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# Inhibitory effect of NO<sub>2</sub> on the selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> over one-pot-synthesized Cu–SSZ-13 catalyst<sup> $\dagger$ </sup>

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The selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> (NH<sub>3</sub>–SCR) on a Cu–SSZ-13 catalyst prepared by a one-pot-synthesis method was inhibited by NO<sub>2</sub> in the low temperature range. NH<sub>4</sub>NO<sub>3</sub> that accumulated on the catalyst surface was the reason for this phenomenon. The key step of the NH<sub>3</sub>–SCR reaction over the catalyst at low temperatures was the formation of nitrate on the Cu sites. However, NO<sub>2</sub>, with its larger kinetic diameter, could not form nitrate species on the Cu sites efficiently, and part of these molecules formed NH<sub>4</sub>NO<sub>3</sub> in combination with NH<sub>4</sub><sup>+</sup> on the Brønsted acid sites. The consumption rate of NH<sub>4</sub>NO<sub>3</sub> by NO was lower than its accumulation under "fast SCR" conditions at low temperatures, making the active sites become blocked by NH<sub>4</sub>NO<sub>3</sub> and inactive. The results of kinetic studies indicate that N<sub>2</sub> formation mainly results from the reaction between NO and NH<sub>3</sub>, even under "fast SCR" reaction conditions.

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# 1. Introduction

Currently, the selective catalytic reduction of  $NO_x$  with  $NH_3$  ( $NH_3$ -SCR) is one of the most promising technologies for  $NO_x$  emission control from diesel engine exhaust. Researchers have conducted many studies to improve the performance of catalysts to meet more and more stringent emission standards, and a great deal of work has been carried out to investigate the active sites and reaction routes of the  $NH_3$ -SCR reaction for different catalyst systems as well.<sup>1–5</sup> A complex reaction pathway was observed during the reduction of  $NO_x$  with  $NH_3$  in previous studies. The main reactions include standard SCR, fast SCR,  $NH_4NO_3$ formation and  $N_2O$  formation. Because the fraction of NO in  $NO_x$  is *ca.* 90% in real diesel exhaust, the "standard SCR" reaction (1) is the most important of the four reactions described above.<sup>6</sup>

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$
 (1)

The SCR performance is always enhanced greatly when the  $NO_2$  fraction in the feed gas is increased to about 50%;

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*E-mail: honghe@rcees.ac.cn; Fax: +86 10 62849123; Tel: +86 10 62849123* † Electronic supplementary information (ESI) available: NH<sub>2</sub>-SCR performance

<sup>†</sup> Electronic supplementary information (ESI) available:  $NH_3$ -SCR performance of the Cu<sub>3,9</sub>-SSZ-13 catalyst; reactions between pre-adsorbed species of  $NH_3$ and NO + O<sub>2</sub>. See DOI: 10.1039/c3cy00924f this is known as the "fast SCR" reaction according to the following stoichiometric equation:<sup>7-10</sup>

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \tag{2}$$

The oxidation of NO to  $NO_2$  has been proposed to be the rate-limiting step in the  $NH_3$ -SCR reaction.<sup>11,12</sup> For this reason, a diesel oxidation catalyst (DOC) is usually put upstream of the SCR catalyst to convert some NO to  $NO_2$  in real applications.<sup>7,13</sup> However, when  $NO_2$  is present in the feed gas,  $N_2O$  is often produced at higher levels through the decomposition of  $NH_4NO_3$ , which is formed easily by reaction between  $NH_3$  and  $NO_2$ . Notably,  $N_2O$  is an undesirable by-product in  $deNO_x$  reactions due to its greenhouse activity and also its ability to destroy the ozone layer.<sup>1,14-16</sup> Thus, researchers seek to develop catalysts with both excellent  $NH_3$ -SCR activity and  $N_2$  selectivity.

