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A comparative study of the activity and hydrothermal stability of Al-rich Cu-SSZ-39 and Cu-SSZ-13



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ABSTRACT

Catalysts Al-rich Cu-SSZ-39 and Cu-SSZ-13 are applied in ammonia selective catalytic reduction (NH₃-SCR) reaction for NOx removal. Al-rich Cu-SSZ-39 maintained its excellent NH₃-SCR activity even after hydrothermal aging at 850 °C for 16 h, whereas Al-rich Cu-SSZ-13 lost its deNOx activities completely when subjected to the same conditions. The main reason is that the active Cu^{2+} species are more stable in the structure of Cu-SSZ-39, because SSZ-39 zeolite contained more paired framework Al, leading to that Cu-SSZ-39 catalysts have more hydrothermally stable Cu^{2+} -2Z species as compared to Cu-SSZ-13, and this makes Cu-SSZ-39 accumulate less CuOx during hydrothermal aging. In addition, the framework Al in SSZ-39 is more stable than that in SSZ-13, and a great amount of Cu^{2+} -2Z species coordinated with paired framework Al in Cu-SSZ-39, which leaves fewer residual uncoordinated Al sites. Moreover, SSZ-39 has a more tortuous channel structure than SSZ-13 does. This inhibits the detached Al(OH)₃ into the framework when cooling down. Therefore, the Al-rich Cu-SSZ-39 with large amounts of stable paired Al shows a competitive potential candidate as an NH₃-SCR catalyst for NOx elimination in practical applications.

1. Introduction

Cu-based small-pore zeolite catalysts have been extensively studied in the past decade due to both their higher deNOx activity and hydrothermal stability in ammonia selective catalystic reduction (NH₃-SCR) technology compared to other zeolite catalysts [1–11]. Among these zeolites, Cu-SSZ-13, which has been implemented as a new-generation SCR catalyst in diesel after-treatment systems, has been especially studied comprehensively from theory to application with regard to structure-activity relationships, reaction mechanism, and hydrothermal stability in NH₃-SCR [12–16]. Nevertheless, this catalyst shows a significant loss of deNOx activity after undergoing hydrothermal aging at 850 °C, especially for Al-rich Cu-SSZ-13 (Si/Al < 8) [8–13,17,18].

Many other small-pore zeolites have been the focus of research in recent years in an attempt to increase the hydrothermal stability [3,5,6,19,20]. Among these, the Cu-LTA zeolites reported first by Hong

et al. [3,8] showed outstanding hydrothermal stability in NH₃-SCR reaction. However, the F-free synthesis of this zeolite still need more efforts. Besides LTA zeolites, SSZ-39 (AEI-type), which has a structure that is extremely similar to that of SSZ-13 (CHA-type) as shown in Fig. 1, also showed excellent hydrothermal stability. The only difference between the AEI and CHA structures is the connection mode of the double 6-rings (D6R). The neighboring D6Rs have mirror symmetry in AEI while being arranged in parallel in CHA, which therefore results in different aei and cha cavities [21]. There have been a few studies on application of the SSZ-39 zeolite with the AEI framework topology for the NH₃-SCR reaction. Moliner and Corma et al. demonstrated the high activity and hydrothermal stability of Cu/Fe-SSZ-39 for deNOx applications [2,19,20]. Sano and co-workers reported that a P-modified AEI zeolite showed excellent hydrothermal stability (hydrothermal treatment at 900 °C for 4 h) with the drawback, however, that NO conversion decreased with increasing P/Al ratio [22]. Ribeiro and Gounder et al. recently compared the hydrothermal stability of SSZ-13 and SSZ-

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Fig. 1. Connection mode in AEI (a) and CHA (b) zeolite, and aei (c) and cha (d) cavities.

39, and demonstrated similar changes before and after hydrothermal aging [5]. To our knowledge, the Si/Al ratios of the reported Cu-SSZ-39 catalysts applied in NH₃-SCR reaction have been relatively high (above 8) [2,5,19,20,22]. Studies on the use of Cu-exchanged Al-rich SSZ-39 (Si/Al < 8) zeolite catalysts for the NH₃-SCR reaction have been scarce.

It is known that the Si/Al ratio can influence the distribution of Cu species and further influence the hydrothermal stability of Cu-SSZ-13 zeolite catalysts [13,16]. When the Si/Al ratio is high, given the random Al distribution subject to Lowenstein's rule, Cu(OH)⁺-Z species, which are located in the 8-membered ring (8MR) balanced by a single Al, should be the only Cu species due to the absence of paired Al. However, for SSZ-13 zeolites with a certain Si/Al ratio that include both isolated and paired Al, the Cu²⁺-2Z species, which are located in the 6-membered ring (6MR) balanced by paired Al, primarily exist in Cu-SSZ-13 catalysts with relatively low Cu loadings, because Cu²⁺ ions occupy the 6MR sites preferentially during the ion-exchange process of SSZ-13, followed by the 8MR sites [12,14,23]. The Cu²⁺ ion species, which are regarded as active SCR sites, are susceptible to accumulating to form CuOx clusters during hydrothermal aging at relatively high temperatures. The formed CuOx not only results in the loss of SCR active sites, but also causes destruction of the long-range order of the zeolite structure [24]. Song et al. and Kim et al. reported that Cu²⁺-2Z is hydrothermally more stable but less active than Cu(OH)⁺-Z [14,16]. Therefore, increasing the percentage of Cu²⁺-2Z species at similar Cu loadings can benefit both the low temperature SCR activity and the hydrothermal stability in the case of certain Si/Al ratios [24]. The Alrich zeolite (Si/Al < 8) contains a large amount of paired Al to accommodate the Cu²⁺-2Z species [13]. Therefore, increasing the amount of Cu2+-2Z active sites that contribute to NH3-SCR activity can be achieved by using the Al-rich zeolite as substrate. Additionally, the residual isolated Al can offer plenty of Brønsted acid sites, which act as a reservoir to provide reactive NH3 molecules to the active sites

Table 1

Physicochemical properties of Cu-exchanged SSZ-39 and SSZ-13 of	catalysts
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[25,26]. However, the high Al content of the zeolite makes it less hydrothermally stable due to dealumination, which limits the utilization of Al-rich Cu-SSZ-13 in actual applications.

