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Distinct NO₂ Effects on Cu-SSZ-13 and Cu-SSZ-39 in the Selective Catalytic Reduction of NO_x with NH_3

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ABSTRACT: Cu-SSZ-13 and Cu-SSZ-39, with similar structures, are both highly active and hydrothermally stable in the selective catalytic reduction of NO_x with NH₃ (NH₃-SCR), attracting great attention for applications on diesel vehicles. In this study, it was interestingly found that NO₂ has distinct effects on the NO_x conversion over Cu-SSZ-13 and Cu-SSZ-39, with an inhibiting effect for Cu-SSZ-13 but a promoting effect for Cu-SSZ-39. The distinct NO₂ effects were found to be associated with the differences in the reactivity of surface NH₄NO₃, a key intermediate for NH₃-SCR, on these two Cu-based small-pore zeolites. Cu-SSZ-13 has excellent standard SCR activity, but the reactivity of surface NH₄NO₃ on the surface and thus inhibit NO_x conversion. Surface Brønsted acid sites play key roles in the reduction of surface NH₄NO₃ by NO, and Cu-SSZ-39 showed much higher surface acidity than Cu-SSZ-13. Compared with Cu-SSZ-13, the intrinsic standard SCR activity of Cu-SSZ-39 was lower but NH₄NO₃ could be reduced by NO



rapidly on Cu-SSZ-39, even faster than the reduction of NO by the adsorbed NH_3 on Cu active sites; thus, NO_x conversion was promoted by NO_2 on Cu-SSZ-39. This work provides an improved understanding of fast SCR on Cu-based small-pore zeolites.

1. INTRODUCTION

Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is the predominate technology for the abatement of NO_x from diesel engine vehicles.^{1–3} Based on different proportions of NO₂ in NO_x, the SCR reactions can be classified into three types, as shown by the following reaction equations

standard SCR(NO₂/NO_x = 0): 4NH₃ + 4NO + O₂

$$\rightarrow$$
 4N₂ + 6H₂O (1)

fast SCR(NO₂/NO_x = 0.5): 2NH₃ + NO + NO₂

$$\rightarrow$$
 2N₂ + 3H₂O

$$NO_2 SCR(NO_2/NO_x > 0.5): 8NH_3 + 6NO_2$$

 $\rightarrow 7N_2 + 12H_2O$ (3)

The effect of NO₂ has attracted great attention, because the fast SCR reaction usually proceeds at a higher reaction rate than the standard SCR reaction, and plays a critical role at low temperatures in boosting deNO_x activity for diesel exhaust after treatment.^{4–7} A diesel oxidation catalyst upstream of the SCR catalyst can partially oxidize NO to NO₂ and thus promote SCR. Koebel *et al.*^{6,8} and Tronconi *et al.*^{9,10} extensively investigated the fast SCR mechanism over the vanadium-based oxide and Fe-based zeolite catalysts. Fast SCR can be described as an overall reaction, in which NH₄NO₃ is an

important intermediate formed by reaction 4 and then reduced by NO following reaction 5, with these two reactions proceeding sequentially. Specifically, reaction 4 can be described as the sum of reactions 6–8 and 11, and reaction 5 has been demonstrated by the dedicated transient reactions 9-11.^{9,11,12} If reaction 4 is faster than reaction 5, the build-up of NH₄NO₃ is observed; if reaction 5 is faster than reaction 4, fast SCR occurs smoothly. The reaction selectivity is determined by the decomposition of NH₄NO₃ to N₂O (reaction 12).^{5,6}

 $2NO_2 + 2NH_3 \rightarrow N_2 + NH_4NO_3 + 2H_2O \tag{4}$

$$NO + NH_4NO_3 \rightarrow NO_2 + N_2 + H_2O$$
(5)

$$2NO_2 \rightleftharpoons N_2O_4 \tag{6}$$

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$$
⁽⁷⁾

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \tag{8}$$

$$NH_4NO_3 \rightarrow NH_3 + HNO_3$$
 (9)