Recently, Cu–CHA materials (such as Cu–SSZ-13 and Cu–SAPO-34), a new type of NH<sub>3</sub>–SCR catalyst, have shown improved NH<sub>3</sub>–SCR activity, N<sub>2</sub> selectivity and hydrothermal stability compared with the existing Cu–zeolite catalysts.<sup>4,5,17–19</sup> Attractively, their small pore structures contribute to a high resistance to small hydrocarbon molecules such as  $C_3H_6$ .<sup>20,21</sup> This feature was helpful for their application under real working conditions. The role of NO<sub>2</sub> and the formation of N<sub>2</sub>O in the NH<sub>3</sub>–SCR reaction catalyzed by Cu–CHA catalysts have also attracted much attention. There was little N<sub>2</sub>O observed in the NH<sub>3</sub>–SCR reaction over the Cu–SSZ-13 catalyst even when a large amount of NO<sub>2</sub> was present in the feed gas.<sup>22</sup> Zhu *et al.* analyzed the relationship between different NH<sub>3</sub>



adsorbed species and the formation of N2 and N2O based on the results of in situ DRIFTS-MS studies over the Cu-SSZ-13 catalyst, suggesting that the formation of N<sub>2</sub>O was associated with the reaction of NO<sub>x</sub> with proton-adsorbed NH<sub>3</sub> via the formation and subsequent thermal decomposition of  $NH_4NO_3$ <sup>23</sup> Kwak *et al.* found that the addition of  $NO_2$  did not significantly increase the rate of NH3-SCR reaction over the Cu-SSZ-13 catalyst, suggesting that the mechanism over this CHA-based catalyst was different from that observed for other zeolites.<sup>24</sup> In the study, the Cu<sup>+</sup>NO<sup>+</sup> species was identified as an important intermediate, which formed in the reaction between Cu<sup>2+</sup> and NO. Different preparation methods were used to prepare Cu-SSZ-13 catalysts with superior NH<sub>3</sub>-SCR performance in previous reports.<sup>25,26</sup> Deka et al. prepared Cu-SSZ-13 catalysts via chemical vapor deposition and wet chemical routes, suggesting that the mononuclear Cu<sup>2+</sup> species was preferred for the formation of  $N_2$ .<sup>25</sup>

The one-pot-synthesis method is also effective in the preparation of a Cu-SSZ-13 sample using a less expensive copperamine complex (Cu-TEPA) as a structure-directing agent (SDA).<sup>26</sup> In this method, the cost of the Cu-SSZ-13 catalyst was decreased greatly with the lower-cost SDA and higher Cu loading efficiency. More importantly, the optimal one-potsynthesized Cu-SSZ-13 catalyst exhibited very good NH<sub>3</sub>-SCR activity, especially in the low temperature range. Thus, Cu-SSZ-13 catalysts with excellent NH<sub>3</sub>-SCR performance and much lower cost could be obtained via this method, which is beneficial for the wide use of Cu-SSZ-13 catalysts. However, there have been few studies on the NH<sub>3</sub>-SCR reaction mechanism relative to the one-pot-synthesized Cu-SSZ-13 catalyst. This paper focuses on the effect of NO2 on the NH<sub>3</sub>-SCR reaction catalyzed by Cu-SSZ-13 prepared by the onepot-synthesis method. Surprisingly, it was found that NO2 inhibited the NH<sub>3</sub>-SCR activity in the low temperature range (<200 °C), which was in contradiction to the promotional effect of NO<sub>2</sub> referred to as "fast SCR".<sup>18,22</sup> The NH<sub>3</sub>-SCR performance was tested under different NO<sub>2</sub>/NO<sub>x</sub> ratios, and the explanations were given based on the results of in situ DRIFTS experiments and kinetic studies. The results indicate that increasing the NO<sub>2</sub> ratio directly in the feed gas is not an effective way to improve NH<sub>3</sub>-SCR performance of the Cu-SSZ-13 catalyst prepared by the one-pot-synthesis method.

## 2. Experimental

#### 2.1 Catalyst preparation and activity test

The initial Cu–SSZ-13 catalyst sample was synthesized using the same procedure as in a previous report.<sup>27</sup> Because of the relatively high Cu content in the initial sample, some posttreatments were necessary to obtain catalysts with suitable Cu loadings. Dilute nitric acid solution was also preferred to adjust the Cu loading in the sample instead of  $NH_4NO_3$ solution. In this study, a suspension of the initial Cu–SSZ-13 sample in nitric acid solution with pH = 1 was stirred for 12 h at 80 °C. After filtration, the sample was dried overnight at 120  $^{\circ}$ C and successively calcined at 600  $^{\circ}$ C to remove the residual template molecules.

