# Distinct NO<sub>2</sub> effects on Cu-SSZ-13 and Cu-SSZ-39 in the selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>

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Summary: Supporting information consists of 21 pages with 1 table and 13 figures.

#### **1 Experimental**

#### 1.1 Activity tests

The SCR activity tests were carried out in a fixed-bed quartz flow reactor at atmospheric pressure. Before the tests, the catalysts were pressed, crushed and sieved to 40–60 mesh. The reaction conditions were controlled as follows: 500 ppm NO for standard SCR (or [NO] =  $[NO_2]$  = 250 ppm for fast SCR), 500 ppm NH<sub>3</sub>, 5 vol. % O<sub>2</sub>, N<sub>2</sub> balance, and 500 mL/min total flow rate. The concentrations of N-containing effluent gases (NO, NH<sub>3</sub>, NO<sub>2</sub>, and N<sub>2</sub>O) were continuously analyzed by an Antaris IGS gas analyzer (Thermo Fisher) equipped with a heated, low-volume multiple-path gas cell. The FTIR spectra were collected throughout and the results were recorded when the SCR reaction reached steady state.

#### **1.2 Characterization**

The elemental composition was determined with an inductively coupled plasma spectrometer (OPTIMA 7000DV) with a radial view of the plasma.

The morphology of the catalyst was examined by scanning electron microscopy (SEM) using a S4800 electron microscope. Transmission electron microscope (TEM) imaging and mapping tests were carried out on a JEOL JEM-ARM2100F electron microscope operating at 200 kV.

The surface areas and pore characteristics of the samples were obtained by  $N_2$  adsorption/desorption analysis at -196 °C using a physisorption analyzer (MicrotracBEL). Prior to the  $N_2$  physisorption, the catalysts were degassed at 300 °C for 2 h.

The  $H_2$  temperature programmed reduction ( $H_2$ -TPR) and the temperature programmed desorption of  $NH_3$  ( $NH_3$ -TPD) experiments were performed on a Micromeritics Autochem 2920

system. Prior to analysis, the samples were pretreated at 300 °C in a flow of Ar (50 mL·min<sup>-1</sup>) for 1 h and cooled down to the room temperature. For H<sub>2</sub>-TPR, the samples were heated from room temperature to 1000 °C in 10 vol. % H<sub>2</sub>/Ar gas flow of 50 mL/min at a heating rate of 10 °C·min<sup>-1</sup>, and H<sub>2</sub> consumption was monitored with a TCD detector. For NH<sub>3</sub>-TPD, the samples were exposed to 2500 ppm NH<sub>3</sub>/He at 50 °C for 1 h, followed by He purge for another 1 h. Finally, the temperature was raised to 650 °C at the rate of 10 °C·min<sup>-1</sup> and the signal was detected by a TCD detector.

NO<sub>2</sub>-TPD results were obtained as part of the NH<sub>3</sub>-SCR activity test. A 50-mg sample of catalyst was pre-treated in air with 20 %  $O_2/N_2$  for 1 h at 500 °C and then cooled down to 30 °C. Afterwards, the sample was exposed to 500 ppm NO<sub>2</sub>/N<sub>2</sub> for 1 h, followed by N<sub>2</sub> purging for another 1 h. Finally, the temperature was raised to 600 °C at the rate of 10 °C·min<sup>-1</sup> and the production of NO<sub>x</sub> was detected by an Antaris IGS gas analyzer.

The pyridine adsorption infrared (Py-FTIR) experiments were performed on a Frontier FT-IR spectrometer. The samples were dehydrated at 350 °C for 2 h under a vacuum of  $1.33 \times 10^{-3}$  Pa, and then the adsorption of pure pyridine vapor was carried out at room temperature for 30 min. After reaching equilibrium, the Py-adsorbed system was evacuated for 0.5 h at 200 °C and 350 °C, respectively, and the corresponding Py-IR spectra were recorded.

In situ diffuse reflectance infrared Fourier transform spectra (*in situ* DRIFTS) were collected on a FTIR spectrometer (Nicolet IS50) equipped with a Smart Collector and an MCT/A detector cooled by liquid nitrogen. The reaction temperature was controlled precisely by an Omega programmable temperature controller. The catalysts were pretreated in 20%  $O_2/N_2$  flow at 500 °C for 30 min, and then cooled down to the desired temperature. The background spectra were collected in flowing  $N_2$  and automatically subtracted from the sample spectra. The reaction conditions were controlled as follows: 300 mL/min total flow rate, 500 ppm NH<sub>3</sub>, 500 ppm NO<sub>x</sub>, 5% O<sub>2</sub>, and N<sub>2</sub> balance. For the experiments on NH<sub>3</sub> or NO<sub>x</sub> adsorption, the sample was saturated with NH<sub>3</sub>/N<sub>2</sub> or NO<sub>x</sub>/N<sub>2</sub> for 40 min, and then purged with N<sub>2</sub> for 30 min. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm<sup>-1</sup>.