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$$HNO_3 + NO \rightarrow NO_2 + HNO_2$$
(10)

$$HNO_{2} + NH_{3} \rightarrow NH_{4}NO_{2} \rightarrow NH_{2}-NO + H_{2}O$$

$$\rightarrow N_{2} + 2H_{2}O$$
(11)

$$\mathrm{NH}_4\mathrm{NO}_3 \to \mathrm{N}_2\mathrm{O} + 2\mathrm{H}_2\mathrm{O} \tag{12}$$

Cu–CHA zeolites have been developed and commercialized for NH₃-SCR in diesel engine exhaust after treatment because of their excellent SCR performance and hydrothermal stability.³ Many studies have focused on the preparation and characterization,^{13,14} deactivation,^{15,16} hydrothermal stability,^{17,18} active sites, and catalytic mechanism of Cu-SSZ-13.^{19,20} Although Cu-SAPO-34 exhibited even better hightemperature SCR activity and stability than Cu-SSZ-13, poor durability in the presence of moisture at low temperatures has restrained its application.²¹

Fast SCR widely occurs on metal oxide catalysts and largepore zeolites^{4,12,22,23} but fails for small-pore CHA zeolites. Concerning the effect of NO₂ on Cu-SSZ-13, Xie *et al.*²⁴ and Shan *et al.*²⁵ showed that NO₂ inhibited the SCR activity because of the accumulation of NH₄NO₃ and pore-plugging. Bendrich *et al.* conducted microkinetics simulations of fast SCR over Cu–CHA and suggested that the oxidation state of the Cu active sites did not change under fast SCR conditions.²⁶ McEwen *et al.* demonstrated that Cu²⁺ was the only evident Cu oxidation state in the fast SCR reaction on Cu-SSZ-13.²⁷

Cu-SSZ-39, with the AEI structure, which is similar to CHA, is another attractive small-pore zeolite catalyst for NH₃-SCR. It was first investigated for NH₃-SCR by Corma et al. in 2012.²⁸ Cu-SSZ-39 showed better SCR activity and hydrothermal stability than Cu-SSZ-13 and was considered to be a very promising candidate for NH₃-SCR.^{29,30} Shan *et al.* found that Cu-SSZ-39 contained more Cu²⁺-2Z species balanced with paired Al than Cu-SSZ-13, which is the reason that Cu-SSZ-39 possesses higher hydrothermal stability.³¹ Du et al. investigated the effects of sulfation on the NH₃-SCR performance of Cu-SSZ-39 and found that the activity of the sulfated catalyst can be recovered partially by high-temperature regeneration.³ Recently, Xu et al. reported a facile synthesis method of SSZ-39 by the transformation of ZSM-5 and Beta zeolites, as well as a direct synthesis method of SSZ-39 using colloidal silica and sodium aluminate as the raw source, instead of using the FAU zeolite. The development of synthetic methods has offered more opportunity for the wide application of Cu-SSZ-39.³³ However, the effects of NO₂ on Cu-SSZ-39 have not yet been reported, and whether the behavior of NH4NO3 on Cu-SSZ-39 is similar to that on Cu-CHA needs to be investigated. In the present work, a comparison study of the effects of NO₂ on Cu-SSZ-13 and Cu-SSZ-39 was carried out and discussed in detail.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. H-SSZ-39 was synthesized from the FAU zeolite by hydrothermal transformation at 140 °C for 72 h using *N*,*N*-dimethyl-3,*S*-dimethylpiperdimum as an organic structure-directing agent (OSDA). Before Cu loading, H-SSZ-39 was filtered, washed, and calcined at 600 °C for 6 h, and then transformed to NH₄-SSZ-39 by ion-exchange at 80 °C for 6 h with NH₄NO₃ solution (0.5 mol/L) for two times. Cu-SSZ-39 was prepared by the ion exchange of NH₄-SSZ-39 with a Cu(NO₃)₂ solution at 80 °C for 5 h and calcination at 550 °C for 5 h. Cu-SSZ-13 was prepared by the one-pot method and then after being treated by 0.1 mol/L NH₄NO₃ at

