fe-ZSM-5 was prepared by conventional liquid ion exchange method. The Fe-ZSM-5 catalyst used in this work was the same sample denoted as Fe-HZ in our previous work, which had high percentaged of isolated Fe^{3+} ions in ion exchanged sites (Shi et al., 2015). Typically, 10 g commercial H-ZSM-5 (SiO_2/Al_2O_3 ratio = 25, BET surface area 320 m^2/g) precursor was added to 17.8 g/L $FeCl_2 \cdot 4H_2O$ solution with constant stirring under a continuous flow of N_2 (200 mL/min) in a water bath at 80°C for 24 hr. The resulting powders were calcined at 600°C for 6 hr in air to obtain Fe-ZSM-5 with 1.27 wt.% Fe loading. The activity tests for this Fe-ZSM-5 catalyst in the standard SCR, fast SCR and NO_2 SCR reactions are illustrated in Appendix A Fig. S1. The activity of the parent H-SSZ-13 in fast SCR is shown in Appendix A Fig. S2.

1.2. In situ DRIFT measurements

In situ FTIR experiments were carried out on a FTIR spectrometer (Nexus 670, Nicolet, USA) equipped with an MCT/A detector cooled by liquid nitrogen and an *in situ* DRIFT spectrum reactor cell with ZnSe window. Before the measurements, the Fe-ZSM-5 sample was pretreated at 550°C in a flow of 10 vol.% O_2/N_2 for 30 min to clean the surface, then cooled down to the test temperature of 140°C and purged in N_2 flow. In experiments on $NO/NO_2/NH_3$ adsorption on clean Fe-ZSM-5, the background spectrum was collected on clean Fe-ZSM-5 in a flowing N_2 atmosphere. In the experiments on NO_2 and NO + O_2 exposure to NH_3 pre-adsorbed Fe-ZSM-5, the background spectrum was collected on NH_3-saturated Fe-ZSM-5 in a flowing of N_2 atmosphere.

2. Results and discussion

2.1. NO_x adsorption and NH_3 on clean Fe-ZSM-5

The DRIFTS spectra of NO_x adsorption over Fe-ZSM-5 have been well documented in the literature (Rivallan et al., 2009; Ahrens et al., 2010; Iwasaki and Shinjoh, 2010a, 2010b; Ruggeri et al., 2012). In order to investigate the NOx adsorption states on the present Fe-ZSM-5 catalyst, the sample was exposed to NO_2 and NO + O_2 in N_2 for 60 min and then purged with N_2 for 60 min at 140°C. The bands from adsorbed NO_x species over Fe-ZSM-5 were assigned according to the previous literature (Rivallan et al., 2009; Ahrens et al., 2010; Iwasaki and Shinjoh, 2010b, 2010c; Ruggeri et al., 2012). As shown in Fig. 1a, in the typical range of surface nitrates (1500-1700 cm^{-1}), two common bands at 1630 and 1574 cm^{-1} appeared in NO + O_2 adsorption, which can be assigned to NO_2 groups and nitrate species adsorbed on Fe sites, respectively (Iwasaki and Shinjoh, 2010c). These ferric nitrate species were stable after purging by N_2 flow. The band at 1888 cm^{-1} is assigned to adsorbed NO species present as Fe^{2+}-NO species, and the broad band centered at 2150 cm^{-1} is attributed to nitrosonium ions (NO^+) weakly
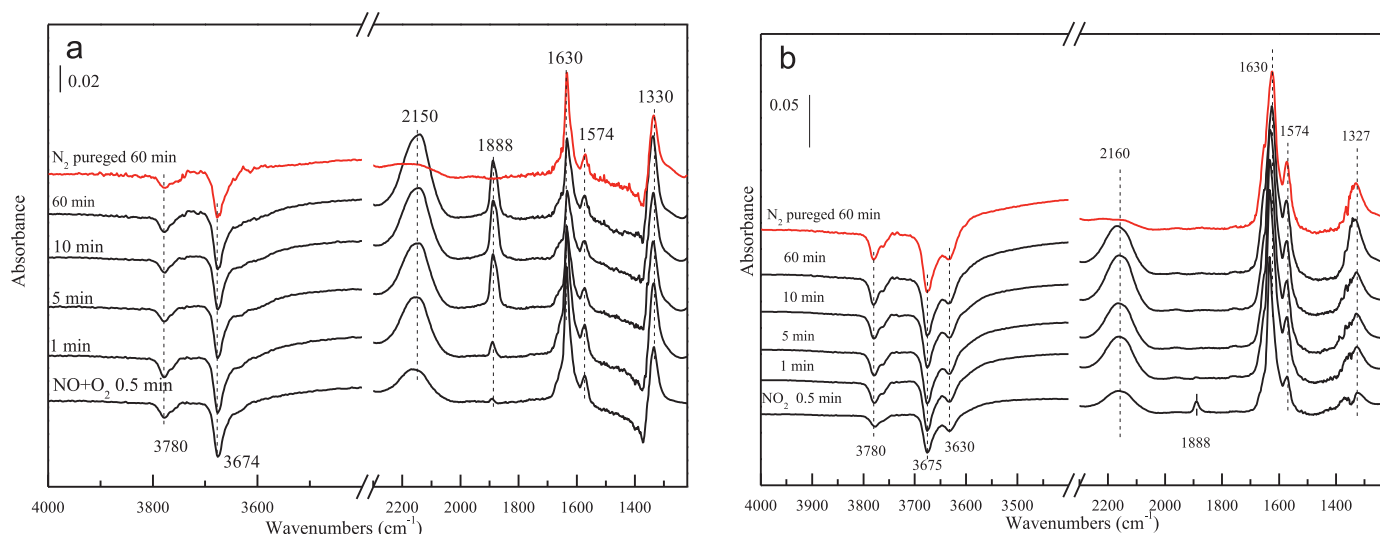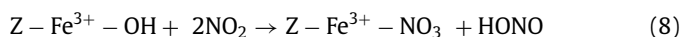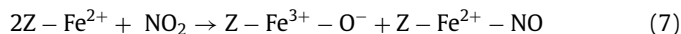
Fig. 1. *In situ* DRIFTS spectra after NO$_x$ adsorption over Fe-ZSM-5 at 140°C: (a) NO + O$_2$ (0.1 vol.% NO, 10 vol.% O$_2$, N$_2$ as balance) and (b) NO$_2$ (0.1 vol.% NO$_2$ in N$_2$).