In the present work, Al-rich (Si/Al ~ 6) SSZ-39 and SSZ-13 zeolites were synthesized and then ion-exchanged with copper nitrate solution to obtain Cu-zeolites. H₂-TPR, EPR, UV–vis, and DRIFTS were conducted to identify the Cu species distributions in the Cu-zeolites. ²⁷Al-NMR, XRD and N₂ adsorption-desorption were utilized to characterize the zeolite framework structure. The catalytic properties of Cu-SSZ-39 and Cu-SSZ-13 were systematically compared with respect to NH₃-SCR activity and hydrothermal stability.

2. Experimental Section

2.1. Catalyst synthesis

The parent Na-SSZ-39 and Na-SSZ-13 zeolites with Si/Al = 6 were synthesized hydrothermally as previously reported in the literature [27,28]. The SEM images (Fig. S1) show the cuboid and cube shapes of Na-SSZ-39 and Na-SSZ-13, respectively, and the particle sizes of the two zeolites are similar with each other (~ 500 nm). The Na-SSZ-39 and Na-SSZ-13 samples were ion-exchanged twice with NH₄NO₃ (0.1 M) solution at 80 °C for 5 h, and the obtained NH₄-SSZ-39 and NH₄-SSZ-13 were subsequently ion-exchanged with Cu(NO₃)₂ solution with varying concentrations (0.01-0.05 M) at ambient temperature for 12 h to prepare Cu-SSZ-39 and Cu-SSZ-13 with different Cu contents. After filtering, washing, drying at 100 °C for 12 h, and calcination at 600 °C for 6 h, two kinds of Cu-SSZ-39 and Cu-SSZ-13 catalysts with different Cu loadings were obtained. Here, we selected only one specific high Cu loading (~3.5 wt.%) of Cu-SSZ-39 and Cu-SSZ-13 for comparison of the hydrothermal stabilities, and the chemical composition was analyzed by ICP and listed in Table 1.

2.2. Characterization

The elemental compositions (Cu loadings, Si/Al and Cu/Al ratios) of the samples, which were dissolved in strong acid, were analyzed by an inductively coupled plasma spectrometer (OPTMIA 2000DV) with a radial view of the plasma. Powder X-ray diffraction (PXRD) was conducted to determine the zeolite structure on a computerized Bruker D8 Advance diffractometer with Cu Ka ($\lambda = 0.15406$ nm) radiation. The data of 20 from 5° to 40° with a step size of 0.02° were collected at ambient temperature. N2 adsorption/desorption isotherms of the samples were measured at 77 K using a Micromeritics ASAP 2020 system, with micropore volumes calculated by the t-plot method. Before each measurement, all the samples were pretreated at 300 °C for 5 h. Solid state ²⁷Al MAS NMR spectra were collected on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP MAS probe head whose X channel was tuned to 104.27 MHz for ²⁷Al, using a magnetic field of 9.39 T at 297 L. The dried and finely powdered samples were packed in the ZrO₂ rotor closed with a Kel-F cap and spun at a 12 kHz rate. A total of 1000 scans were recorded with 2 s recycle delay for each sample. All ²⁷Al MAS NMR chemical shifts were referenced to the resonance of Al(H₂O)₆³⁺ solution. High-resolution

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Sample	Cu loading (wt.%) ^a	Cu/Al ^a	Si/Al ^a	N_2 BET surface areas $(m^2/g)^b$			Micropo	re volumes (m ³ /	g) ^c		
				Fresh	HTA-750	HTA-800	HTA-850	Fresh	HTA-750	HTA-800	HTA-850
Cu-SSZ-39 Cu-SSZ-13	3.39 3.45	0.29 0.29	6.5 6.1	438 545	410 413	395 305	233 47	0.181 0.198	0.146 0.147	0.140 0.107	0.082 0

^a elemental analysis by ICP-OES.

^b calculated by BET method.

^c micropore volumes were determined by the t-plot method.

transmission electron microscopy (HRTEM) images were obtained on a JEM2100PLUS microscope with 200 kV acceleration voltage.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy experiments were carried out using molecular ammonia as the probe (NH₃-DRIFTS) using a Nicolet Is10 instrument equipped with s Smart Collector and an MCT/A detector. The samples were pretreated at 500 °C in air for 60 min and cooled down to 35 °C. Afterwards, the background was collected in pure N2 and automatically subtracted from the sample spectrum prior to NH₃ adsorption with the concentration of 500 ppm. All spectra were recorded from 4000 to 650 cm^{-1} by accumulating 100 scans with a resolution of 4 cm^{-1} . The electron paramagnetic resonance (EPR) of the samples was recorded at 153 K on a Bruker E500 X-band spectrometer. All catalysts were placed into quartz tubes for the measurement. Hydrogen temperature-programmed reduction (H2-TPR) was carried out on a Micromeritics AutoChem 2920 chemisorption analyzer. ~50 mg samples were put into a quartz reactor and pretreated in air at 500 °C for 60 min. After cooling down to 50 °C, 10 % H₂/Ar was introduced at a flow rate of 50 mL/min. A linear temperature ramp of 10 °C/min from 100 °C to 1000 °C was used and the hydrogen consumption was monitored by a thermal conductivity detector (TCD). UV-vis-NIR diffuse reflectance spectra were obtained in the range of 200 - 1400 nm on a Shimadzu UV3600Plus spectrometer at the ambient temperature.