#### 2 Results



Figure S1. NH<sub>3</sub>-SCR performance of (a) H-SSZ-13 and (b) H-SSZ-39 zeolites. Reaction conditions: 500 ppm NO<sub>x</sub> (500 ppm NO for standard SCR or 250 ppm NO + 250 ppm NO<sub>2</sub> for fast SCR), 500 ppm NH<sub>3</sub>,  $[O_2] = 5$  vol. %, N<sub>2</sub> balance, and GHSV = 400,000 h<sup>-1</sup>

To investigate the effects of NO<sub>2</sub>, activity tests were conducted on H-SSZ-13 and H-SSZ-39 under standard SCR and fast SCR conditions, respectively, and the results are shown in Figure S1. In the absence of NO<sub>2</sub>, there was almost no NO<sub>x</sub> conversion observed for H-SSZ-13 or H-SSZ-39, indicating that only the standard SCR reaction occurred on Cu active sites, i.e., NO only reacted with the NH<sub>3</sub> species adsorbed on Cu sites to form N<sub>2</sub>. However, under fast SCR condition, the NO conversion sharply increased at temperatures above 250 °C, indicating that the fast SCR reaction can take place at the acid sites in the absence of Cu species. The NO conversion was still lower than the NO<sub>2</sub> conversion, which may be due to the accumulation or partial decomposition of NH<sub>4</sub>NO<sub>3</sub>, resulting in excessive consumption of NH<sub>4</sub>NO<sub>3</sub>.



Figure S2. TPD results after NH<sub>3</sub> and NO<sub>2</sub> adsorption at 130 °C for Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39. Adsorption conditions:  $[NO_2] = [NH_3] = 500$  ppm, N<sub>2</sub> balance, total flow rate = 500 mL/min. Reaction conditions: heating rate = 10 °C min<sup>-1</sup>

Figure S2 shows the TPD results after adsorption of  $NH_3$  and  $NO_2$ . The decomposition temperatures of  $NH_4NO_3$  on  $Cu_{1.8}$ -SSZ-13 and  $Cu_{1.8}$ -SSZ-39 were almost the same, but the amounts of  $N_2O$  and  $NH_3$  generated on  $Cu_{1.8}$ -SSZ-13 were both much higher than those on  $Cu_{1.8}$ -SSZ-39, due to more  $NH_4NO_3$  accumulation on  $Cu_{1.8}$ -SSZ-13.



**Figure S3.** *In situ* DRIFTS results of NH<sub>3</sub> adsorption at 200 °C over (a) Cu<sub>1.8</sub>-SSZ-13 and (b) Cu<sub>1.8</sub>-SSZ-39 and (c) IR spectra of T-O-T vibration regions (1000-850 cm<sup>-1</sup>) after NH<sub>3</sub>

## adsorption.

The *in situ* DRIFTS results of NH<sub>3</sub> adsorption on Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39 catalysts are shown in Figure S3. The same NH<sub>3</sub> adsorbed species were observed on Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39. The band at 1446 cm<sup>-1</sup> was assigned to NH<sub>4</sub><sup>+</sup> adsorbed at the Brønsted acid sites, and the bands at 1617 and 1264 cm<sup>-1</sup> were attributed to NH<sub>3</sub> species coordinated at the Lewis acid sites.<sup>1</sup> The bands at 3372, 3322 and 3273 cm<sup>-1</sup> were attributed to the N-H stretching vibration of NH<sub>4</sub><sup>+</sup>, and the band at 3184 cm<sup>-1</sup> was due to NH<sub>3</sub> adsorbed on Cu<sup>+</sup>.<sup>2</sup> The band at 897 cm<sup>-1</sup> was associated with the T-O-T framework vibration perturbed by Cu cations.<sup>3</sup> The consumption bands at 3609 and 3576 cm<sup>-1</sup> were attributed to the depletion of Si-OH-A1 by NH<sub>3</sub>.<sup>4</sup> Specifically, the bands at 3609 and 3576 cm<sup>-1</sup> were assigned to Si-OH-Al groups positioned at cages and at 6MR, respectively.<sup>5</sup> According to the intensity of the consumption band at 3609 cm<sup>-1</sup>, Cu<sub>1.8</sub>-SSZ-39 had more Si-OH-Al groups positioned at cages.