adsorbed on acid sites (Rivallan et al., 2009; Iwasaki and Shinjoh, 2010c; Malpartida et al., 2010; Ruggeri et al., 2012). The two NO-related bands disappeared after the NO + O$_2$ flow was turned off and the sample was purged by N$_2$. The bands at 1330 cm^{-1} can probably assigned to nitrite groups (NO$_2^-$) (Sun et al., 2002; Iwasaki and Shinjoh, 2010c; Sun et al., 2001). In the OH stretching region (3800-3500 cm^{-1}), the negative bands at 3780 cm^{-1} and 3674 cm^{-1} can be assigned to terminal silanols (Si-OH) and OH groups linked with ion-exchanged Fe (Fe-OH), due to the consumption of Si-OH and Fe-OH sites (Iwasaki and Shinjoh, 2010c).

The NO$_2$ adsorption over clean Fe-ZSM-5 showed similar nitrate bands at 1630 and 1574 cm^{-1} to those observed for NO + O$_2$ adsorption, but with much higher intensity, as shown in Fig. 1b. This confirms that NO$_2$ adsorption over Fe-ZSM-5 formed the same surface species as NO + O$_2$ adsorption. In addition, the higher nitrate concentrations formed in NO$_2$ adsorption indicate that the oxidation of NO to NO$_2$ should benefit the formation of nitrates. However, the NO oxidation activity of Fe-ZSM-5 was relatively low at 140°C. In the OH stretching region, an additional band at 3630 cm^{-1} was detected. It has been reported that the band related to Al-O(H)-Si bridged hydroxyl groups appears at ~3610 cm^{-1}, and our experiments on NH$_3$ adsorption exhibited this band at ~3610 cm^{-1} (Appendix A Fig. S1). Although the band at 3630 cm^{-1} appeared at higher wavenumbers, we tentatively assigned this band to Al-O(H)-Si bridged hydroxyl groups (Brønsted acid), considering that the IR band of Al-O(H)-Si appeared next to that of Fe-OH (Ahrens et al., 2010; Iwasaki and Shinjoh, 2010b). The results suggest that the replacement of protons on Brønsted acid sites can occur in NO$_2$ adsorption, evidenced by the NO$^+$ band at ~2160 cm^{-1} (Ruggeri et al., 2012). It was noted that the band at 1888 cm^{-1} related to the Fe^{2+}-NO species complex was temporarily observed at the beginning of exposure of NO$_2$ to Fe-ZSM-5, then the band vanished within 1 min. The release of NO accompanying NO$_2$ adsorption on Fe-ZSM-5 has also been proved by transient flow reactor experiments in the literature (Grossale et al., 2008; Iwasaki and Shinjoh, 2010c). The formation of Fe^{2+}-NO species in NO$_2$ adsorption can be attributed to the interaction of NO$_2$ with Fe^{2+} in the zeolite catalyst as indicated in reaction (7) (Ahrens et al., 2010; Iwasaki and Shinjoh, 2010c; Ruggeri et al., 2012). The formation of ferric nitrates over Fe-ZSM-5 during exposure to NO$_2$ can be illustrated as shown in reaction (8) (Ruggeri et al., 2012).

$$2Z-Fe^{2+} + NO_2 \rightarrow Z-Fe^{3+}-O^- + Z-Fe^{2+}-NO \qquad (7)$$

$$Z-Fe^{3+}-OH + 2NO_2 \rightarrow Z-Fe^{3+}-NO_3 + HONO \qquad (8)$$

Since FTIR studies of NH$_3$ adsorption on Fe-ZSM-5 can be found in numerous publications, the steady-state DRIFTS spectra of NH$_3$ adsorption on the present Fe-ZSM-5 and parent H-ZSM-5 at 140°C are shown in Appendix A Fig. S3. The results showed that NH$_3$ adsorbed on the Brønsted acidic sites showed a band of NH$_4^+$ at ~1482 cm^{-1} with the appearance of a negative band corresponding to the OH stretch at 3606 cm^{-1} (Sun et al., 2001; Long and Yang, 2002; Castoldi et al., 2011). It can be seen that the area of the band at 3606 cm^{-1} for the Fe-ZSM-5 catalyst was lower than that of the H-ZSM-5 catalyst, due to ion exchange of Fe ions into H-ZSM-5. The NH$_3$ coordinated at Lewis acid sites (Al^{3+} and Fe^{3+}) showed broad features in the 3500-3100 cm^{-1} region, and the weak band at 1612 cm^{-1} can be assigned to NH$_3$ coordinatively linked to Fe Lewis acid sites (Sun et al., 2001; Long and Yang, 2002; Castoldi et al., 2011). On the basis of the above results of NO + O$_2$, NO$_2$ and NH$_3$ adsorption over clean Fe-ZSM-5, in the next section, we will compare and discuss the spectroscopy of NO$_2$ and NO + O$_2$ adsorption on NH$_3$ pre-adsorbed Fe-ZSM-5.