2.3. NH₃-SCR activity test

Tests of catalytic activity were conducted in a fixed-bed quartz flow reactor at atmospheric pressure. The catalysts with particle size of 40–60 mesh were placed in the tube reactor. The total flow rate was held at 500 mL/min, with gas composition of 500 ppm NO, 500 ppm NH₃, 5 vol.% O₂, 5 vol.% H₂O and N₂ as balance gas. 80 mg zeolite samples were used for the tests, with gas hourly space velocity (GHSV) of ~250,000 h⁻¹. The inlet and outlet gas compositions were monitored by an online Nicolet Is10 spectrometer equipped with a heated, low-volume (0.2 L) multiple-path gas cell (2 m). The NOx conversion was then calculated based on the equation below:

$$NOx \text{ conversion} = \left(1 - \frac{[NOx]_{out}}{[NOx]_{in}}\right) \times 100\% (x = 1, 2)$$

To investigate the hydrothermal stability, the samples were hydrothermally aged in flowing air containing 10 vol. % H_2O at 750 °C (HTA-750), 800 °C (HTA-800) and 850 °C (HTA-850) for 16 h.

The standard SCR reaction rates (r) were normalized on a per sample weight basis, using the first-order kinetic equation:

$$r = -\frac{F}{W}\ln(1-x)$$

Where, W represents the catalyst weight (g), F represents the NO flow rate (mol/s), and x represents the NO conversion. The activation energies (Ea) and pre-exponential factors (A) were calculated based on the Arrhenius equation:

$$k = \frac{r}{[NO]_0} = Ae^{(-Ea/RT)}$$

3. Results

3.1. NH₃-SCR performance

The NOx conversion of fresh and hydrothermally aged Cu-SSZ-39 and Cu-SSZ-13 samples in the standard NH₃-SCR reaction are depicted in Fig. 2, as a function of temperature from 150 to 550 °C under GHSV of 250,000 h⁻¹. At temperatures below 250 °C, the fresh Cu-SSZ-13 showed higher NOx conversion than Cu-SSZ-39, with values of 78 % and 56 %, respectively, at 175 °C. In contrast, at temperatures above 350 °C, Cu-SSZ-39 exhibited higher activity than Cu-SSZ-13, achieving

nearly 100 % NOx conversion before showing a slight decrease at 500 °C. After hydrothermal aging, the activities of both Cu-SSZ-39 and Cu-SSZ-13 decreased, but Cu-SSZ-39 showed markedly higher hydrothermal stability than Cu-SSZ-13. The difference was more pronounced after hydrothermal aging at 800 °C. In this case, Cu-SSZ-39 showed NOx conversion above ~80 % within the temperature range of 225–550 °C, while the NOx conversion of Cu-SSZ-13 decreased to ~ 60 % over the whole temperature range. Of particular interest is the fact that elevated temperature (850 °C) hydrothermal aging caused Cu-SSZ-13 to lose NOx conversion totally, while Cu-SSZ-39 still showed similarly high deNOx activity as obtained for aging at 800 °C. Clearly, Cu-SSZ-39 was more resistant to hydrothermal aging and maintained high NOx conversion over the whole temperature range, even after extremely harsh hydrothermal aging at 850 °C.

Additionally, both types of catalysts showed excellent selectivity to N₂ in the NH₃-SCR reaction, with N₂O production (Fig. S2) less than 10 ppm regardless of hydrothermal aging. The excellent hydrothermal stability is reproducible for Cu-SSZ-39 with different Cu loadings under higher GHSV of 400,000 h^{-1} (Fig. S3). After deep hydrothermal aging at 850 °C, only Cu_{1.1}- and Cu_{1.9}-SSZ-13 with low Cu contents showed low NOx conversion, while Cu-SSZ-39 with Cu contents from 1.3 to 3.5 wt.% all maintained relatively high NOx conversion. Cu-SSZ-13 catalysts with other Si/Al ratios and Cu loadings were also evaluated, with the results shown in Fig. S4a. After hydrothermal aging at 850 °C, maximum NOx conversions of ~82 %, ~70 %, and ~4 % were observed for Cu_{3.0}-SSZ-13-7.5, Cu_{1.9}-SSZ-13-10 and Cu_{4.8}-SSZ-13-4.5, respectively, indicating that 850 °C hydrothermal aging can significantly deactivate Cu-SSZ-13 irrespective of the Si/Al ratio or Cu loading, as was found in previous literature.^{8,14,18} The influence of CO was also investigated, with the results shown in Fig. S4b. In the presence of 500 and 1000 ppm CO, the low-temperature NOx conversion of Cu-SSZ-39 showed only a slight decrease and the changes in the concentration of CO showed hardly any influence on NOx conversion over Cu-SSZ-39. To highlight the advantage of the Al-rich Cu-SSZ-39 zeolite applied to NH₃-SCR reaction, moreover, we also evaluated the Cu-SSZ-39 zeolite with relatively high Si/Al (\sim 8.5), and the results are shown in Fig. S4c. The fresh Cu_{3.5}-SSZ-39 sample with Si/Al of 6.5 showed obviously higher NOx conversion than the Cu-SSZ-39 with Si/Al of 8.5. After hydrothermal aging at 850 °C, Al-rich Cu-SSZ-39 (Si/Al~6.5) still showed a wider operating temperature window than the aged Cu-SSZ-39 with Si/ Al of 8.5, although slightly higher low-temperature NOx conversion was observed over Cu_{2.5}-SSZ-39-8.5. These results revealed that Al-rich Cu-SSZ-39 zeolite catalyst has a competitive potential candidate as an NH₃-SCR catalyst for NOx elimination in practical applications.

