Study on the Performance of the Zr-Modified Cu-SSZ-13 Catalyst for Low-Temperature NH$_3$-SCR

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ABSTRACT: Cu-SSZ-13 and Zr-modified Cu-SSZ-13 catalysts with different Zr/Cu mass ratios were prepared by ion-exchange and impregnation methods, respectively. The NH$_3$-SCR performance tests were performed using the catalyst performance evaluation device to investigate the effects of different Zr/Cu mass ratios on the catalyst ammonia-selective catalytic reduction (NH$_3$-SCR) performance. X-ray diffraction, ICP-OES, BET, NH$_3$ temperature-programmed desorption (NH$_3$-TPD), H$_2$ temperature-programmed reduction (H$_2$-TPR), X-ray photoelectron spectrometry, and in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) were used to characterize the catalysts. The results show that the prepared Cu-SSZ-13 catalyst had good catalytic activity. Zr introduction was carried out on this basis. The results showed that proper Zr doping improved the catalytic activity at low temperatures and widened the high-temperature stage, with an optimal activity stage at a Zr/Cu mass ratio of 0.2. The NO$_x$ conversion efficiency was close to 100% at 200 °C and over 80% at 450 °C. The active species were well dispersed on the catalyst surface, and the metal modification did not change the crystal structure of the zeolite. The NH$_3$-TPD results showed that the Zr-modified catalyst had more abundant acid sites, and the H$_2$-TPR results indicated that the Cu species on the catalyst had excellent reducibility at low temperatures. The interaction between Cu and Zr could regulate the Cu$^+$ and Cu$^{2+}$ proportion on the catalyst surface, which facilitated the increase in the Cu$^+$ for fast SCR reaction at low temperatures. With abundant acid sites and both SCR reactions following the Eley–Rideal (E–R) and Langmuir–Hinshelwood (L–H) mechanism on the catalyst surface at a low temperature of 150 °C, more abundant acid sites and reaction paths created favorable conditions for NH$_3$-SCR reactions at low temperatures.

1. INTRODUCTION

With the increasingly stringent emission requirements of vehicles, the diesel particulate filter (DPF) system was used to remove the particulate matter to meet the regulations. Due to the characteristics of vanadium-based SCR catalysts, the high-temperature durability was terrible. Evaporation of vanadium metal and catalyst deactivation existed above 550 °C, which was a great hazard to the environment and human health. In light of this, V-based catalysts were not suitable for current diesel after-treatment systems. Cu-SSZ-13 molecular sieve catalysts with transition-metal Cu as the active component had been widely used in lean combustion diesel engines and commercial vehicle after-treatment systems. Cu-SSZ-13 molecular sieve catalysts with transition-metal Cu as the active component had been widely used in lean combustion diesel engines and commercial vehicle after-treatment systems. The Cu-based zeolite catalysts performed well in hydrothermal resistance and de-NO$_x$ at low temperatures. Besides, the Cu-SSZ-13 catalyst could also avoid irreversible deactivation and vanadium metal evaporation in the case of DPF regeneration.

In addition to single metal Cu-SSZ-13 catalysts loaded with Cu, researchers further enhanced the performance of Cu-SSZ-13 catalysts by doping with other metals. Fe-based catalysts had excellent NH$_3$-SCR performance at high temperatures. Using different preparation and doping methods, iron and copper active components could co-exist in the composite catalyst. Due to the strong interaction between Fe and Cu species, Fe–Cu/SSZ-13 composite catalysts could widen the SCR reaction temperature range and improve the NH$_3$-SCR activity compared to Cu-SSZ-13 catalysts. Ce doping could also improve the performance of Cu-SSZ-13 catalysts, and the appropriate amount of Ce doping could stabilize the zeolite structure and Cu active center to improve the
hydrothermal stability of the catalysts.\textsuperscript{12,13} H\textsubscript{2} temperature-programmed reduction (H\textsubscript{2}-TPR) experiments and in situ IR results showed that the doping of Ce could improve the redox performance of the catalysts. The synergistic utility between Cu and Ce species could enhance the surface adsorption of NH\textsubscript{3} and NO\textsubscript{2}\textsuperscript{-} to improve the NH\textsubscript{3}-SCR performance of the catalyst. Other metal doping-modified Cu-SSZ-13 catalysts were also studied. The synergistic effect of active metals with suitable multi-metal modification could also improve the catalytic performance. Liu et al.\textsuperscript{15} first prepared Cu-SSZ-13 catalysts by ion exchange and then used the impregnation method to introduce Mn and Ce metals into Cu-SSZ-13 to obtain Mn–Ce/Cu-SSZ-13 catalysts. Utilizing in situ IR and other characterization methods found that the synergistic interaction between Mn/Cl/Cu converted the bridged nitrate adsorbed on the catalyst surface into monodentate nitrate, which improved the performance of Cu-SSZ-13 catalysts at low temperatures.