2.2. NO$_2$ reaction with NH$_3$ pre-adsorbed Fe-ZSM-5

Ruggeri et al. (2012) studied the FTIR dynamics during exposure of NH$_3$-saturated commercial Fe-ZSM-5 to NO$_2$ at 200°C. Since the reactivity between NO$_2$ and pre-adsorbed NH$_3$ was quite high at 200°C, they only observed the fast disappearance of the band corresponding to NH$_4^+$ adsorbed on Brønsted acidic sites (1450 cm^{-1}) and the formation of surface ferric nitrates (band at 1620 cm^{-1}). In this work, in order to observe more details of the reaction of pre-adsorbed NH$_3$ with NO$_2$, we decreased the experimental temperature to 140°C, and especially, a background spectrum was collected of NH$_3$ saturated Fe-ZSM-5 at the same temperature. In detail, Fe-ZSM-5 was first exposed to NH$_3$/N$_2$ flow until close to adsorption saturation, and a background spectrum was obtained after purging in N$_2$ for at least 3 hr. Before exposure to NO$_2$, the spectrum collected on the NH$_3$-saturated catalyst surface was a straight line without visible bands against this background spectrum. In this way, on exposure to NO$_2$ flow, the dynamic changes of bands could provide information on the reaction of NO$_2$ with adsorbed NH$_3$. Fig. 2 shows the *in situ* DRIFTS spectra after Kubela-Munk (K-M) transformation for NO$_2$ adsorption over the NH$_3$ pre-adsorbed Fe-ZSM-5 at 140°C in 30 min. In order to clarify the changes in the IR dynamics, Fig. 2a and b illustrates the spectra in the time ranges of 0-5 and 5-30 min, respectively. As shown in Fig. 2a, in the range of nitrates, besides the bands at 1630 and 1574 cm^{-1} which can be characterized for NO$_x$ adsorption on clean Fe-ZSM-
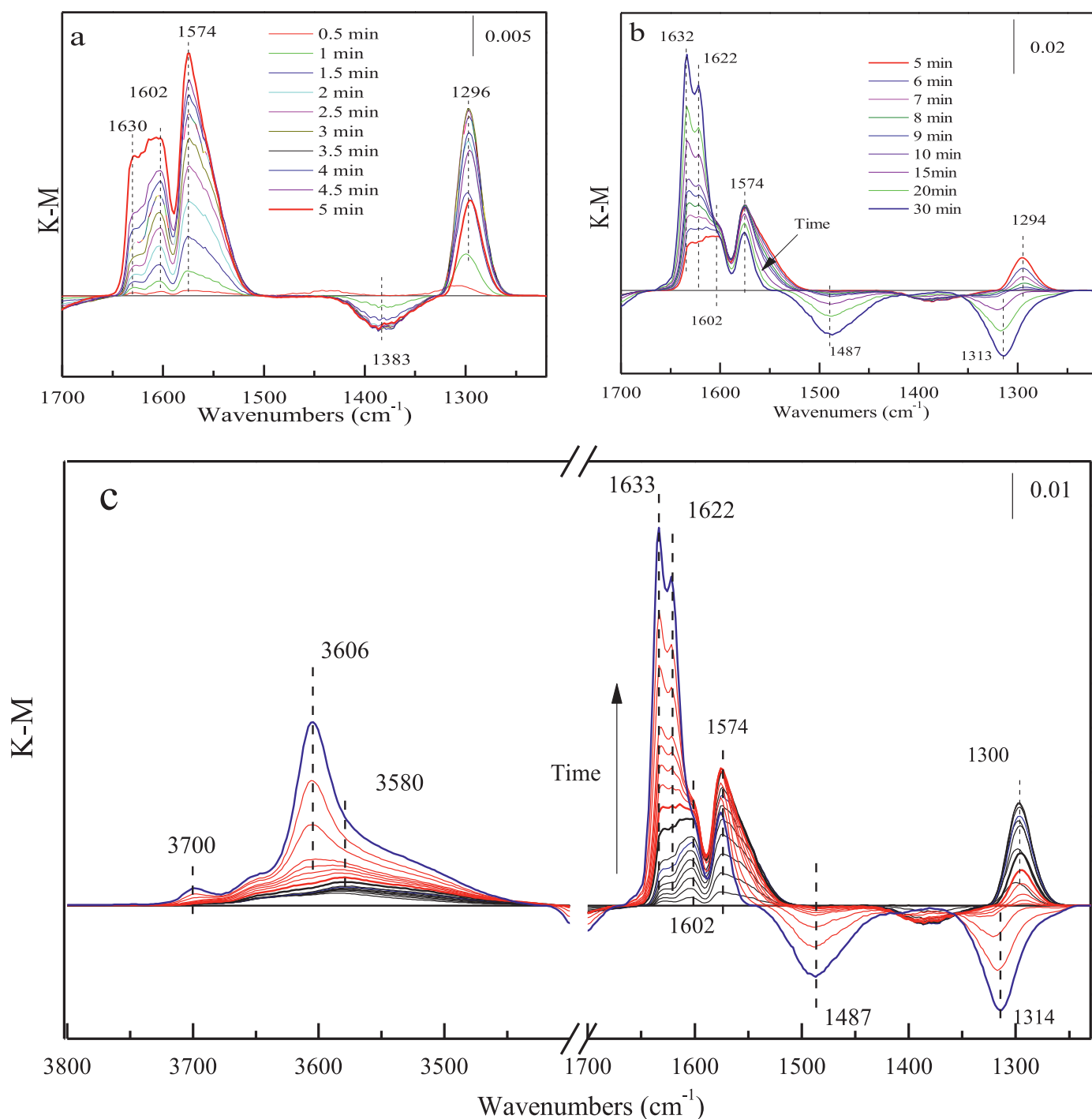
Fig. 2. *In situ* DRIFTS spectra after NO_2 adsorption over NH_3 pre-adsorbed Fe-ZSM-5 at 140°C: (a) 0-5 min, (b) 5-30 min, and (c) 0-30 min (black colour: 0-5 min). Feed: 0.1 vol.% NO_2, N_2 as balance. K-M: Kubela-Munk.