3.2. Textural properties

The zeolite framework structures of fresh and hydrothermally aged Cu-SSZ-39 and Cu-SSZ-13 catalysts were examined by XRD, N2 adsorption-desorption and NMR measurements. As shown by the XRD results in Fig. 3, the hydrothermal aging at 750 °C hardly changed the crystallinity of the Cu-SSZ-39 and Cu-SSZ-13 catalysts, while on increasing the hydrothermal aging temperature to 800 and 850 °C, a slight decrease of diffraction peak intensities was observed for Cu-SSZ-39, indicating a slight decrease in crystallinity. Notably, the Cu-SSZ-13 sample hydrothermally aged at 800 °C almost lost its typical zeolite structure, which thus induced a significant decrease in NOx reduction efficiency. After hydrothermal aging at 850 °C, more seriously, the zeolite structure of Cu-SSZ-13 collapsed, which induced the complete loss of NH₃-SCR performance. The results of N₂ adsorption-desorption confirmed that all samples exhibited the typical isotherm of microporous materials, except for the Cu-SSZ-13 sample hydrothermally aged at 850 °C with collapsed framework structure (Fig. S5). As shown in Table 1, hydrothermal aging at 750 and 800 °C slightly decreased the BET surface areas (438-395 m²/g) and micropore volumes (0.181-0.140 cm³/g) of Cu-SSZ-39. On further increasing the hydrothermal aging



Fig. 2. NOx conversion as a function of temperature in NH₃-SCR reaction over fresh, 750, 800, and 850 °C hydrothermally aged (a) Cu-SSZ-39 and (b) Cu-SSZ-13 catalysts. Conditions: 500 ppm NO, 500 ppm NH₃, 5 vol. % H₂O, and 5 vol.% O₂ balanced with N₂, GHSV = 250, 000 h⁻¹.

temperature to 850 °C, however, the surface areas and micropore volumes of Cu-SSZ-39 decreased distinctly. As for Cu-SSZ-13, it was clear that the decrease in BET surface areas and micropore volumes induced by hydrothermal aging was more severe compared with Cu-SSZ-39. Indeed, the Cu-SSZ-13 sample aged at 850 °C almost lost its micropore features. Again, the XRD and N₂ adsorption-desorption results confirmed that the zeolite structure of Cu-SSZ-39 was more stable than that of Cu-SSZ-13 during hydrothermal aging.

Furthermore, ²⁷Al solid-state NMR was carried out to determine the local Al environment, with the results shown in Fig. 4. Generally, the peak at ~58 ppm is ascribed to 4-coordinated framework Al (denoted as FAl hereafter), and the peaks at ~ 45 ppm and ~ 0 ppm are attributed to 5- and 6-coordinated extra-framework Al (denoted as EFAl hereafter), respectively. [29] It can be seen that for Cu-SSZ-39, hydrothermal aging at 750 °C and 800 °C resulted in a slight decrease in the intensity of the peak assignable to FAl, indicative of slight dealumination. Even after undergoing hydrothermal aging at 850 °C, about 80 % of FAl was still maintained in Cu-SSZ-39. On the other hand, more severe dealumination occurred for Cu-SSZ-13, with around 65 % of FAl being detached from the zeolite framework after hydrothermal aging at

800 °C. When the aging temperature reached 850 °C, the FAl sites of Cu-SSZ-13 even totally disappeared accompanied by the appearance of EFAl, which is consistent with the XRD results showing that the zeolite structure collapsed at this hydrothermal aging temperature.

3.3. Acid sites

NH₃ shows specific adsorption on Cu-SSZ-13 and Cu-SSZ-39, therefore serving as an IR probe molecule to characterize the features of zeolitic Brønsted acid sites and active Cu sites 30. As shown in Fig. 5a and b, the negative peaks at 3735 and 3661 cm⁻¹ correspond to the consumption of silica O-H (Si-OH) and aluminum O-H (Al-OH) bond stretching vibrations due to NH₃ adsorption on the fresh Cu-SSZ-13 and Cu-SSZ-39, respectively, and the peaks at 3615 and 3578 cm are attributed to Brønsted O-H (Si-OH-Al) [30,31]. The Cu-SSZ-39 catalyst showed a slight decrease of Brønsted acid sites after hydrothermal aging at 750 °C, and the trend of decrease continued with the increase of hydrothermal aging temperature. Even after hydrothermal aging at 850 °C, it should be noted that the Cu-SSZ-39 catalyst maintained its Brønsted acid sites, attributed to the existence of certain amounts of FAl



Fig. 3. XRD patterns of (a) Cu-SSZ-39 and (b) Cu-SSZ-13 before and after hydrothermal aging at 750, 800, and 850 °C.