The SCR activity tests of the sieved powder catalysts were carried out in a fixed-bed quartz flow reactor at atmospheric pressure. 50 mg samples of catalysts were used, and the gas hourly space velocity (GHSV) was *ca.* 400 000 h<sup>-1</sup>. The reaction conditions were controlled as follows:  $[NO_x] = [NO] + [NO_2] = 500$  ppm, 500 ppm NH<sub>3</sub>, 5 vol.% O<sub>2</sub>, balance N<sub>2</sub>. The total flow rate was held at 500 mL min<sup>-1</sup>. The effluent gas including NO, NH<sub>3</sub>, NO<sub>2</sub> and N<sub>2</sub>O was continuously analyzed using an online NEXUS 670-FTIR spectrometer equipped with a heated, low volume (0.2 L) multiple-path gas cell (2 m). The FTIR spectra were collected throughout and the results were recorded when the SCR reaction reached a steady state. Then, the NO<sub>x</sub> conversion and N<sub>2</sub>O concentration were calculated accordingly.

$$NO_x \text{ conversion} = \left(1 - \frac{[NO]_{out} + [NO_2]_{out}}{[NO]_{in} + [NO_2]_{in}}\right) \times 100\%$$

#### 2.2 In situ DRIFTS experiments

The in situ DRIFTS experiments were performed using an FTIR spectrometer (Nicolet Nexus 670) equipped with a Smart Collector and an MCT/A detector. The reaction temperature was controlled precisely by an Omega programmable temperature controller. Prior to each experiment, the catalyst was pretreated at 550 °C for 20 min in a flow of 20 vol.% O<sub>2</sub>/N<sub>2</sub> and then cooled down to 120 °C. The background spectrum was collected in flowing N<sub>2</sub> and automatically subtracted from the sample spectrum. In order to identify the adsorbed species, the catalysts were exposed to a flow of 1000 ppm NH<sub>3</sub>/N<sub>2</sub> or 1000 ppm NO (NO<sub>2</sub>) + 5 vol.%  $O_2/N_2$  (200 mL min<sup>-1</sup>) at 120 °C for 0.5 h, followed by a N<sub>2</sub> purge for another 0.5 h. The reaction conditions were controlled as follows: 1000 ppm  $NO_x$ , 1000 ppm  $NH_3$ , 5 vol.%  $O_2$ , balance  $N_2$  (200 mL min<sup>-1</sup>), and NO<sub>x</sub> + O<sub>2</sub> was composed of 1000 ppm NO + 5 vol.% O<sub>2</sub>/N<sub>2</sub> or 500 ppm NO + 500 ppm NO<sub>2</sub> + 5 vol.%  $O_2/N_2$ . To investigate the reactions in detail, the  $NO_x + O_2$  adsorbed species were set as background, and then NH<sub>3</sub> was introduced to the reaction cell. If the absorbance was negative, the corresponding surface species were consumed. Conversely, there were new species generated on the catalyst surface, if the absorbance was positive. All spectra were recorded by accumulating 100 scans with a resolution of  $4 \text{ cm}^{-1}$ .

#### 2.3 Kinetic studies

The kinetic data for "standard SCR" and "fast SCR" were evaluated in a differential reactor with a 4 mm inner diameter at atmospheric pressure. About 5 mg of the catalyst diluted with 20 mg of SiC was loaded with a catalyst bed length of *ca.* 2 mm. Under different conditions, the NO<sub>x</sub> conversion was kept less than 20% in the temperature range tested. To eliminate the effects of diffusion, a total gas flow rate of 500 mL min<sup>-1</sup> and a particle size of 40–60 mesh were used. The

"standard SCR" gas mixture was composed of 500 ppm NO, 500 ppm NH<sub>3</sub>, 5 vol.% O<sub>2</sub>, and balance N<sub>2</sub>, while the "fast SCR" gas mixture was composed of 250 ppm NO, 250 ppm NO<sub>2</sub>, 500 ppm NH<sub>3</sub>, 5 vol.% O<sub>2</sub>, and balance N<sub>2</sub>. The effluent gas was also analyzed using an online NEXUS 670-FTIR spectrometer as described above. NO<sub>x</sub> reduction rates (mol g s<sup>-1</sup>) were calculated as:

$$r_{\rm NO_x} = X_{\rm NO_x} Y_{\rm NO_x, in} V_{\rm gas} / m_{\rm cat}$$

where  $X_{NO_x}$  is the NO<sub>x</sub> conversion,  $Y_{NO_x}$  is the NO<sub>x</sub> molar fraction in the inlet gas,  $V_{\text{gas}}$  is the total flow rate in moles per second, and  $m_{cat}$  is the mass of the catalyst in grams.