80 °C for 5 h.²⁵ The Cu contents of Cu-SSZ-13 and Cu-SSZ-39 were controlled to similar levels at about 1.8%, as determined by ICP, and these two samples were named Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39. H-SSZ-13 was synthesized using N,N,N-trimethyl-1-adamantanamine iodide as the organic template.³⁵

2.2. Activity Test and Kinetic Experiments. The NH₃-SCR performance of as-obtained catalysts was evaluated in a continuous-flow fixed-bed reactor system. The reaction conditions were controlled as follows: 500 ppm NO_x (500 ppm NO for standard SCR or 250 ppm NO + 250 ppm NO₂ for fast SCR), 500 ppm NH₃, 5 vol % O₂, and N₂ balance, with a total flow rate of 500 mL/min and a gas hourly space velocity (GHSV) of 400,000 h⁻¹. The concentrations of reactants and products were measured by a gas analyzer (Antaris IGS, Thermo Fisher) equipped with a heated, low-volume multiple-path gas cell.³⁶ The NO, NO₂, and NO_x conversion levels were calculated by the following equations:

NO conversion =
$$\left(1 - \frac{[NO]_{outlet}}{[NO]_{inlet}}\right) \times 100\%$$

NO₂ conversion = $\left(1 - \frac{[NO_2]_{outlet}}{[NO_2]_{inlet}}\right) \times 100\%$
NO_x conversion = $\left(1 - \frac{[NO]_{outlet} + [NO_2]_{outlet}}{[NO]_{inlet} + [NO_2]_{inlet}}\right)$
 $\times 100\%$

In the kinetic experiments, to eliminate the effects of masstransfer limitations and ensure the kinetic data obtained within kinetically regime, the particles of samples and a total flow rate were selected as 60–80 mesh and 500 mL/min, respectively. The feed gas contained 500 ppm NO_x (500 ppm NO for standard SCR or 250 ppm NO + 250 ppm NO₂ for fast SCR), 500 ppm NH₃, 5 vol % O₂, and N₂ balance. The catalyst (10– 17 mg) was loaded in a quartz reactor with an inner diameter of 3 mm. The length of the catalyst bed was 3–4 mm. The data were collected at steady state after the reaction proceeded for 200 min. When the NO_x conversion was kept below 20%, the apparent activation energy (E_a) was calculated based on the Arrhenius plot of the reaction rate (r) versus 1/T (T is the temperature).

2.3. Characterization. Inductively coupled plasma (ICP), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N_2 physisorption, H_2 -TPR, NH_3 -TPD, and NO_2 -TPD measurements of catalysts were carried out, and the experimental details are shown in Supporting Information.

In situ diffuse reflectance infrared Fourier transform spectra (*in situ* DRIFTS) were recorded on a Nicolet IS50 FTIR spectrometer equipped with a liquid N₂ cooled MCT/A detector and computer-controlled reaction chamber temperature controller. The reaction temperature was controlled precisely by an Omega programmable temperature controller. Prior to each test, the catalyst was pretreated in air flow at 500 °C for 0.5 h before test. The DRIFT spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹. The reaction conditions were controlled as follows: 300 mL/min total flow rate, 500 ppm NH₃, 500 ppm NO_x, 5 vol % O₂, and N₂ balance. For the experiments of NH₃ or NO_x adsorption, the samples were saturated with NH₃/N₂ or NO_x/N₂ for 40 min and then purged with N₂ for 30 min. To investigate the

Conversion (%)

100 100 (b) (a) -80 Cu__-SSZ-13 80 Cu₁₈-SSZ-39 Conversion (%) NO,/NO_ = 0 NO₂/NO₂ = 0 60 60 NO conversion NO conversion 40 40 NO_/NO_ = 1/2 NO_/NO_ = 1/2 NO conversion NO conversion 20 20 NO₂ conversion NO₂ conversion 0 L 100 0 ∟ 100 200 400 400 500 300 500 200 300 Temperature (°C) Temperature (°C)

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Figure 1. NH₃-SCR performance of (a) Cu_{1.8}-SSZ-13 and (b) Cu_{1.8}-SSZ-39 catalysts. Reaction conditions: 500 ppm NO_x (500 ppm NO for standard SCR or 250 ppm NO + 250 ppm NO₂ for fast SCR), 500 ppm NH₃, $[O_2] = 5$ vol %, N₂ balance, and GHSV = 400,000 h⁻¹.