Fig. 4. ²⁷Al solid-state NMR profiles of (a) Cu-SSZ-39 and (b) Cu-SSZ-13 before and after hydrothermal aging at 750, 800, and 850 °C.

and further confirming the ²⁷Al-NMR and XRD results. After hydrothermal aging of Cu-SSZ-13 catalysts at 800 °C, in contrast, the IR feature assignable to FAl was hardly observed, and completely disappeared after hydrothermal aging at 850 °C. In good agreement with the results of DRIFTS measurements, the ¹H-NMR spectra (Fig. S6) results showed that more Brønsted acid sites are preserved over hydrothermally aged Cu-SSZ-39 catalysts (especially at 850 °C) than Cu-SSZ-13 catalysts.

3.4. Active Cu^{2+} species

By using NH₃ adsorption, meanwhile, perturbation of the zeolite T-O-T (T represents framework Si or Al atoms) stretching vibrations by ion-exchanged Cu²⁺ ions in the form of Cu²⁺-2Z and Cu(OH)⁺-Z can be observed, giving the opportunity to distinguish the two types of Cu²⁺ ions [30,32]. As shown in Fig. 5c and d, the negative peaks at 950 and ~900 cm⁻¹ observed on Cu-SSZ-13 are ascribed to zeolite T-O-T vibrations perturbed by Cu(OH)⁺-Z next to the 8-membered ring (8MR) and Cu²⁺-2Z next to the 6-membered ring (6MR), respectively [30,32]. Considering that the two zeolites have the same cavity compositions

(cha and aei cavities shown in Fig. 1) and similar curve shapes in DRIFTS and H₂-TPR (discussed later, shown in Fig. 7a and b), we surmised that two types of Cu²⁺ species next to 6MR and 8MR also exist in Cu-SSZ-39. Here, the peaks at 950 and \sim 900 cm⁻¹ are attributed to the Cu(OH)⁺-Z next to 8MR and the Cu²⁺-2Z next to 6MR in Cu-SSZ-39, respectively. Although the sensitivity factors of the two bands are different, the relative amounts of Cu species in two zeolites could be identified. For instance, the IR profiles of the fresh Cu-SSZ-39 and Cu-SSZ-13 were deconvoluted, and typical results are shown in Fig. S7. The percentage of Cu²⁺-2Z species in fresh Cu-SSZ-39 catalysts was 75.2 %, while that in fresh Cu-SSZ-13 catalysts was only 51.8 %. This indicated that fresh Cu-SSZ-39 contains more Cu²⁺-2Z species than fresh Cu-SSZ-13 with the same Cu loadings. After hydrothermal aging at 750 °C, both the catalysts showed a slight decrease in the intensity of peaks attributed to Cu(OH)⁺-Z and Cu²⁺-2Z species. This result indicates a slight loss of interaction between these active Cu²⁺ ions and the zeolites, thus inducing the aggregation of Cu²⁺ species to form small amounts of CuOx clusters. Further elevating the hydrothermal aging temperatures to 800 and 850 °C, the peaks attributed to Cu(OH)⁺-Z and Cu²⁺-2Z species almost disappeared for Cu-SSZ-13, while these peaks were still



Fig. 5. In-situ DRIFTS spectra of O–H bond ($3800-3500 \text{ cm}^{-1}$) and T-O-T bond vibration regions ($1000-850 \text{ cm}^{-1}$) after NH₃ adsorption saturation at 35 °C on Cu-SSZ-39 and Cu-SSZ-13 before and after hydrothermal aging.



Fig. 6. EPR profiles of Cu-SSZ-39 and Cu-SSZ-13 before and after hydrothermal aging.

maintained for Cu-SSZ-39. These results clearly indicate that Cu-SSZ-39 possesses a stronger ability to preserve the active Cu²⁺ species in the form of isolated ions, avoiding the formation of CuOx clusters during hydrothermal aging. To highlight this issue, the formation of CuOx clusters induced by hydrothermal aging was further analyzed by UV–vis-NIR measurements. For samples hydrothermally aged at a given temperature (Fig. S8), UV–vis-NIR measurements showed that the Cu-SSZ-13 catalysts contained much greater amounts of CuOx clusters than the Cu-SSZ-39 catalysts did.

An EPR experiment was carried out at 153 K to identify the Cu²⁺ species. To make all Cu²⁺ species EPR active, the test samples were left untreated and exposed to the humid ambient conditions, in which case all the existing Cu^{2+} active species could be identified [16]. It was reported that the transformation of Cu^{2+} species to CuOx clusters during hydrothermal aging results in the loss of EPR signal intensity, due to the EPR silent CuOx clusters [16]. As shown in Fig. 6a and c, the peak intensities of both catalysts showed a marked decrease after hydrothermal aging, indicating the transformation from EPR-active Cu^{2+} species to EPR-silent CuOx clusters. The decrease continued progressively with increasing hydrothermal aging temperature, indicating that much greater amounts of CuOx clusters formed. It was noted that unlike the Cu-SSZ-39 catalyst, a new peak at ~3360 G appeared at high magnetic field (Fig. 6c) after hydrothermal aging at 800 and 850 °C for the Cu-SSZ-13 catalyst. Kim et al. [14] also observed this new peak on severely aged Cu-SSZ-13 catalysts. Probably, this peak can be attributed to increased Cu²⁺ ion mobility due to the weakened coordination between the Cu²⁺ species and zeolite, [12] resulting from degradation of the zeolite structure as shown in XRD and ²⁷Al-NMR results (Figs. 3 and 4). By contrast, the preserved zeolite structure of Cu-SSZ-39 did not induce the appearance of this new peak even after hydrothermal aging at 850 °C. Additionally, the hyperfine features at low field are magnified and shown in Fig. 6b and d. Only one spectral feature (A species, g =2.39 and A_{\parallel} = 134 G) was observed for Cu-SSZ-39 catalysts, whether