### Results and discussion

#### 3.1 NH<sub>3</sub>-SCR performance of the Cu-SSZ-13 catalyst under different NO<sub>2</sub>/NO<sub>x</sub> ratio conditions

The elemental content was analyzed using an inductively coupled plasma instrument (OPTMIA 2000DV) with a radial view of the plasma. There was 3.9% Cu content by weight remaining in the obtained catalyst, which was denoted as Cu<sub>3.9</sub>-SSZ-13. The catalyst showed excellent NH<sub>3</sub>-SCR performance under "standard SCR" conditions (Fig. S1<sup>†</sup>). In order to investigate the effect of NO2, the activity tests were carried out from 150 to 550 °C with different NO<sub>2</sub>/NO<sub>x</sub> ratios in the feed gas, as shown in Fig. 1. In the low temperature range ( $\leq 200$  °C), the NH<sub>3</sub>-SCR performance of the catalyst became poorer with the increase of the  $NO_2$  ratio. When the  $NO_2/NO_x$ ratio was changed from 0 to 0.5, the  $NO_r$  conversion decreased from 92.7% to 4.8% at 200 °C. During the activity test, a small amount of N<sub>2</sub>O formed (less than 10 ppm) under "standard SCR" conditions, while under "fast SCR" conditions (NO<sub>2</sub>/NO<sub>x</sub> = 1/2), more N<sub>2</sub>O was observed at temperatures higher than 250 °C, and the N<sub>2</sub>O level increased significantly at temperatures from 200 to 250 °C, especially from 225 to 250 °C (Fig. S2<sup>†</sup>), implying the possible rapid



NO,/NO\_=1/2

20

ž

0 250 300 350 400 450 500 150 200 550 Temperature (°C)

NO,/NO\_=1/2

decomposition of NH<sub>4</sub>NO<sub>3</sub> which might be an important reaction intermediate for the SCR process at high temperatures. It was surprising that the improvement of NH<sub>3</sub>-SCR activity under "fast SCR" reaction conditions was reversed, that is, NO<sub>2</sub> did not promote the activity of the Cu-SSZ-13 catalvst prepared by the one-pot-synthesis method but instead inhibited the reaction. This inhibitory effect was still distinct in the presence of 5% H<sub>2</sub>O (Fig. S3<sup>†</sup>). Compared with the effect of NO2 on metal oxide catalysts, transition metalexchanged zeolite catalysts (such as Cu-ZSM-5 and Fe-ZSM-5) and even the Cu-SSZ-13 catalyst prepared by ion exchange method in previous reports, the conclusion was entirely opposite.<sup>7,8,18,28,29</sup> These observations suggested that the mechanism of the NH3-SCR reaction over this catalyst was different, and more research is needed to investigate the true reason for the inhibitory effect of NO<sub>2</sub> on the NH<sub>3</sub>-SCR reaction.