Figure 2. Arrhenius plots of the SCR reaction rates over (a) $Cu_{1.8}$ -SSZ-13 and (b) $Cu_{1.8}$ -SSZ-39 versus inverse temperature. Reaction conditions: (1) standard SCR ($NO_2/NO_x = 0$): [NO] = [NH_3] = 500 ppm, [O_2] = 5 vol %, N_2 balance, 17 mg of the catalyst, total flow rate = 500 mL, and GHSV = 1,000,000 h⁻¹ and (2) fast SCR ($NO_2/NO_x = 0.5$): [NO] = [NO_2] = 250 ppm, [NH_3] = 500 ppm, [O_2] = 5 vol %, N_2 balance, 10 mg of the catalyst, total flow rate = 500 mL/min, and GHSV = 1,700,000 h⁻¹.



Figure 3. NO and NO₂ reaction rates over (a) Cu_{1.8}-SSZ-13 and (b) Cu_{1.8}-SSZ-39 under standard SCR and fast SCR. Reaction conditions: (1) standard SCR (NO₂/NO_x = 0): [NO] = [NH₃] = 500 ppm, [O₂] = 5 vol %, N₂ balance, 17 mg of the catalyst, total flow rate = 500 mL, and GHSV = 1,000,000 h⁻¹ and (2) fast SCR (NO₂/NO_x = 0.5): [NO] = [NO₂] = 250 ppm, [NH₃] = 500 ppm, [O₂] = 5 vol %, N₂ balance, 10 mg of the catalyst, total flow rate = 500 mL/min, and GHSV = 1,700,000 h⁻¹.

reactions between NO and pre-adsorbed NH_3 and NO_2 , NH_3/N_2 and NO_2/N_2 were fed to DRIFTS cell simultaneously for 1 h and then purged with N_2 for another 30 min. After that, the pre-adsorbed catalysts were exposed to NO/N_2 for 1 h. For TPD experiments, the background spectra were collected in flowing N_2 at intervals of 100 °C from 100–500 °C. After the adsorption of NH_3 and NO_2 at 30 °C for 1 h and then purging with N_2 , the samples were heated to 500 °C. During the temperature ramp, DRIFT spectra of samples were collected after subtracting the corresponding background spectra at every target temperature.

3. RESULTS AND DISCUSSION

3.1. Catalytic Activity. The NH₃-SCR activities of Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39 under standard SCR and fast SCR are shown in Figure 1. When NO₂/NO_x = 0.5 in the feed, below 250 °C, the SCR activity of Cu_{1.8}-SSZ-13 was significantly inhibited, and the conversion percentages of NO

and NO₂ were both very low. Above 250 °C, the NO_x conversion of Cu_{1.8}-SSZ-13 increased sharply to 100%, which was associated with the decomposition of NH₄NO₃ and the recovery of activity. For Cu_{1.8}-SSZ-39, the NO conversion under standard SCR was relatively low, and significantly lower than that under fast SCR conditions at temperatures above 190 °C. Moreover, the ratio of NO conversion: NO₂ conversion under fast SCR was close to 1:1, indicating that fast SCR occurred smoothly on Cu_{1.8}-SSZ-39, which is different from the case with Cu_{1.8}-SSZ-13. Besides, for Cu_{1.8}-SSZ-39, the NO₂ conversion is slightly higher than NO conversion above 185 °C, which may be due to the accumulation or decomposition of a small amount of NH₄NO₃, apart from the reaction with NO. In addition, under standard SCR conditions, there was almost no NO_x conversion observed for H-SSZ-13 or H-SSZ-39, while NO conversion sharply increased above 250 °C in the presence of NO₂, indicating that the standard SCR reaction only occurred on Cu active sites and the fast SCR reaction can

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Figure 4. TPSR of 500 ppm NO passing over pretreated (a) Cu_{1.8}-SSZ-13 and (b) Cu_{1.8}-SSZ-39 by 500 ppm NH₃ and 500 ppm NO₂ at 130 °C.