5, a band at 1602 cm^{-1} appeared immediately after exposure to NO_2. The bands related to nitrates gradually increased with time. The band at 1602 cm^{-1} can be assigned to an ammonium nitrite (briefly denoted as NH_4NO_2 in this work) due to the reaction between NO_2 species and NH_4^+ ions (Long and Yang, 2002; Devadas et al., 2006). Simultaneously, a band at 1296 cm^{-1} increased with time and then decreased after 4 min. Following the results of Sun et al. (2001, 2002), the band at 1296 cm^{-1} can be assigned to the NO_2^- group.

In the SCR reaction over Fe-zeolite catalysts, the ammonium nitrite species was considered to be an intermediate species that

can decompose to N_2 and H_2O (Devadas et al., 2006; Grossale et al., 2008; Kim et al., 2014; Beale et al., 2015). According to the results from transient reaction experiments, Grossale et al. (2008, 2009) proposed that the temperature threshold of formation/decomposition of ammonium nitrites, thus forming N_2, is estimated to be around 100°C. In theory, the decomposition of ammonium nitrites should result in the consumption of NH_4^+ ions. The results of Long and Yang (2002) showed that in the reaction of NO_2 with adsorbed NH_3 over Fe-ZSM-5, the appearance of the band of intermediate ammonium nitrites (1602 cm^{-1}) along with the decrease of the band corresponding to NH_4^+ on Brønsted
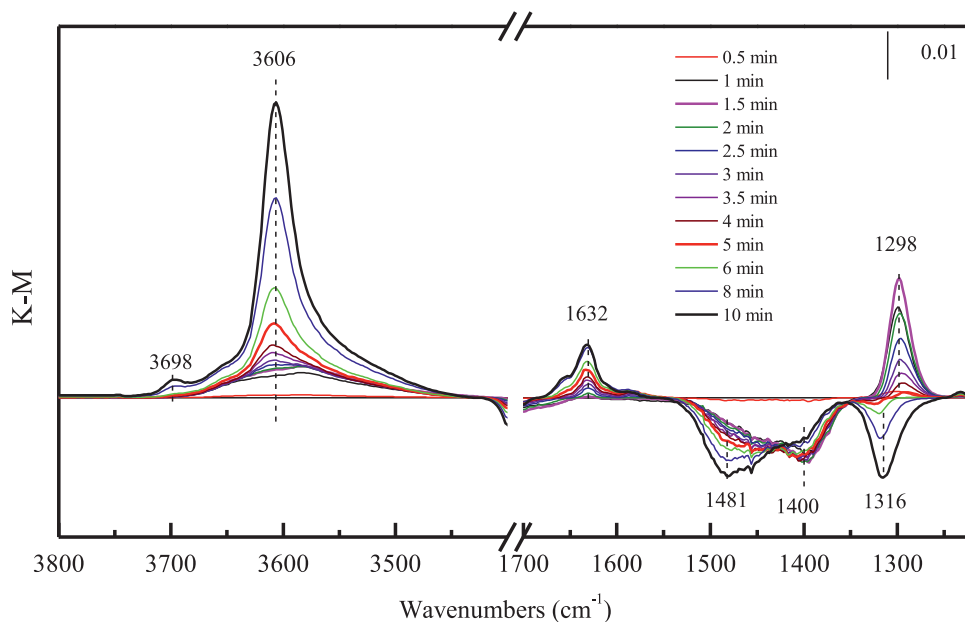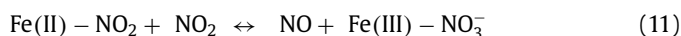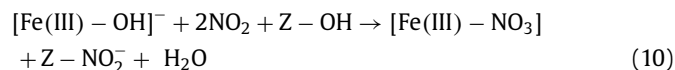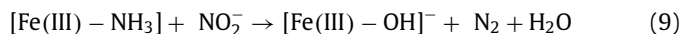
Fig. 3. *In situ* DRIFT spectra after NO_2 adsorption over NH_3 pre-adsorbed H-ZSM-5 at 140°C. Feed: 0.1 vol.% NO_2, N_2 as balance.