The modifications of Cu-SSZ-13 by transition metals of Fe and Mn and lanthanide metals represented by Ce were widely studied. However, the modification of Cu-SSZ-13 by other transition metals was less studied. There were many studies related to the application of Zr in oxide catalysts. The introduction of Zr could improve the N\textsubscript{2} selectivity of catalysts.\textsuperscript{16} The collaboration between Cu and other metals could enhance the catalyst structure stability,\textsuperscript{17} improve the reduction performance, and strengthen the surface acid sites of the catalysts to enhance the NH\textsubscript{3}-SCR activity.\textsuperscript{18} Some researchers have also introduced Zr into zeolite catalysts. Peng et al. utilized different methods to introduce Zr into Cu-SSZ-13 catalysts (Cu-SSZ-13 was prepared using ion exchange). They found that the introduction of highly dispersed ZrO\textsubscript{2} could improve the high-temperature catalyst performance without having any effect on the low-temperature performance of the catalyst. The interaction between Zr and Cu could reduce the oxidation of NH\textsubscript{3}.\textsuperscript{19} Chen et al. introduced Zr and Fe into SSZ-13 zeolite using a one-pot method, and Zr/Fe-SSZ-13 catalysts with small amount of Zr doping were obtained. The introduction of Zr was found to improve the relative crystallinity of Fe-SSZ-13 catalysts, inhibit the migration and agglomeration of iron ions, and improve the hydrothermal stability of the catalysts.\textsuperscript{20}

In this study, a small amount of Zr was introduced into the Cu-SSZ-13 catalyst obtained by ion exchange through the impregnation method. Zr-modified Cu-SSZ-13 catalysts with different Zr/Cu mass ratios were obtained. The NH\textsubscript{3}-SCR performance was investigated. The catalysts were characterized by X-ray diffraction (XRD), ICP-OES, BET, X-ray photoelectron spectrometry (XPS), in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and so on to investigate the factors affecting the NH\textsubscript{3}-SCR performance.

2. EXPERIMENT

2.1. Preparation of Cu-SSZ-13 and Zr-Modified Catalysts. A H-SSZ-13 molecular sieve with a Si/Al ratio of 6.5 was used, and the typical Cu loading mass fraction should be 2–3\% for a low Si/Al ratio.\textsuperscript{19} The Cu-SSZ-13 catalyst was prepared using the ion exchange method, and it was reported that the best balance of high-temperature durability and SCR activity could be achieved with a Cu loading mass fraction of about 2.2\%.\textsuperscript{19} The design target Cu loading mass fraction was 2.2\%. Copper acetate monohydrate (Tianjin Beichen, AR) was used as the precursor. After a lot of experimental attempts and ICP-OES verification, the Cu-SSZ-13 catalyst with a Cu loading mass fraction of about 2.2\% was obtained. The experiment was as follows: the copper acetate solution was prepared according to the calculation. The mass concentration of Cu\textsuperscript{2+} was 4.42 g/L, and the mass ratio of Cu\textsuperscript{2+} to molecular sieve was 4.5\% which was put into the corresponding H-SSZ-13 molecular sieve, placed in a magnetic stirrer with heating and stirring at 73 ± 2 °C, and started for 4 h when the temperature reached 73 °C. Then, the catalyst was washed with deionized water after ion exchange, dried in an oven at 105 °C for 8 h, and calcined in a muffle furnace at 550 °C for 6 h after grinding. Under these conditions, we conducted several preparations of 30 g of samples, and the Cu content fluctuates between 2.179 and 2.246\%. At last, the sample was ground again to obtain a Cu-SSZ-13 zeolite catalyst, marked as Cu–S. The Zr-modified Cu-SSZ-13 catalyst was prepared using the impregnation method. First, the pore volume of 1 g of Cu-SSZ-13 molecular sieve was titrated with deionized water to obtain the volume of water absorption. The Zr/Cu mass ratio of the modified catalyst was set to 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0, respectively. The corresponding zirconium nitrate pentahydrate (Macklin, AR) solution was configured. Then, the solution was added dropwise to the samples while stirring. The samples were dried at 105 °C for 8 h in an oven. After that, the samples were calcined at a temperature of 550 °C for 6 h. The catalysts were ground to obtain Zr/Cu-SSZ-13 catalysts labeled as Zr\textsubscript{0.1}Cu–S, Zr\textsubscript{0.2}Cu–S, Zr\textsubscript{0.4}Cu–S, Zr\textsubscript{0.6}Cu–S, Zr\textsubscript{0.8}Cu–S, and Zr\textsubscript{1.0}Cu–S, respectively.