#### 3.2 NH<sub>3</sub> adsorption

In situ DRIFTS spectra were collected to characterize the surface species during NH<sub>3</sub> adsorption on the Cu<sub>3.9</sub>-SSZ-13 catalyst at 120 °C for 0.5 h, followed by a N<sub>2</sub> purge for 0.5 h. As shown in Fig. 2, strong IR bands at 1458 and 1621  $cm^{-1}$ were observed. The band at 1458  $\text{cm}^{-1}$  was assigned to NH<sub>4</sub><sup>+</sup> species adsorbed on the Brønsted acid sites, whereas the band at 1621 cm<sup>-1</sup> was due to NH<sub>3</sub> coordinately linked to the Lewis acid sites.<sup>12</sup> There were four bands in the range from 3100 cm<sup>-1</sup> to 3400 cm<sup>-1</sup>, which were assigned to N-H stretching vibrations. In detail, the band at 3178 cm<sup>-1</sup> was due to NH<sub>3</sub> adsorbed on Cu species. The bands at 3270 and 3332  $\text{cm}^{-1}$  were attributed to  $\text{NH}_4^+$  species, and the band at 3384 cm<sup>-1</sup> was assigned to NH<sub>3</sub> molecules.<sup>30-32</sup> Meanwhile, the negative bands at 3567, 3602, 3654 and 3745 cm<sup>-1</sup> were assigned to OH vibrations, corresponding to the Brønsted acid sites.<sup>32-35</sup> The NH<sub>3</sub> adsorbed species observed on the Cu-SSZ-13 catalyst prepared by the one-pot-synthesis method were similar to those seen on other Cu-CHA catalysts.



Fig. 2 In situ DRIFT spectra of species on the Cu<sub>3.9</sub>-SSZ-13 catalyst during exposure to NH<sub>3</sub> at 120 °C.

100

80

60

40

20

0

NO、conversion (%)

#### 3.3 NO<sub>x</sub> adsorption

In order to identify the adsorbed NO<sub>x</sub> species on the Cu-SSZ-13 catalyst and further investigate the difference caused by different NO<sub>x</sub> sources, the sample was exposed to NO +  $O_2$  or NO<sub>2</sub> + O<sub>2</sub> for 0.5 h and then purged in N<sub>2</sub> for 0.5 h. When the Cu<sub>3.9</sub>-SSZ-13 catalyst was exposed to NO + O<sub>2</sub>, three types of nitrate species were mainly observed, as shown in Fig. 3(a). They were assigned to monodentate nitrates  $(1504 \text{ cm}^{-1})$ , bidentate nitrates (1573 and 1596 cm<sup>-1</sup>) and bridging nitrates (1631 cm<sup>-1</sup>).<sup>36-40</sup> All nitrate species formed simultaneously as soon as NO<sub>r</sub> was introduced to the catalyst, indicating the good oxidation ability of the catalyst. When the sample was exposed to  $NO_2 + O_2$ , the adsorption progress was totally different, as shown in Fig. 3(b). Only bridging nitrates (1631 cm<sup>-1</sup>) were formed on the catalyst surface in the first 4 min. Then, monodentate nitrates (1502 cm<sup>-1</sup>) and bidentate nitrates (1575 and 1598 cm<sup>-1</sup>) formed gradually. Only a small amount of nitrate species formed in 5 min using  $NO_2 + O_2$ , while much more nitrate species formed under the same conditions with NO +  $O_2$ . Thus, it was apparent that the formation speed of nitrate species was much slower when NO was replaced by  $NO_2$  in the feed gas.

# 3.4 *In situ* DRIFTS experiments under "standard SCR" and "fast SCR" conditions

The *in situ* DRIFTS experiments were carried out to determine the species on the catalyst surface under real  $NH_3$ -SCR reaction conditions at 120 °C. The reaction time was controlled at 0.5 h, and the spectra were collected throughout. The stable surface species under different reaction conditions are shown in Fig. 4. When the  $NH_3$ -SCR reaction was conducted under "standard SCR" conditions, typical bands at 1479, 1620, 2825, 3062, 3186, 3270 and 3327 cm<sup>-1</sup> were observed (Fig. 4(a)). According to the peak assignments described above, the peaks at 1620, 3186, 3270 and 3327 cm<sup>-1</sup> were assigned to  $NH_3$  adsorbed species, and the formation of a peak at 1479 cm<sup>-1</sup> should be due to the combination of



Fig. 3 In situ DRIFT spectra of species on the Cu<sub>3.9</sub>-SSZ-13 catalyst during exposure to NO + O<sub>2</sub> (a) and NO<sub>2</sub> + O<sub>2</sub> (b) at 120 °C.



Fig. 4 In situ DRIFT spectra of stable species on the  $Cu_{3.9}$ -SSZ-13 catalyst under "standard SCR" conditions (a) and "fast SCR" conditions (b) at 120 °C.