Figure 5. In situ DRIFTS results of NO introduction after the adsorption of NH₃ and NO₂ at 200 °C over (a) Cu_{1.8}-SSZ-13 and (b) Cu_{1.8}-SSZ-39.

take place at the acid sites in the absence of Cu species (Figure S1).

Kinetic experiments were performed over Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39 under standard SCR and fast SCR conditions, and the results are shown in Figure 2. For Cu_{1.8}-SSZ-13, the activation energies of standard SCR and fast SCR were almost the same. For Cu_{1.8}-SSZ-39, the activation energy of standard SCR was *ca.* 55.5 kJ/mol, while the activation energy of fast SCR was different in two different temperature ranges. When the temperature was below 190 °C, the activation energy was *ca.* 21.5 kJ/mol, while above 190 °C, the activation energy was *ca.* 118.3 kJ/mol. This result indicated two different reaction mechanisms for Cu_{1.8}-SSZ-39 under fast SCR conditions and confirmed the participation of NH₄NO₃ as the rate-limiting step.³⁷

The reaction rates of NO and NO₂ in the kinetic experimental range under standard SCR and fast SCR conditions were compared, as shown in Figure 3. Under standard SCR conditions, the intrinsic activity of Cu_{1.8}-SSZ-13 was higher than that of Cu_{1.8}-SSZ-39. For Cu_{1.8}-SSZ-13, both the NO and NO₂ reaction rates under fast SCR conditions were much lower than the NO reaction rate under standard SCR conditions in the range from 160 to 230 °C, with the NO reaction rate under fast SCR conditions being particularly low, indicating that the fast SCR reaction almost did not occur and the presence of NO₂ inhibited the conversion of NO. On the other hand, for Cu_{1.8}-SSZ-39, the NO₂ reaction rate of fast SCR was higher than the NO reaction rate of standard SCR in the whole temperature range, but the NO reaction rate of Cu_{1.8}-SSZ-39 in the fast SCR reaction was much lower at low temperatures (below 184 °C). With the temperature increasing above 184 °C, the NO reaction rate significantly increased to be close to the NO₂ reaction rate, indicating that the fast SCR reaction occurred smoothly. In addition, the NO reaction rate of Cu_{1.8}-SSZ-39 under fast SCR conditions was higher than that under standard SCR conditions above 184 °C, indicating

that the reaction between NO and $\rm NH_4NO_3$ was faster than that between NO and adsorbed $\rm NH_3$ species on Cu active sites.

3.2. Reactivity of NH₄NO₃. The activity tests and kinetics experiments demonstrated that the fast SCR reaction did occur smoothly on Cu_{1.8}-SSZ-39, and the NO reaction rate (above 184 °C) of fast SCR was higher than that of standard SCR, while the SCR reaction over Cu_{1.8}-SSZ-13 was inhibited by NO₂ because of the blockage of pores by NH₄NO₃. Therefore, the reactivity of NH4NO3 with NO was further investigated in this study, as shown in Figure 4. At 130 $^\circ$ C, 500 ppm NH₃ and 500 ppm NO₂ were fed together to Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39 for 1 h and then purged by N_{24} and thus NH_4NO_3 was accumulated in situ. After that, NO was introduced to the catalysts and the temperature ramped, and NO₂ was generated simultaneously when NO was consumed, indicating that NO can react with the formed NH4NO3. Compared with Cu1.8-SSZ-13, the reaction temperature of NO with NH₄NO₃ was markedly lower on Cu_{1.8}-SSZ-39 and more NO₂ was produced, indicating that the accumulated NH₄NO₃ on Cu_{1.8}-SSZ-39 was more reactive. As shown in Figure 4b, the N₂O production due to NH₄NO₃ decomposition for Cu_{1.8}-SSZ-13 is up to 230 ppm, which is much higher than that for Cu_{1.8}-SSZ-39 (with less than 50 ppm). This result suggested that the reactivity of NH₄NO₃ on Cu_{1.8}-SSZ-13 was much lower than that on Cu_{1.8}-SSZ-39 when reacting with NO, leading to the accumulation of NH₄NO₃ and pore-blocking, and thus inhibited the reaction between NO and the NH₃ coordinated on Cu active sites. The TPD results after the adsorption of NH₃ and NO₂ (Figure S2) showed that the amounts of N₂O and NH₃ generated on Cu_{1.8}-SSZ-13 were both greater than those on Cu_{1.8}-SSZ-39 because of more NH₄NO₃ accumulation on Cu_{1.8}-SSZ-13. Only after the decomposition of NH₄NO₃ with the increase of temperature could the SCR activity be recovered on Cu₁₈-SSZ-13.