2.2. Catalyst Performance Measurement. Cu-SSZ-13 sample and modified Zr/Cu-SSZ-13 catalyst NH\textsubscript{3}-SCR performance tests were carried out on a VDRT-200 SCR catalyst evaluation device; the inlet gas flow was composed of 0.1\% NO, 0.1\% NH\textsubscript{3}, and 5\% O\textsubscript{2} by volume fractions and N\textsubscript{2} as balance gas. The gas flow was dominated at 200 mL min\textsuperscript{-1} in the gas hourly space velocity (GHSV) of 24,000 h\textsuperscript{-1}, which was controlled using a mass flowmeter. 300 mg (about 0.5 mL) of the catalyst was added into the reactor. The catalyst efficiency was calculated using eq 1

\[
\eta = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\%.
\]  

(1)

2.3. Catalyst Characterization. The XRD measurement in the 2θ range of 5°–40° was performed on the DX-2700B X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm). The scanning speed was set to 2°/min, and the tube voltage and current were set to 50 kV and 30 mA, respectively.

The catalyst was tested by ICP-OES on a PerkinElmer Avio200 inductively coupled plasma optical emission spectrometer. 50 mg of the sample was dissolved in a mixed solution of hydrochloric acid and sulfuric acid, digested completely using a microwave digester and compared with the standard solution to obtain the actual metal content of the catalyst.

N\textsubscript{2} adsorption was carried out at 77 K using a V-Sorb 2800 automatic specific surface area analyzer to measure the BET surface areas, micropore diameters, and volumes (using single-point maximum adsorption and t-plot method).

NH\textsubscript{3} temperature-programmed desorption (NH\textsubscript{3}-TPD) and H\textsubscript{2}-TPR were carried out on a Vodo-VDsorb-911i instrument. For the NH\textsubscript{3}-TPD measurement, 0.05 g of the sample was pretreated at 500 °C under pure He gas flow of 30 mL min\textsuperscript{-1}.
for 1 h to remove the impurities adsorbed on the sample surface. Then, it was cooled to 100 °C and saturated with 5% NH₃/N₂ gas for 45 min. After being purged by He gas flow (30 mL min⁻¹) for 1 h to remove the physically adsorbed NH₃ desorption of NH₃ was carried out from 100 to 700 °C at 10 °C min⁻¹. For the H₂-TPR measurement, 0.05 g of the sample was pretreated at 500 °C under pure He gas flow of 30 mL min⁻¹ for 1 h to remove the impurities adsorbed on the sample surface, then cooled to 50 °C. Subsequently, the reduction process was performed from 50 to 900 °C at 10 °C min⁻¹ in 10% H₂/Ar flow (10 mL min⁻¹).

The surface atomic concentration and element valence of catalysts were recorded using an X-ray photoelectron spectrometer (Thermo Escalab 250Xi) with Al Kα as the radiation source. Semi-quantitative analysis of the surface element content was obtained.

In situ DRIFTS was performed on a Shimadzu IRTracer-100 Fourier transform spectrometer with a spectra collection range of 4000–650 cm⁻¹ and a resolution of 4 cm⁻¹. A mercury-cadmium-telluride detector was used for in situ cell IR detection (cooling by liquid nitrogen). The sample was mixed with KBr at a mass ratio of 1:50 and sent into the reactor, which was purged for 40 min at 400 °C under an Ar atmosphere. Subsequently, it was cooled to 150 °C to start the experiment. The gas flow was composed of 5% O₂, 1% NH₃, and 1% NO with Ar as the balance gas, and the total inlet gas flow was dominated at 100 mL min⁻¹ using the flow controller.

3. RESULTS AND DISCUSSION

3.1. Catalytic Activity Measurements. The NO conversion of the synthesized Cu-SSZ-13 and Zr/Cu-SSZ-13 catalysts prepared in different Zr/Cu mass ratios is displayed in Figure 1. It showed that the Cu–S sample prepared using the ion-exchange method and Zr-modified catalysts using the impregnation method presented superior NH₃-SCR activity at a temperature range of 250–400 °C. The catalyst labeled as ZrₓCu–S performed excellent NH₃-SCR at 200 °C with approximate 100% NOx conversion efficiency. At a temperature of 450 °C, ZrₓCu–S could also keep the NO conversion above 80%. The NO conversion efficiency of most of the catalysts decreased sharply when the temperature increased to 450 °C, which might be due to the oxidation of the NH₃ after the temperature reached 400 °C, leading to the decrease in NOx conversion. A moderate amount of Zr doping can improve the NOx conversion of Cu-SSZ-13 catalysts, and Zr-doped-modified catalysts perform better NH₃-SCR activity than Cu-SSZ-13 at higher temperatures. However, an excessive Zr doping could also lead to a decrease in NOx conversion at high temperatures. Compared with the origin Cu–S catalyst, the impregnated Zr-modified Cu–S catalyst with a Zr/Cu mass ratio of 0.2 improved low-temperature NO conversion performance and broadened the high-temperature reactive interval.