hydrothermally aged or not. This feature was also observed for the fresh and 750 °C hydrothermally aged Cu-SSZ-13 catalysts (A species, g_{\parallel} = 2.39 and $A_{\parallel} = 132$ G). The A species was ascribed to the active Cu^{2+} ions in the NH₃-SCR reaction [12,14,16]. However, for the Cu-SSZ-13 samples after hydrothermal aging at 800 and 850 °C, the A species almost disappeared, accompanied by the appearance of B species ($g_{\parallel} =$ 2.32 and $A_{\parallel} = 156$ G), which is ascribed to $Cu^{2+}-Al_2O_3$ [14]. This indicated that EFAl formed (also can be seen in Fig. 4) and coordinated to Cu^{2+} , therefore deactivating the $\mathrm{NH}_3\text{-}\mathrm{SCR}$ performance; while Cu-SSZ-39 preserved its active A species even after hydrothermal aging at 800 and 850 °C, resulting in good deNOx efficiency in the NH₃-SCR reaction (Fig. 2). The EPR results showed that the Cu-SSZ-39 catalyst preserved more active Cu²⁺ ions and formed less CuOx than the Cu-SSZ-13 catalyst after hydrothermal aging. However, the EPR results could only give the qualitative analysis of the active Cu²⁺ species and CuOx clusters. The quantitative analysis of different Cu²⁺ species and CuOx need to be characterized by H2-TPR measurement.

The copper species distributions in Cu-SSZ-39 and Cu-SSZ-13 were further identified by H₂-TPR (Fig. 7). For the fresh Cu-SSZ-13 catalyst, the H₂ consumption peaks at 200 and 300 °C were attributed to the reduction of Cu(OH)⁺-Z next to 8MR and Cu²⁺-2Z next to 6MR, respectively, while the peak at 890 °C was derived from the reduction of Cu⁺ to Cu⁰ [23,32,33]. Similarly, two peaks at 180 °C and 295 °C were observed when the fresh Cu-SSZ-39 catalyst was reduced by H₂, confirming the presence of Cu(OH)+-Z species next to 8MR and Cu²⁺-2Z species next to 6MR, respectively. On the basis of the deconvolution of H_2 -TPR profiles (Fig. S9), the relative amounts of Cu^{2+} species were calculated and listed in Table 2. In the fresh Cu-SSZ-39 catalyst, both active Cu(OH)+-Z and Cu2+-2Z species existed. Moreover, the percentage of Cu²⁺-2Z to total Cu species for Cu-SSZ-39 was up to 86.1 %, much higher than that for the fresh Cu-SSZ-13 catalyst (37.2 %), which is in good agreement with the results of DRIFTS (Fig. 5). Considering that $Cu^{2+}-2Z$ is more stable than $Cu(OH)^+-Z$, the high percentage of



Fig. 7. H2-TPR profiles of (a) Cu-SSZ-39 and (b) Cu-SSZ-13 before and after hydrothermal aging at 750, 800, and 850°C.

 Table 2

 Cu species and their distribution determined by H₂-TPR analysis.

Catalysts	Cu(OH) ⁺ -Z (8 mr)	Cu ²⁺ -2Z (6 mr)	CuOx
Cu-SSZ-39	0.139	0.861	0
Cu-SSZ-39-HTA-750	0.012	0.988	0
Cu-SSZ-39-HTA-800	0.040	0.491	0.469
Cu-SSZ-39-HTA-850	0	0.542	0.458
Cu-SSZ-13	0.628	0.372	0
Cu-SSZ-13-HTA-750	0.011	0.853	0.136
Cu-SSZ-13-HTA-800	0.291	0	0.709
Cu-SSZ-13-HTA-850	0	0	1

Cu²⁺-2Z species thus benefits the hydrothermal stability of the Cu-SSZ-39 catalyst. [14,16,24] The reduction peak of Cu⁺ to Cu⁰ for fresh Cu-SSZ-39 appeared at 925 °C, 35 °C higher than that for fresh Cu-SSZ-13, with this reduction occurring at 890 °C. This is further evidence that the stability of the zeolite structure of Cu-SSZ-39 is better than that of Cu-SSZ-13, since the reduction of Cu⁺ to Cu⁰ occurs when the zeolite structure begins to collapse [12,34].

Previous studies have revealed that hydrothermal aging of Cu-SSZ-13 can induce the transformation of Cu^{2+} active species from 8MR to 6MR sites and to CuOr clusters, [14,16,35] which was also observed in our study. As shown in Table 2, after hydrothermal aging at 750 °C, the relative amount of Cu(OH)⁺-Z species in Cu-SSZ-13 decreased from 62.8 % to 1.1 %, accompanied by an increase in the amount of CuO_x to 13.6 %. During this process, meanwhile, the percentage of $Cu^{2+}-2Z$ increased from 37.2% to 85.3%, indicating the transformation of active Cu^{2+} species from 8MR to 6MR and to CuO_x . After aging at the same temperature of 750 °C, the transformation of Cu species in Cu-SSZ-39 from 8MR to 6MR also occurred, while no peak related to CuO_x was observed. Such transformation leads to the predominance of stable Cu²⁺-2Z entities in the Cu-SSZ-39 catalyst aged at 750 °C, giving the relative amount of 98.8 %. As for Cu-SSZ-39, it should be recalled that the DRIFTS, UV-vis, and EPR results indicated that hydrothermal aging at 750 °C results in the formation of a trace amount of CuO_x clusters, which were not detected by H2-TPR measurements. It is likely that the H₂ consumption due to the trace amount of CuO_x clusters was obscured by the reduction of the large amounts of Cu²⁺ species. Further increasing the hydrothermal aging temperature to 800 and 850 °C, most of the Cu^{2+} species in Cu-SSZ-13 catalysts converted to CuO_r clusters. However, 53.1 % and 54.2 % of active Cu²⁺ species were preserved for the Cu-SSZ-39 catalysts aged at 800 and 850 °C, respectively. Indeed,