3.3. In situ DRIFTS Study of the NO Reaction after the Adsorption of NH₃ and NO₂. In situ DRIFTS studies of NH₃

adsorption, NO + O₂ adsorption, and NO₂ + O₂ adsorption at 200 °C were applied to investigate the surface adsorbed species on Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39 catalysts under different conditions, and the results are shown in Figures S3–S5, respectively. The same NH₃ adsorbed species were observed on Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39 (Figure S3). However, distinct NO_x adsorbed species were identified by the *in situ* DRIFTS of NO_x adsorption (Figures S4 and S5) and NO₂-TPD (Figure S6), which indicated that more physically adsorbed NO_x species or monodentate nitrate occurred on Cu_{1.8}-SSZ-13, while more bidentate nitrate and bridge nitrate species were adsorbed on Cu_{1.8}-SSZ-39.

In order to investigate the reaction process of NH₄NO₃ and NO, NO was introduced to the Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39 catalysts after NH₃ + NO₂ adsorption and N₂ purging at 200 °C, and the in situ DRIFTS results are shown in Figure 5. When NO was introduced to the Cu₁₈-SSZ-13 catalyst with pre-adsorbed NH₃ and NO₂, in the first 5 min, the bands assigned to bridge nitrate (1609 and 1622 cm^{-1}) and bidentate nitrate (1575 and 1597 cm⁻¹) declined in intensity.³⁸ The bands appearing at 1633 and 1338 cm⁻¹ may be attributed to the adsorbed NO₂ and ionic nitrate species, respectively.³ Meanwhile, more NO⁺ species were detected (2194, 1751, and 1933 cm^{-1}). Specifically, the band at 2194 cm^{-1} may be attributed to NO⁺ adsorbed on acid sites, and the bands at 1751 and 1933 cm⁻¹ may be assigned to NO adsorbed on Cu⁺ sites and NO adsorbed on Cu²⁺ sites, respectively.⁴⁰ These bands gradually decreased with continuous exposure to NO, indicating that NO could react with the adsorbed NH₄NO₃. On the Cu_{1.8}-SSZ-39 catalyst, after the adsorption of NH₃ and NO₂, the bands assigned to nitrate species (1622, 1575, and 1597 cm⁻¹) were clearly observed. When NO was introduced, the bands for nitrate species decreased significantly, and only a small amount of NO⁺ (2184 cm⁻¹) appeared, indicating that NO reacted with NH₄NO₃ rapidly on Cu_{1.8}-SSZ-39. Thus, just a trace of NO adsorption was observed on Cu18-SSZ-39. On the other hand, the reaction between NO and NH₄NO₃ was relatively slow, and more NO adsorption was observed on the acid sites and Cu sites of Cu_{1.8}-SSZ-13. Therefore, the reactivity of NH4NO3 with NO on Cu18-SSZ-39 was much higher than that on Cu_{1.8}-SSZ-13, which resulted in the distinctly different NO₂ effects on these two catalysts.