acid sites (1461 cm^{-1}) was observed. In this work, since the NH$_3$-saturated surface was used as background, consumption of NH$_4^+$ on Brønsted acid sites should be expected to show a negative band at around 1487 cm^{-1} and a positive OH bridging band at 3606 cm^{-1}. However, as shown in Fig. 2a, a negative band at ~1487 cm^{-1} could not be detected during the time range of 0-5 min after exposure to NO$_2$. In addition, according to the results of Grossale et al. (2009), the disproportionation of NO$_2$ to form nitrates and nitrites as in reaction (3) could be essentially unaffected by pre-adsorbed NH$_3$ on Fe-ZSM-5. Taking these things into account, we deduced that the NH$_4^+$ in the intermediate NH$_4$NO$_2$ might originate from/compensate for another source of NH$_3$ (such as NH$_3$ bound to Lewis acid sites) on the catalyst surface. It is worth mentioning that the band of the NH$_4$NO$_2$ intermediate (1602 cm^{-1}) increased simultaneously with the bands of nitrates (1630 and 1574 cm^{-1}) in the time range of 0-5 min. This indicates that the rate of formation of the NH$_4$NO$_2$ intermediate is faster than the rate of its decomposition to N$_2$ and water in this time range. The band at 1296 cm^{-1} related to NO$_2^-$ increased with exposure time to NO$_2$ and then decreased at around 5 min. As shown in Fig. 2a, the change of the band intensity of NO$_2^-$ was not coincident with nitrite intermediates at 1602 cm^{-1} during the whole time range of 0-5 min. In addition, the band of NO$_2^-$ can also be observed for NO$_2$ exposure to NH$_3$ pre-adsorbed H-ZSM-5 (Fig. 3). It is reasonable to assume that the formation of NO$_2^-$ species was not related to Fe sites. The weak negative band at 1383 cm^{-1} might result from the distorted NH$_4^+$ ions on some sites due to the formation of NH$_4$NO$_3$ speices over the catalyst surface.

Fig. 2b shows the IR spectra in the time range of 5-30 min. It can be seen that the bands related to NO$_2$ groups (1633 and 1622 cm^{-1}) increased with further exposure to NO$_2$. It was noted that, starting from ~6 min, the negative band at 1480 cm^{-1} in the spectra arose with the appearance of the bridging OH band at 3606 cm^{-1}. This indicates the consumption of the NH$_4^+$ on Brønsted acid sites starting at this time. Simultaneously, a slow decrease of the band at 1574 cm^{-1} can be observed, indicating that a portion of ferric nitrates was reacted away. The decrease of the band at 1574 cm^{-1} along with the prominent appearance of a negative band at 1487 cm^{-1} can be explained by part of the ferric nitrates being reduced by NO (released on NO$_2$ adsorption) to ferric nitrites, and then reacting with adjacent NH$_4^+$ on Brønsted acid sites to form

the intermediate NH$_4$NO$_2$. However, at 140°C, the formation of NH$_4$NO$_3$ or strongly interacting ammonia-nitrate ad-species should block the reactivity of nitrates with NO, known as the NH$_3$ blocking effect (Grossale et al., 2008, 2009). Furthermore, NH$_4$NO$_3$ cannot decompose at the experimental temperature (140°C). Therefore, the ferric nitrate species (1622 and 1574 cm^{-1}) can remain on the catalyst surface due to the formation of NH$_4$NO$_3$, which blocked the reduction of nitrates to nitrites by NO. In addition, the production of NO by NO$_2$ disproportionation should also stop after exposure to NO$_2$ at a certain time. As shown in Fig. 2, bands related to ferric nitrates could be observed after 30 min. This indicates that when NH$_3$ is removed from Fe sites, ferric nitrate species are formed according to reactions (9) and (10). In addition, ferric nitrite species could be oxidized to nitrates with further exposure to NO$_2$ as shown in reaction (11).

$$[Fe(III) - NH_3] + NO_2^- \rightarrow [Fe(III) - OH]^- + N_2 + H_2O \qquad (9)$$

$$[Fe(III) - OH]^- + 2NO_2 + Z - OH \rightarrow [Fe(III) - NO_3]$$
$$+ Z - NO_2^- + H_2O \qquad (10)$$

$$Fe(II) - NO_2 + NO_2 \leftrightarrow NO + Fe(III) - NO_3^- \qquad (11)$$

The experimental results at 250°C are shown in Appendix A Fig. S4. It can be seen that the NO$_2$ group band at 1630 cm^{-1} was the only dominant nitrate species, and all the peaks associated with adsorbed NH$_3$ species were rapidly consumed in 5 min with the reappearance of the Brønsted acid OH stretch at 3610 cm^{-1}. This indicates that the pre-adsorbed NH$_3$ can directly react with NO$_2$ gas at 250°C.