Figure S3c showed the IR spectra in the zeolite T-O-T bond vibration region after NH<sub>3</sub> adsorption on the Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39. The negative peaks at 942 and 897 cm<sup>-1</sup> observed on the two catalysts were assigned to the zeolite T-O-T vibrations perturbed by Cu(OH)<sup>+</sup>- Z next to 8-membered ring (8MR) and Cu<sup>2+</sup>-2Z next to the 6-membered ring (6MR), respectively. Specifically, the band at 942 cm<sup>-1</sup> was very weak, while the band at 897 cm<sup>-1</sup> was relatively strong, indicating that the main Cu species for both Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39 were Cu<sup>2+</sup> in 6MR, consistent with the H<sub>2</sub>-TPR results.



**Figure S4.** *In situ* DRIFTS results of NO + O<sub>2</sub> adsorption at 200 °C over (a) Cu<sub>1.8</sub>-SSZ-13 and (b) Cu<sub>1.8</sub>-SSZ-39.

The *in situ* DRIFTS results of NO + O<sub>2</sub> adsorption on Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39 catalysts are shown in Figure S4. The band at 2190 (2184) cm<sup>-1</sup> may be assigned to NO<sup>+</sup> species. The band at 1622 cm<sup>-1</sup> was attributed to bridge nitrate, and the bands at 1597 and 1575 cm<sup>-1</sup> were attributed to bidentate nitrate.<sup>6</sup> After exposure to NO + O<sub>2</sub> and N<sub>2</sub> purging, the surface species on Cu<sub>1.8</sub>-SSZ-13 was mainly NO<sup>+</sup> species and the peak of nitrate was very weak. However, after the introduction of NO + O<sub>2</sub> to Cu<sub>1.8</sub>-SSZ-39 and N<sub>2</sub> purging, the major species on the surface of Cu<sub>1.8</sub>-SSZ-39 were bridge nitrate and bidentate nitrate, while the adsorption peak of NO<sup>+</sup> species was very weak, indicating that the adsorbed NO<sub>x</sub> species on the surfaces of Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39 were different.



**Figure S5.** *In situ* DRIFTS results of NO<sub>2</sub> + O<sub>2</sub> adsorption at 200 °C over (a) Cu<sub>1.8</sub>-SSZ-13 and (b) Cu<sub>1.8</sub>-SSZ-39.

Figure S5 shows the *in situ* DRIFTS results of  $NO_2 + O_2$  adsorption results of  $Cu_{1.8}$ -SSZ-13 and  $Cu_{1.8}$ -SSZ-39 catalysts at 200 °C. Bands assigned to NO<sup>+</sup> species (2190 cm<sup>-1</sup>), bridge nitrate (1622 and 1609 cm<sup>-1</sup>) and bidentate nitrate (1597 and 1575 cm<sup>-1</sup>) were observed. For both  $Cu_{1.8}$ -SSZ-13 and  $Cu_{1.8}$ -SSZ-39, the adsorption behaviors of  $NO_2 + O_2$  were similar to those of NO +  $O_2$ . After the adsorption of  $NO_2 + O_2$ , the main surface species on  $Cu_{1.8}$ -SSZ-13 was the NO<sup>+</sup> species, while the main species on  $Cu_{1.8}$ -SSZ-39 were bridge nitrate and bidentate nitrate.



Figure S6. NO<sub>2</sub>-TPD results of Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39. Adsorption conditions:  $[NO_2] = 500 \text{ ppm}$ , N<sub>2</sub> balance, 500 mL/min. Reaction conditions: heating rate = 10 °C·min<sup>-1</sup>

The NO<sub>2</sub>-TPD results of Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39 are shown in Figure S6. Two desorption peaks of NO<sub>x</sub> species were observed for both Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39. The peak at 100 °C was attributed to physically adsorbed NO<sub>x</sub> or monodentate nitrate,<sup>7,8</sup> while the peak at 325 °C may be assigned to bidentate nitrate and bridge nitrate.<sup>9,10</sup> In contrast, the amount of monodentate nitrate on Cu<sub>1.8</sub>-SSZ-13 was more than that on Cu<sub>1.8</sub>-SSZ-39, while the amounts of bidentate nitrate and bridge nitrate on Cu<sub>1.8</sub>-SSZ-39, while the amounts of in accordance with the *in situ* DRIFTS results of NO<sub>x</sub> adsorption (Figure S4 and Figure S5).