NH<sub>3</sub> species at 1458 cm<sup>-1</sup> and some nitrate species at 1504 cm<sup>-1</sup>. In line with previous studies, it was supposed that peaks at 2825 and 3062 cm<sup>-1</sup> could be assigned to NH<sub>4</sub><sup>+</sup> from NH<sub>4</sub>NO<sub>3</sub>.<sup>41,42</sup> Surface NH<sub>4</sub>NO<sub>3</sub> species could participate in the NH<sub>3</sub>-SCR reaction, following the equations: NH<sub>4</sub>NO<sub>3</sub> + NO  $\rightarrow$  NH<sub>4</sub>NO<sub>2</sub> + NO<sub>2</sub>, NH<sub>4</sub>NO<sub>2</sub>  $\rightarrow$  N<sub>2</sub> + H<sub>2</sub>O.<sup>43-45</sup>

In order to confirm the assignment of peaks at 2825 and  $3062 \text{ cm}^{-1}$ , the *in situ* DRIFTS experiment was carried out to record the reactions between NO and the Cu<sub>3.9</sub>-SSZ-13 catalyst (*ca.* 2 wt% NH<sub>4</sub>NO<sub>3</sub> loaded on the surface). Because the spectrum of the catalyst loaded with NH<sub>4</sub>NO<sub>3</sub> was set as the background, the negative peaks at 3270, 3041, 2832 and 1446 cm<sup>-1</sup> should be assigned to NH<sub>4</sub><sup>+</sup> from NH<sub>4</sub>NO<sub>3</sub> (Fig. 5). According to the nitrate species assignments above (Fig. 3), the positive peaks in the range from 1500 to 1700 cm<sup>-1</sup> were attributed to the formation of new nitrate species. Thus, on the basis of the results in Fig. 2 and 5, it was concluded that NH<sub>3</sub> adsorbed species and a small amount of NH<sub>4</sub>NO<sub>3</sub> formed on the catalyst surface under "standard SCR" conditions (Fig. 4(a)).



Fig. 5 Reduction of  $NH_4NO_3$  loaded on the  $Cu_{3.9}\text{-}SSZ\text{-}13$  catalyst by NO and  $O_2$  at 120  $^\circ\text{C}.$ 

The stable species on the catalyst surface under "fast SCR" reaction conditions were also recorded, as shown in Fig. 4(b). The peaks at 3323, 3189 and 3270 cm<sup>-1</sup> indicated the adsorption of NH<sub>3</sub> species, and the peaks at 2827, 3061 and 3270 cm<sup>-1</sup> proved that NH<sub>4</sub>NO<sub>3</sub> was also deposited on the catalyst surface under these conditions. Compared with the results under "standard SCR" conditions (Fig. 4(a)), the intensity of the peak at 3270 cm<sup>-1</sup> was higher, which should be due to the larger amount of NH<sub>4</sub>NO<sub>3</sub> on the surface. More notably, a much larger amount of nitrate species was observed in the low wavenumber range (such as peaks at 1562, 1593 and 1633  $\text{cm}^{-1}$ ). All of these results proved that more NH4NO3 accumulated on the catalyst surface under "fast SCR" than under "standard SCR" conditions. Because NH<sub>4</sub>NO<sub>3</sub> could block the pores and deactivate the active sites of the Cu<sub>3.9</sub>-SSZ-13 catalyst, it was adverse for the  $deNO_x$  process. Therefore, the much greater amount of NH<sub>4</sub>NO<sub>3</sub> deposited on the catalyst surface was the main reason for the NO<sub>2</sub> inhibitory effect on NH<sub>3</sub>-SCR reaction in the low temperature range.

#### 3.5 Reactions between pre-adsorbed species of NO<sub>x</sub> and NH<sub>3</sub>

In this study, the reactions between pre-adsorbed species of  $NO_x$  and  $NH_3$  at 120 °C were chosen to represent the reactions in the low temperature range (Fig. 6). Because similar nitrate species were formed on the catalyst surface, regardless of whether NO + O<sub>2</sub> or NO<sub>2</sub> + O<sub>2</sub> contacted the catalyst (Fig. 3), nitrate species from NO + O<sub>2</sub> were chosen to react with NH<sub>3</sub> in this section. As shown in Fig. 6(a), upon the introduction of a NH<sub>3</sub> flow, the nitrate species (negative peaks at 1504, 1571 and 1596 cm<sup>-1</sup>) decreased quickly with reaction time, especially in the first 10 min. New species (positive peaks at 1625 and 1458 cm<sup>-1</sup>) could also be detected, which were caused by NH<sub>3</sub> adsorbed on the Lewis acid sites that were now free of nitrates and Brønsted acid sites, respectively. At the end of the reaction (shown in Fig. 6(b)), the stable species (3318, 3270, 3184, 3060, 2831, 1620 and 1471 cm<sup>-1</sup>) were observed on the catalyst surface.