When NO + O₂ was introduced to the Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39 with pre-adsorbed NH₃ and NO₂ (Figure S7), the reaction process was almost the same as that with the introduction of NO (without O₂), with NO rapidly reacting with NH₄NO₃ on Cu_{1.8}-SSZ-39.

3.4. Structure-activity Relationship. Both TPD results (Figure S2) and *in situ* DRIFTS results of TPD (Figure S8) after NH₃ and NO₂ adsorptions showed that NH₄NO₃ has similar stability on Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39. Therefore, based on the results of TPSR, activity, kinetic experiments, and *in situ* DRIFTS, it can be concluded that NO₂ can promote NO_x conversion on Cu_{1.8}-SSZ-39 above 180 °C, while inhibiting that on Cu_{1.8}-SSZ-13, which is associated with the different reactivity of NH₄NO₃ on these two catalysts. In order to investigate the structure–activity relationship, a comparison of structural properties and redox abilities as well as acid properties was conducted for Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39.

The SEM (Figure S9) and TEM mapping (Figure S10) results showed that $Cu_{1.8}$ -SSZ-13 and $Cu_{1.8}$ -SSZ-39 had similar morphologies, and highly dispersed Cu species were observed on the catalysts. As shown in Table S1, the Cu contents of the

two catalysts were both about 1.8%, while the Si/Al ratios of Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39 were 4.5 and 8.2, respectively. Cu_{1 8}-SSZ-13 showed a higher BET surface area and micropore volume (718 m²/g and 0.31 m³/g) than those of Cu₁₈-SSZ-39 (650 m²/g and 0.26 m³/g). The H₂-TPR results of Cu₁₈-SSZ-13 and Cu_{1.8}-SSZ-39 are shown in Figure S11. Three H₂ consumption peaks at around 343 °C (325 °C), 495 °C (687 °C), and 860 °C (982 °C) were observed for Cu_{1.8}-SSZ-13 (Cu₁₈-SSZ-39), which can be assigned to the reduction of Cu²⁺ located in 6MR to Cu⁺, low-stability Cu⁺ to Cu⁰, and high-stability Cu⁺ to Cu⁰, respectively.⁴¹ These results indicated that the main Cu active sites on both Cu18-SSZ-13 and Cu_{1.8}-SSZ-39 were isolated Cu²⁺ in 6MR, as confirmed by in situ DRIFTS (Figure S3c). The NH₃-TPD results (Figure S12) showed that $Cu_{1,8}$ -SSZ-13 and $Cu_{1,8}$ -SSZ-39 had a similar acid strength, and three NH₃ desorption peaks at around 170, 325, and 506 °C were observed for both of the catalysts, which were assigned to physically adsorbed NH₃, NH₃ adsorbed on Lewis acid sites (mainly Cu^{2+}), and NH_3 adsorbed on Brønsted acid sites, respectively.⁴² The above-mentioned characterization results indicated that Cu_{1.8}-SSZ-39 and Cu₁₈-SSZ-13 had similar structures, morphologies, acid strengths, and Cu distributions.

Previous studies have shown that fast SCR is related to the acid sites and is less sensitive to the nature of the cations^{3,43} and the decomposition of NH4NO3 can be enhanced by acidity.44-46 Savara et al. proposed that the acid sites (including Brønsted and Lewis acid sites) catalyzed the reduction of NH₄NO₃ by NO over Y zeolites in DeNO_x systems. $^{47}\,\mathrm{NH_3}$ can inhibit the reaction between $\mathrm{NH_4NO_3}$ and NO by blocking the Brønsted acid sites.⁴⁸ The role of acid sites may be the reversible binding of NH₃ to promote the decomposition of NH4NO3 by reaction 9 and the reduction of HNO₃ by reactions 10 and 11.⁴⁷ For the Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39 catalysts, the NO₂ molecules (three-dimensional lengths $3.35 \times 3.85 \times 5.42$ Å) exhibit geometric dimensions similar to the channel opening of the CHA or AEI structure (about 3.8 \times 3.8 Å), and thus, NO₂ molecules have difficulty entering the CHA or AEI pores.²⁵ NO₂ reacted with NH₃ on the Brønsted acid sites to form N₂, H₂O, and NH₄NO₃ at low temperatures, and then NH4NO3 accumulated on the surface of the catalyst.^{48,49} From the above discussion, it has been demonstrated that the reaction between NH₄NO₃ and NO on the small-pore zeolites can be related to the surface acid sites, mainly the surface Brønsted acid sites. In this work, Py-FTIR was performed to determine the surface Brønsted and Lewis acid sites for Cu_{1.8}-SSZ-39 and Cu_{1.8}-SSZ-13 (Figure S13 and Table 1). The results indicated that Cu_{1.8}-SSZ-39 had more Brønsted acid sites on the surface than Cu_{1.8}-SSZ-13, which may be due to the fact that Cu_{1.8}-SSZ-39 had more Si-OH-Al groups positioned at cages (more accessible for pyridine)