 Cu^{2+} -2Z was always predominant whether before or after aging for the Cu-SSZ-39 catalyst. In other words, active Cu^{2+} species in Cu-SSZ-39 catalysts preferentially occupied 6MR sites, thus exhibiting excellent hydrothermal stability.

4. Discussion

4.1. Al and Cu distribution in SSZ-39 and SSZ-13 zeolite

The FAl species distribution (isolated and paired FAl) in zeolites can influence the distribution of Cu species during the ion exchange process, and eventually affect the catalytic performance of Cu-zeolite catalysts [16]. To identify the distribution of paired FAl species in parent zeolites, we carried out a Co^{2+} ion exchange process with H-SSZ-39 and H-SSZ-13 substrates, in which Co^{2+} can be only present as Co^{2+} -2Z balanced with paired FAl [13,36]. The elemental compositions of parent and Co^{2+} -exchanged SSZ-39 and SSZ-13 are displayed in Table S1. The results showed no change in the Al content and Si/Al ratio after the ion-exchange process in $Co(NO_3)_2$ solution. However, the Co-SSZ-39 and Co-SSZ-13 samples showed different Co/Al ratios of 0.20 and 0.15, respectively. This confirmed that although the SSZ-39 and SSZ-13 substrates have the same Si/Al and Al contents, the distributions of FAl in the two zeolites are different, and demonstrated that more paired Al existed in the SSZ-39 substrate compared to SSZ-13.

SSZ-39 and SSZ-13 have extremely similar framework structures, both containing a large cage (aei and cha cavities) and a double 6 mr prism as shown in Fig. 1. The large cages of SSZ-39 and SSZ-13 have the same composition, including 12 four-membered rings, 2 six-membered rings and 6 eight-membered rings. For Cu-SSZ-13, the Cu(OH)⁺-Z species located next to 8MR are balanced by a single Al, while the $Cu^{2+}-2Z$ species located next to 6MR are balanced by paired Al [16,37]. As discussed before, the parent SSZ-39 had more paired Al than the parent SSZ-13. Therefore, Cu-SSZ-39 had a lower percentage of Cu (OH)⁺-Z but higher percentage of Cu²⁺-2Z compared to Cu-SSZ-13 for similar Cu loadings. The H2-TPR experiments of Cu-zeolites with Cu loadings of 3.5 wt% verified this difference in Cu distributions for the two catalysts (Table S2). We have also conducted the H2-TPR measurements of Cu-SSZ-39 and Cu-SSZ-13 with other Cu loadings (Fig. S10). It is clearly seen that Cu-SSZ-39 contained more Cu^{2+} -2Z species than Cu-SSZ-13 did in the case of similar Cu loadings.

To highlight this difference, the normalized standard SCR reaction rates, activation energies and pre-exponential factors were calculated in the low NO_x conversion region (< 20 %, Fig. S11). As shown in Fig. 8, it



Fig. 8. (a) Normalized standard SCR reaction rates as a function of temperature and (b) Arrhenius plots of Cu-SSZ-39 and Cu-SSZ-13 before and after hydrothermal aging.

was found that the fresh Cu-SSZ-13 catalyst exhibited a higher reaction rate than fresh Cu-SSZ-39. This result indicates that a larger percentage of active Cu (OH)⁺-Z species existed in Cu-SSZ-13 compared to Cu-SSZ-39. because $Cu^+(OH)$ -Z species are more active than Cu^{2+} -2Z species in the SCR reaction [14,24]. Moreover, the fresh Cu-SSZ-13 catalyst had a significantly larger pre-exponential factor than fresh Cu-SSZ-39, which also indicated that more Cu(OH)⁺-Z existed in Cu-SSZ-13 due to the higher accessibility to reactants of Cu(OH)⁺-Z compared with Cu²⁺-2Z [16]. In addition, Cu-SSZ-39 showed a slightly lower activation energy (51.8 kJ/mol) than Cu-SSZ-13 (71.4 kJ/mol). In the NH₃-SCR reaction, Paolucci et al. [38] reported that the rate-limiting process of Cu-SSZ-13 was the migration of $Cu(NH_3)^{2+}$ through the 8MR, which is influenced by the mobility and effective diffusion distances of Cu ions. Therefore, different Cu distributions and zeolite topology gave rise to different limitations on the movable $Cu(NH_3)^{2+}$ species, which resulted in a small difference in the NH₃-SCR reaction activation energy between Cu-SSZ-39 and Cu-SSZ-13 zeolite catalysts [13,15,38]. After hydrothermal aging, an increase trend of Ea from ~50 to ~70 kJ/mol was observed for the Cu-SSZ-39 catalysts, probably indicative of reaction pathway change. However, the Ea of Cu-SSZ-13 hardly changed after hydrothermal aging at 750 °C, but significantly decreased after hydrothermal aging at 800 °C due to the formation of large amounts of CuOx and collapse of the structure.