Fig. 6 Reactions between pre-adsorbed nitrate species and NH<sub>3</sub> at 120 °C on the Cu<sub>3.9</sub>-SSZ-13 catalyst: (a) the reaction process recorded with nitrate species as the background; (b) the stable species maintained on the catalyst surface with N<sub>2</sub> as the background.

Clearly, the species were similar to those existing under "standard SCR" conditions (Fig. 4(a)), indicating that the reactions between nitrate species and gaseous  $NH_3$  played an important role in the  $NH_3$ -SCR reaction for the Cu-SSZ-13 catalyst.

Grossale *et al.* reported that NH<sub>3</sub> could react with nitrate species on the surface of Fe–SZM-5 directly at temperatures higher than 220 °C, according to the following equation:  $5NH_3 + 3HNO_3 \rightarrow 4N_2 + 9H_2O$ .<sup>15</sup> The results in this study proved that the reaction could occur at a high rate at a much lower temperature (120 °C) over the Cu–SSZ-13 catalyst. Therefore, if NO<sub>x</sub> could come in contact with the Cu sites and then form nitrate species efficiently, they could be consumed by NH<sub>3</sub> rapidly.

# 3.6 Kinetic diameter of NO<sub>2</sub> and the effect on NH<sub>3</sub>-SCR reaction

The kinetic diameters of molecules play a very important role in predicting their diffusion and adsorption into zeolites, and they are obtained commonly from experimental data. However, the corresponding data are lacking for NO<sub>2</sub>. Liu reported one method to estimate the average diameter of a molecule which is thought to be similar to the molecular kinetic diameter, giving a kinetic diameter for NO<sub>2</sub> in the range from 0.401 to 0.502 nm.<sup>46</sup> A space-filling model (CPK model) has also been used to calculate the kinetic diameter of molecules. Considering the uncertainty of the CPK model, we further calibrated the cross-sectional area using the model and experimental values of Ar, Kr, Xe, N<sub>2</sub>, H<sub>2</sub>O, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>6</sub>, and CO<sub>2</sub>.<sup>47</sup> The calibrated cross-sectional area of NO<sub>2</sub> was 0.206 nm<sup>2</sup>. Thus, the kinetic diameter of NO2 could be estimated as 0.512 nm. These two results indicate that the kinetic diameter of NO2 was larger than 0.38 nm. Thus, different from NO with a kinetic diameter of 0.32 nm, the speed for NO<sub>2</sub> to enter the Cu-CHA pores and form nitrate species was much slower, as shown in Fig. 3(b). If some NO<sub>2</sub> molecules could not form nitrate species on the Cu sites efficiently and react with NH<sub>3</sub>, they could combine with NH<sub>4</sub><sup>+</sup> on the other sites to form NH<sub>4</sub>NO<sub>3</sub>. The formation of NH<sub>4</sub>NO<sub>3</sub> resulting from the reaction between nitrate species and NH4<sup>+</sup> was very fast, but its consumption rate was much slower over the Cu<sub>3.9</sub>-SSZ-13 catalyst (Fig. S4<sup>†</sup>). Ciardelli reported that NH<sub>4</sub>NO<sub>3</sub> is an important intermediate in the "fast SCR" reaction, and the reaction between NH<sub>4</sub>NO<sub>3</sub> and NO is the rate-determining step of the reaction at low temperatures. If the formation of NH<sub>4</sub>NO<sub>3</sub> was faster than its decomposition, the "fast SCR" phenomenon would not be obvious.<sup>2</sup> Unfortunately, less NO could be used for its decomposition under "fast SCR" reaction conditions. Thus, much NH<sub>4</sub>NO<sub>3</sub> accumulated on the catalyst surface under "fast SCR" reaction conditions, and active sites were blocked until NH4NO3 could be decomposed at a higher temperature. Therefore, the key step for the NH<sub>3</sub>-SCR reaction over the Cu-SSZ-13 catalyst in the low temperature range was the formation of nitrate on the Cu sites. Increasing the NO<sub>2</sub> ratio directly in the feed gas was not an effective way to improve the NH3-SCR performance of the Cu-SSZ-13 catalyst prepared by the one-pot-synthesis method.