Table 1. Acidity Properties of $Cu_{1.8}$ -SSZ-13 and $Cu_{1.8}$ -SSZ-39 Determined by Py-FTIR Characterization

	acidity (mmol/g)			
	total acid sites		total moderate and strong acid sites	
samples	Brønsted acid sites	Lewis acid sites	Brønsted acid sites	Lewis acid sites
Cu _{1.8} -SSZ-13	0.01716	0.00726	0.01295	0.00432
Cu _{1.8} -SSZ-39	0.06466	0.01728	0.04885	0.01170

(Figure S3). Under fast SCR conditions, when normalized to the amount of surface Brønsted acid sites (Figure 6), the NO



Figure 6. Normalized NO and NO₂ reaction rates by surface Brønsted acid sites over Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39 under fast SCR. Reaction conditions: $[NO] = [NO_2] = 250$ ppm, $[NH_3] = 500$ ppm, $[O_2] = 5$ vol %, N₂ balance, 10 mg of the catalysts, total flow rate = 500 mL/min, and GHSV = 1,700,000 h⁻¹.

reaction rate of Cu_{1.8}-SSZ-39 is higher than that of Cu_{1.8}-SSZ-13 above 185 °C. This result confirmed that the reactivity of NH_4NO_3 toward NO on Cu_{1.8}-SSZ-39 is higher than that on Cu_{1.8}-SSZ-13.

The corresponding mechanisms of the NO_2 effects are summarized in Figure 7. Under standard SCR conditions, the



Figure 7. Effects of NO₂ on the NH₃-SCR reactions over Cu-SSZ-13 and Cu-SSZ-39.

reaction between NO and adsorbed NH_3 on the Cu active sites over Cu-SSZ-13 is faster than that over Cu-SSZ-39. However, under fast SCR conditions, the different reactivities of NH_4NO_3 with NO results in the distinct NO_2 effects on the two catalysts. The NH_4NO_3 on the acid sites was reduced fast by NO on Cu-SSZ-39, and thus NO_2 promoted the SCR activity. For Cu-SSZ-13, the reaction between NH_4NO_3 and NO was slow, which resulted in the accumulation of NH_4NO_3 and pore-plugging, and the SCR activity is inhibited by NO_2 .

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c06256.

Detailed activity tests, characterization methods, NH_3 -SCR performance of H-SSZ-13 and H-SSZ-39 zeolites, TPD results after NH_3 , and NO_2 adsorption at 130 °C,

in situ DRIFTS results of NH₃/NO + O₂/NO₂ + O₂ adsorption at 200 °C, NO₂-TPD results, *in situ* DRIFTS results of NO + O₂ adsorption after the adsorption of NH₃ and NO₂ at 200 °C, *in situ* DRIFTS results of TPD after the adsorption of NH₃ and NO₂ at 30 °C, SEM images, TEM images, and mapping results, H₂-TPR results, NH₃-TPD results, Py-FTIR spectra, specific surface areas, and Cu contents of Cu_{1.8}-SSZ-13 and Cu_{1.8}-SSZ-39 (PDF)

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Notes

The authors declare no competing financial interest.

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