4.2. Hydrothermal stability

The hydrothermal stability of Cu-zeolites is considered to be mainly related to the topology of the zeolite structure, Si/Al ratio and Cu loading (or Cu/Al) [4,5,14,16,28,39]. As for the Al-rich Cu-SSZ-13 zeolites, although they have excellent NH₃-SCR performance [25,40-42], their low hydrothermal stability has always been a drawback, due to their facile dealumination when subjected to hydrothermal aging. In fact, lowering the Si/Al ratio can increase the amount of paired Al and further increase the accommodation of Cu²⁺-2Z species, which benefit both the low-temperature NH3-SCR performance and the hydrothermal stability [24]. Large CuO_x clusters derived from the transformation of Cu(OH)⁺-Z and Cu²⁺-2Z species can induce structural damage, which is thought to be the principal cause for the deactivation of Cu-SSZ-13 during hydrothermal aging [14,43]. Fig. 9 shows HRTEM images of the Cu-SSZ-39 and Cu-SSZ-13 catalysts after hydrothermal aging at 800 °C, illustrating their different morphologies. As can be seen, the CuOx clusters formed on Cu-SSZ-13-800, showing

poorer dispersity and larger accumulated particle sizes than those on Cu-SSZ-39-800. This indicated that the Cu species in Cu-SSZ-13 are more moveable during hydrothermal aging, leading to the formation of the larger CuOx clusters. These CuOx clusters with bigger size thus damage the zeolite structure of Cu-SSZ-13, which was also observed in the XRD results (Fig. 3). Thanks to the small particle size and high dispersity of the clusters, however, the zeolite structure of SSZ-39 was well maintained despite the formation of CuOx clusters. The evidence presented here as well as previous results achieved in Cu-SSZ-13 catalysts [14,16] both confirm that Cu^{2+} -2Z species are more hydrothermally stable than $Cu(OH)^+$ -Z species. Therefore, the more Cu^{2+} -2Z species are present in Cu-based small-pore zeolites, the less formation of CuO_x clusters occurs after hydrothermal aging. It follows that Cu-SSZ-39 with more paired Al has higher hydrothermal stability than Cu-SSZ-13.

Besides the active Cu²⁺ species, the tendency for dealumination should be also considered for the hydrothermal stability. A lowered Si/ Al ratio often results in the presence of residual aluminum uncoordinated with Cu²⁺. The residual aluminum in Al-rich Cu-zeolite is vulnerable to dealumination during hydrothermal aging, thus lowering the stability. Here, Cu-SSZ-39 gives an Al-rich zeolite the opportunity to be applied in the NH₃-SCR reaction. On one hand, the greater amount of Cu²⁺-2Z species coordinated with paired framework Al in Cu-SSZ-39 leaves fewer residual uncoordinated Al sites, compared to Cu-SSZ-13 with the same Cu loadings. On the other hand, SSZ-39 has a more tortuous channel structure than SSZ-13 does (schematic diagram shown in Fig. S12). This structure can inhibit the detached Al(OH)₃ from exiting the pores of the AEI zeolite framework, which would result in reincorporation of Al(OH)₃ into the framework when cooling down [28]. To eliminate the influence of Cu species, we carried out ²⁷Al-NMR measurements on pure H-SSZ-39 and H-SSZ-13 zeolite before and after hydrothermal aging (Fig. S13). It can be seen that H-SSZ-39 showed less dealumination than H-SSZ-13 when subjected to the same hydrothermal aging conditions, indicating that the FAl in pure SSZ-39 zeolite is more stable than that in SSZ-13 zeolite. This result could also explain why Cu-SSZ-39 showed higher hydrothermal stability than Cu-SSZ-13 at low Cu loading, where Cu²⁺-2Z species dominate in both catalysts, since Cu-SSZ-13 showed more severe dealumination (Fig. S14) and resulted in more loss of acid sites.



Fig. 9. HRTEM images of (a) Cu-SSZ-39-800 and (b) Cu-SSZ-13-800.

5. Conclusion

The NH₃-SCR activity and hydrothermal stability of Cu-exchanged SSZ-39 and SSZ-13 zeolites have been investigated. Cu-SSZ-39 showed comparable deNOx efficiency but significantly higher hydrothermal stability than Cu-SSZ-13. Compared to SSZ-13 with large amounts of Cu (OH)⁺-Z species balanced with isolated Al, SSZ-39 contained a larger percentage of Cu²⁺-2Z species balanced with paired Al next to 6MR, when ion-exchanged to produce the same Cu loading. The Cu²⁺-2Z species are more stable and have a lower tendency to form CuOx clusters during hydrothermal aging. Moreover, the framework Al of SSZ-39 is more hydrothermally stable than that in SSZ-13 because it has less Al that is not coordinated with copper species and a more tortuous channel structure. In addition, compared to Cu-SSZ-13 with high Si/Al. the Al-rich Cu-SSZ-39 catalysts showed an excellent NH₃-SCR performance in a wide temperature range. Therefore, the Cu-SSZ-39 zeolite catalyst shows strong potential as an NH₃-SCR catalyst for actual application due to its good NOx conversion and outstanding hydrothermal stability.

Author contribution

Yulong Shan prepared the catalyst. Yulong Shan and Wenpo Shan performed the characterizations, catalytic tests and wrote the paper. Xiaoyan Shi and Jinpeng Du participated the discussion and analysis of the experimental data. Yunbo Yu and Hong He designed this research, analyzed the data.

Declaration of Competing Interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

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