#### 3.7 Kinetic studies

In order to further prove the conclusions gained from the in situ DRIFTS results, we carried out some kinetic studies. The apparent activation energy  $(E_a)$  for NH<sub>3</sub>-SCR on the Cu<sub>3 9</sub>-SSZ-13 catalyst was estimated using the data obtained in the temperature range where NO<sub>x</sub> conversion increased rapidly. When the  $NO_2/NO_r$  ratio was 0 or 1/2 in the feed gas, the tested temperature range was set at 160-200 °C or 210-250 °C, respectively. Based on the Arrhenius plot of the rate (R) versus inverse temperature (Fig. 7) at different  $NO_2/NO_r$  ratios,  $E_a$  was determined to be ~60 and ~89 kJ mol<sup>-1</sup> for  $NO_2/NO_x = 0$  and  $NO_2/NO_x = 1/2$ , respectively. Therefore,  $E_a$  of "standard SCR" was much lower than that of "fast SCR". The higher performance of "standard SCR" over the Cu-SSZ-13 catalyst correlated well with its lower activation barrier. The presence of NO<sub>2</sub> in the feed gas increased the apparent activation energy, thereby decreasing the activity of  $NO_x$  reduction.

Based on the Arrhenius plot of the rate (*R*) versus inverse temperature (Fig. 8) for NO and NO<sub>2</sub> when the NO<sub>2</sub>/NO<sub>x</sub> ratio was 1/2, the apparent activation energy was determined to be ~63 and ~110 kJ mol<sup>-1</sup>, respectively. Since the reaction between



Fig. 7 Arrhenius plots of rate (R) of NO<sub>x</sub> reduction versus inverse temperature under different NO<sub>2</sub>/NO<sub>x</sub> ratio conditions.



Fig. 8 Arrhenius plots of rate (*R*) versus inverse temperature of NO and NO<sub>2</sub> reduction when the NO<sub>2</sub>/NO<sub>x</sub> ratio was 1/2.

NO and NH<sub>3</sub> showed lower  $E_a$  and higher reaction activity than the reaction between NO<sub>2</sub> and NH<sub>3</sub>, it is reasonable to conclude that the N<sub>2</sub> formation mainly came from the reaction between NO and NH<sub>3</sub> under "fast SCR" conditions.

## 4. Conclusions

The Cu<sub>3.9</sub>-SSZ-13 catalyst prepared by the one-pot-synthesis method exhibited excellent NH3-SCR activity under "standard SCR" conditions. However, poorer SCR performance was observed in the low temperature range with the increase of the NO<sub>2</sub> concentration in the feed gas. The results of in situ DRIFTS experiments indicate that the inhibitory effect was caused by NH<sub>4</sub>NO<sub>3</sub> deposition. The reactions between nitrate species and gaseous NH<sub>3</sub> played an important role in the NH<sub>3</sub>-SCR reaction at low temperatures for the catalyst. Thus, the key step of the reaction was the formation of nitrate on the Cu sites. However, because the kinetic diameter of NO<sub>2</sub> was larger than the pores of the CHA structure, some NO<sub>2</sub> could not form nitrate on the Cu sites efficiently to react with NH<sub>3</sub> but combined with NH<sub>4</sub><sup>+</sup> on the Brønsted acid sites to form NH<sub>4</sub>NO<sub>3</sub>. The consumption rate of NH<sub>4</sub>NO<sub>3</sub> by NO was slower than its formation under "fast SCR" conditions, resulting in much accumulated NH4NO3 on the catalyst surface blocking active sites. The results of kinetic studies indicate that the apparent activation energy was high when NO<sub>2</sub> was present in the feed gas, and the reaction between NO and NH<sub>3</sub> was dominant under "fast SCR" conditions.

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