In order to identify the surface species related to Fe sites that formed during exposure to NO$_2$, the experiment involving NO$_2$ exposure to NH$_3$ pre-adsorbed H-ZSM-5 was carried out. As indicated by the results shown in Fig. 3, during this run, only very weak bands at 1630 cm^{-1} associated with NO$_2$ groups could be observed in the nitrate range. This confirmed that the high intensity of bands related to nitrate species at 1630 and 1574 cm^{-1}, as well as the intermediate NH$_4$NO$_2$ at 1602 cm^{-1} observed in Fig. 2, originated from Fe species. The results for H-ZSM-5 showed that the OH bridging band (3606 cm^{-1}) and the negative bands related
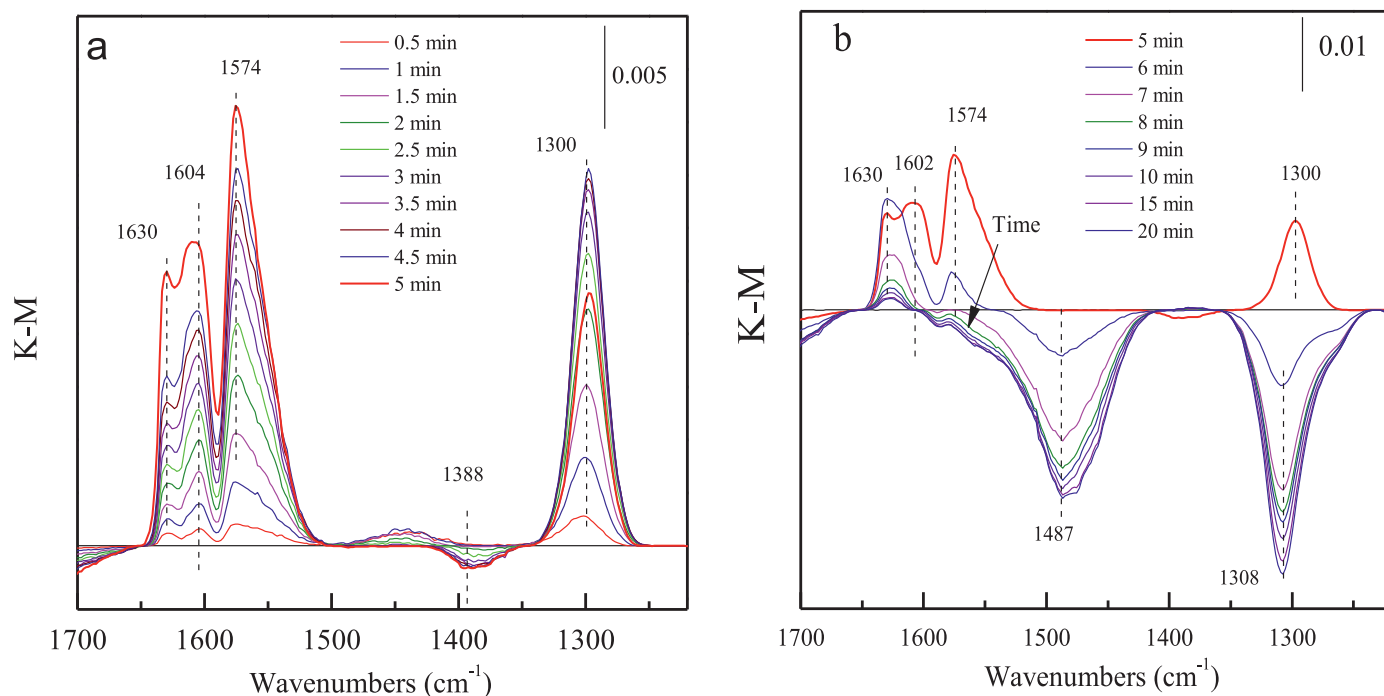
Fig. 4. *In situ* DRIFT spectra after NO + O$_2$ adsorption over NH$_3$ pre-adsorbed Fe-ZSM-5 at 140°C: (a) 0-5 min and (b) 5–20 min. Feed: 0.1 vol.% NO$_2$, N$_2$ as balance.

to NH$_4^+$ appeared rapidly after exposure to NO$_2$. The band at 1300 cm^{-1} assigned to nitrites suggests that the adsorbed NH$_3$ can be consumed through the direct reaction of nitrites with NH$_4^+$ on Brønsted acid sites as shown in the reaction (12) below (Ruggeri et al., 2014).

$$Z-ONH_4 + HNO_2 \rightarrow [NH_4NO_2] + Z-OH \rightarrow N_2 + 2H_2O + Z-OH \qquad (12)$$
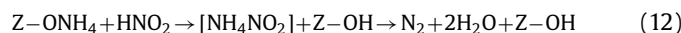
2.3. NO adsorption on pre-adsorbed NH$_3$

The oxidation of NO to NO$_2$ has been considered to be the key step in the standard SCR reaction over Fe-ZSM-5 (Long and Yang, 2002; Ruggeri et al., 2013; Iwasaki and Shinjoh, 2010a). Furthermore, according to the results of experiments using chemical trapping techniques, Ruggeri et al. (2014) proposed that nitrites/HONO formed on the catalyst surface, rather than gaseous NO$_2$ produced from NO oxidation, should be the common intermediates in the NO oxidation, standard and fast SCR reactions over Fe-ZSM-5. However, direct proof of ammonium nitrite (NH$_4$NO$_2$) intermediates in the standard SCR reaction was difficult to obtain by IR spectroscopic techniques due to its high activity and low quantity. It was reported that the protonated NH$_4$NO$_2$ species can decompose even at room temperature (Li et al., 2006). In addition, the IR absorbance features of the zeolite framework in the range of ~1300 cm^{-1} would strongly overlap the characteristic bands of adsorbed nitrite species over Fe-ZSM-5 (Rivallan et al., 2009). Therefore, the IR bands related to the intermediate ammonia nitrite species were almost invisible in the reaction of NO + O$_2$ with adsorbed NH$_3$ over Fe-ZSM-5, in which significant changes in the NH$_4^+$ adsorbed on Brønsted acid sites were observed (Long and Yang, 2002). In order to confirm the formation of nitrites in NO oxidation, in the experiments of Ruggeri et al. (2014), a Fe-ZSM-5 + BaO/Al$_2$O$_3$ physical mixture, in which the formed nitrites can be trapped by BaO, was exposed to NO + O$_2$ at 120°C. Then the formation of nitrites was evidenced by the observation of an equimolar mix of NO and NO$_2$ in the following temperature programmed decomposition experiments (Ruggeri et al., 2014). In the current study, direct detection of the IR bands of nitrites was realized in the NO reaction with

pre-adsorbed NH$_3$ by subtraction of the NH$_3$ saturated Fe-ZSM-5 background spectrum.