Figure S7. In situ DRIFTS results of NO +  $O_2$  adsorption after the adsorption of NH<sub>3</sub> and NO<sub>2</sub> at 200 °C over (a) Cu<sub>1.8</sub>-SSZ-13 and (b) Cu<sub>1.8</sub>-SSZ-39

When NO +  $O_2$  was introduced to the Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39 with pre-adsorbed NH<sub>3</sub> and NO<sub>2</sub> (Figure S7), the reaction process was almost the same as for the introduction of NO (without O<sub>2</sub>), with NO rapidly reacting with NH<sub>4</sub>NO<sub>3</sub> on Cu<sub>1.8</sub>-SSZ-39.



Figure S8. In situ DRIFTS results of TPD after the adsorption of  $NH_3$  and  $NO_2$  at 30 °C over (a) Cu<sub>1.8</sub>-SSZ-13 and (b) Cu<sub>1.8</sub>-SSZ-39

Figure S8 shows the *in situ* DRIFTS results of TPD after NH<sub>3</sub> and NO<sub>2</sub> adsorption on Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39. After NH<sub>3</sub> and NO<sub>2</sub> were adsorbed on Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39 at 30 °C, typical bands at 1485, 1256, 3279, 1569, 1589, 3038, 2822, 3609, and 897 cm<sup>-1</sup> appeared. The bands at 1485, 1256 and 3279 cm<sup>-1</sup> were assigned to NH<sub>3</sub> adsorbed species;<sup>1,2</sup> the negative bands at 3609 and 897 cm<sup>-1</sup> were attributed to the consumption of Si-OH-Al by NH<sub>3</sub> and the T-O-T framework vibration by Cu, respectively;<sup>3,4</sup> the bands at 1569 and 1589 cm<sup>-1</sup> were attributed to bidentate nitrate species.<sup>6</sup> The bands at 3038 and 2822 cm<sup>-1</sup> could be attributed to the NH<sub>4</sub><sup>+</sup> from NH<sub>4</sub>NO<sub>3</sub>,<sup>11</sup> confirming the formation of NH<sub>4</sub>NO<sub>3</sub> on these two catalysts.

With the increase of temperature, the intensity of each adsorption peak decreased gradually, due to the decomposition of  $NH_4NO_3$  and the desorption of  $NH_3$ . On  $Cu_{1.8}$ -SSZ-13, the band at 1485 cm<sup>-1</sup> significantly decreased above 300 °C and redshifted to 1441 cm<sup>-1</sup>, which may be due to the desorbed  $NH_3$  being physically adsorbed on  $NH_4^+$ .<sup>12</sup> Moreover, the band at 1485 cm<sup>-1</sup> on  $Cu_{1.8}$ -SSZ-39 significantly diminished and redshifted to 1441 cm<sup>-1</sup> at 200 °C.



Figure S9. SEM of (a, b) Cu<sub>1.8</sub>-SSZ-13 and (c, d) Cu<sub>1.8</sub>-SSZ-39







Figure S11.  $H_2$ -TPR results of  $Cu_{1.8}$ -SSZ-13 and  $Cu_{1.8}$ -SSZ-39



Figure S12. NH<sub>3</sub>-TPD results of Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39



Figure S13. Py-FTIR spectra of Cu<sub>1.8</sub>-SSZ-13 and Cu<sub>1.8</sub>-SSZ-39 catalysts at (a) 200 °C and (b) 350 °C

The Py-FTIR was carried out to investigate the surface acid sites, and the results are shown in Figure S13. The Py-FTIR spectra at 200 °C and 350 °C correspond to total acid sites as well as total moderate and strong acid sites. The bands at ca. 1540 and 1450 (1455) cm<sup>-1</sup> are assigned to the adsorption of pyridine on Brønsted (B) and Lewis (L) acid sites, respectively.<sup>13,14</sup>

Samples	ABET	V	Cu content	Si/Al
	$(m^2/g)$	$(cm^3/g)$	(%)	molar ratio
Cu <sub>1.8</sub> -SSZ-13	718	0.31	1.79	4.5
Cu <sub>1.8</sub> -SSZ-39	650	0.26	1.85	8.2

Table S1. Specific surface areas and Cu contents of  $Cu_{1.8}$ -SSZ-13 and  $Cu_{1.8}$ -SSZ-39

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