As shown in Fig. 4a, bands related to nitrates at 1630 and 1574 cm^{-1}, as well as intermediate ammonium nitrite species at 1602 cm^{-1}, can be clearly observed after flowing the NO + O$_2$ mixture over NH$_3$ pre-adsorbed Fe-ZSM-5. From the results in the time range of 0-5 min shown in Fig. 4a, it can be seen that the spectral features were very similar to those observed in the case of exposure to NO$_2$ (Fig. 2a). It can be seen that the bands of NO$_2$ groups (1630 cm^{-1}) and ferric nitrates (1574 cm^{-1}), as well as the intermediate NH$_4$NO$_2$ (1602 cm^{-1}), increased with time in the first 5 min. Similarly, the negative band of NH$_4^+$ on Brønsted acid sites did not appear in this time range. The results provide clear evidence that the NO oxidation to form surface nitrates and nitrites is a key pathway in the standard SCR reaction, and that the intermediates are the same as those in the NO$_2$ reaction with pre-adsorbed NH$_3$. Our results confirm that the intermediates in the standard SCR reaction should be generated from the oxidation of NO. The lower intensity of those bands in this case indicates that less nitrates were formed in NO + O$_2$ compared with exposure to NO$_2$, due to the low NO oxidation activity of Fe-ZSM-5 at 140°C.

It is worth noting that the bands related to changes of NH$_4^+$ on Brønsted acid sites (negative bands at ~1487 cm^{-1} and positive band at ~ 3610 cm^{-1}) cannot be observed in the early stage of the reaction, as shown in Figs. 2a and 4a. This indicates that the NH$_4^+$ on Brønsted acid sites was less active at low temperature. Recently, Zhang et al. (2019) found that for Cu-SSZ-13, NH$_3$ adsorbed on Lewis acid sites is more active than NH$_4^+$ on Brønsted acid sites in reaction with nitrogen oxides at low temperature, and they presumed that NH$_3$ adsorbed on Lewis acid sites can react with NO directly via a NO-assisted NH$_3$ activation pathway. We considered that this should be a common mechanism for the SCR reaction over ion-exchanged zeolite catalysts: NO first reacts predominantly with NH$_3$ coordinated to Lewis acid sites related to metal active sites. The results from Chen et al. (2016) provided clear evidence for that NH$_3$ bound to the Lewis acid sites can be protonated and transformed into the intermediate NH$_4^+$ in the standard SCR reaction. Taken together, a reaction pathway involving NH$_3$ adsorbed
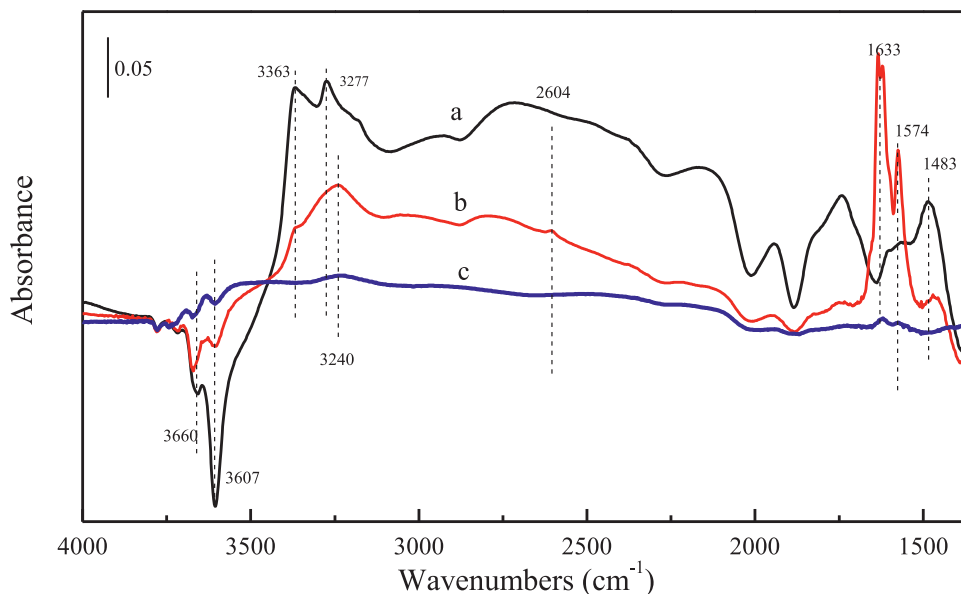
Fig. 5. Comparison of *in situ* DRIFT spectra after NO_x reacted with NH_3 followed by N_2 purging at 140°C: (a) NH_3 adsorption, (b) NO_2 reaction with pre-adsorbed NH_3, and (c) $NO + O_2$ reaction with pre-adsorbed NH_3. Background spectrum was collected on clean Fe-ZSM-5.

on Fe sites with NO might also occur as shown in reaction (13). Then, the NH_2NO can decompose into N_2 and H_2O, and H^+ can transfer to adjacent adsorbed NH_3 to form NH_4^+.

$$Fe(III) - NH_3 + \ NO \ \rightarrow Fe(II) - \ NH_2NO \ + \ H^+ \qquad (13)$$
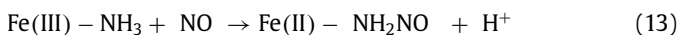
On the other hand, the dynamic spectra after 5 min were different from those observed with NO_2 exposure. As shown in Fig. 4b, the bands at 1574 and 1602 cm^{-1} sharply decreased and became invisible in ~2 min, accompanied by the appearance of negative bands of NH_4^+ ions at 1487 cm^{-1} and OH bridging bands at 3606 cm^{-1}. At the same time, the band at 1630 cm^{-1} decreased at a relatively slow rate, and a very weak band remained after 20 min. The significant decrease of the band at 1574 cm^{-1} at around ~5 min should be attributed to the occurrence of the reduction of nitrates by NO to form nitrites, after which the ferric nitrites would react with NH_4^+ adsorbed on Brønsted acid sites to form N_2 and water. as shown in reaction (4).

It should be noted that the bands related to nitrate species at 1630 and 1574 cm^{-1} were almost undetectable after 10 min exposure to $NO + O_2$. Contrarily, $NO + O_2$ adsorption on clean Fe-ZSM-5 catalysts at 140°C exhibited bands of 1633 and 1574 cm^{-1}. This indicates that the oxidation of NO to form nitrates over the catalyst surface became difficult after the pre-adsorbed NH_3 was completely consumed in the $NO + O_2$ flow. According to Delahay et al. (2005), re-oxidation of Fe^{2+} species was the slow step in the Fe^{3+}/Fe^{2+} species cycle in the standard SCR reaction. The undetectable nitrate species on the Fe-ZSM-5 in $NO + O_2$ at the end of the run indicate that the re-oxidation of Fe^{2+} species should be rather difficult at 140°C. Moreover, it should be noted that H-ZSM-5 realized NO_x reduction in the fast SCR reaction at 200°C (Appendix A Fig. S2), but the NO conversion was markedly lower compared to Fe-ZSM-5. This further suggests that the oxidation of NO over Fe active sites is crucial for reduction of NO at low temperature, even under fast SCR reaction conditions.

In order to identify the remaining surface species after NO_2 and $NO + O_2$ reacted with pre-adsorbed NH_3 over Fe-ZSM-5, after the reaction gas was switched off and followed by a N_2 purge, the spectra were collected using the clean catalyst surface as background. As shown in Fig. 5, in the case of NO_2 exposure (line b), bands related to nitrates at 1630 and 1574 cm^{-1}, as well as negative bands related to Brønsted acid sites at 3610 and 3660 cm^{-1},
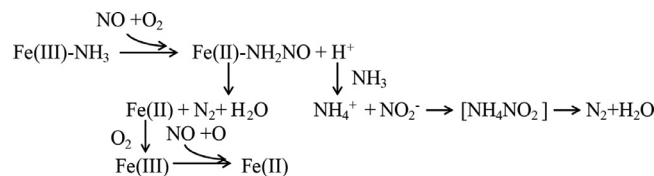
Scheme 1. Proposed pathways for the $NO + O_2$ exposures to NH_3 pre-adsorbed Fe-ZSM-5.

can be observed with high intensity. This indicates that a certain amount of nitrates and part of the NH_3 adsorbed on Brønsted acid sites remained after the reaction of NO_2 with pre-adsorbed NH_3 at 140°C. However, in the case of $NO + O_2$ (line c), the negative bands related to OH groups and bands in the nitrate range were almost undetectable. This indicates that the pre-adsorbed NH_3 was almost completely consumed through reaction during exposure to $NO + O_2$ at 140°C. On the other hand, high intensity nitrate bands at 1633 and 1574 cm^{-1} can be observed on the catalyst surface after exposure to NO_2, while a very small amount of ferric nitrates was formed in the case of exposure to $NO + O_2$. The results in Fig. 5 confirm that a certain amount of NH_4NO_3 remained over the NH_3 pre-adsorbed Fe-ZSM-5 after exposure to NO_2, and the Fe sites became inactive after the reaction of pre-adsorbed NH_3 with $NO + O_2$. The possible reaction pathways of $NO + O_2$ reacted with NH_3 pre-adsorbed over Fe-ZSM-5 at low temperature can be summarized in Scheme 1.

3. Conclusions

By *in situ* DRIFTS studies, we present evidence for the formation of common surface nitrate and nitrite species, as well as NH_4NO_2 intermediates, in the reaction of $NO + O_2$ and NO_2 with pre-adsorbed NH_3 over Fe-ZSM-5 at 140°C. The results confirm the occurrence of NO oxidation to form ferric nitrates and nitrite species in the reaction of $NO + O_2$ with NH_3. The re-oxidation of Fe(II) to Fe(III) is difficult at this low temperature. This should be the primary cause for the low activity of Fe-ZSM-5 in the standard SCR reaction. The addition of NO_2 can promote the formation of surface nitrates and nitrites; however, when NH_3 is present, the further reaction of ferric nitrates to

form nitrites is blocked due to formation of ammonium nitrates. Additionally, the reactions involving NH_4^+ adsorbed on Brønsted acid sites should be slow pathways in the SCR reaction at this temperature.

Declaration of Competing Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of the manuscript entitled.

Acknowledgments

Appendix A. Supplementary data

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jes.2020.02.029.

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