3.2. XRD Test. In order to verify whether the lattice structure of the catalyst samples changed after Cu/Zr doping, XRD tests were carried out, and the results are shown in Figure 2. All samples showed distinctive peaks at 2θ = 9.86, 14.07, 16.11, 17.92, 20.74, 25.16, and 30.87°, which were consistent with the CHA structure peaks of SSZ-13 (2θ = 9.5, 14.0, 16.1, 17.8, 20.7, 25.0, and 30.7°). It was indicated that the doping of Cu and Zr did not change the crystal structure of the molecular sieve significantly. The diffraction peak of 2θ = 9.5° presented a minor weakness with the increase in the metal loading, which might be due to the combination of metal ions with the zeolite framework, resulting in the deformation of the crystal octet ring and weakening of the planar (1 0 0) diffraction intensity. The diffraction peaks of CuO (2θ = 35.60 and 38.80°) and Cu₂O (2θ = 36.44°) were not observed in the pattern, which indicated that Cu species were well dispersed in Cu–S and Zr-modified Cu–S catalysts. M-ZrO₂ and t-ZrO₂ diffraction peaks of 2θ = 28.2 and 30.2° respectively were not observed in the diffraction patterns, which indicated that the element of Zr may be uniformly dispersed as nanoparticles on the catalyst surface or present in the zeolite pores in the ionic form.

3.3. BET and ICP-OES Measurements. The parameters of the H-SSZ-13 molecular sieve and Cu–S and Zr-modified Cu–S catalysts with Cu and Zr element mass fraction, specific surface area, and pore structure are shown in Table 1. A larger specific surface area of the catalyst could provide more active sites for the NH₃-SCR reaction, which was beneficial to the NH₃-SCR reaction. After the Zr introduction, the specific surface area decreased significantly with the increase in the metal loading, which might be the increase in metal doping resulting in pore blockage. The larger the micropore volume and smaller the pore size, the more favorable the NH₃-SCR reaction was. ZrₓCu–S demonstrated a larger pore volume and smaller pore size, which was one of the reasons for its superior NOx conversion efficiency. Abnormal data of ZrₓCu–S might be the corrosion of micropores during metal modification.

ICP-OES analysis showed that all the samples had a stable Cu loading of about 2.2%, which was consistent with the experimental design goals. However, the XRD pattern did not show the diffraction peaks of introduced metal, it also confirmed that the introduced metal elements were present in the pore channels in the ionic form or uniformly dispersed on the catalyst surface in the form of nanoparticles, which facilitated the NH₃-SCR reaction.

3.4. NH₃-TPD Measurement. The NH₃-TPD measurement was conducted to probe the acidity of Cu–S and Zr-modified catalysts, and the results are shown in Figure 3. All the catalysts exhibited three distinct NH₃ desorption peaks (A, B, C)
B, and C). The peak located near 185 °C could be attributed to the desorption of NH$_3$ adsorbed at weak Lewis acid sites;\textsuperscript{26,27} the B peak appeared at ∼300 °C and could be assigned to the desorption of NH$_3$ from Cu$^{2+}$ and strong Lewis acid sites; and the desorption peak C near 481 °C should be the desorption of NH$_3$ adsorbed at Brønsted acid sites.\textsuperscript{27,28} The fitted profile was integrated and calculated to obtain the total NH$_3$ desorption. We found that Zr$_{0.8}$Cu$^{-}$S had the largest integral area among all catalysts, followed by Zr$_{0.2}$Cu$^{-}$S. Compared with the Cu$^{-}$S sample, the integral area of the A and B peaks (Lewis acid sites) of Zr$_{0.2}$Cu$^{-}$S was increased by 7%. Zr modification enhanced the NH$_3$ adsorption capacity. Lewis acid sites played an important role in the NH$_3$-SCR reaction at low temperatures, and we speculated that the rich Lewis acid site was one of the reasons for the excellent NH$_3$-SCR performance of Zr$_{0.2}$Cu$^{-}$S at low temperatures.

3.5. H$_2$-TPR Measurement. Figure 4 shows the H$_2$-TPR results of Cu$^{-}$S and Zr/Cu-SSZ-13 catalysts. All the lines demonstrated four reduction peaks. Generally, the reduction of Cu$^{2+}$ has two steps: in the first, Cu$^{2+}$ is reduced to Cu$^{+}$, and then, Cu$^{+}$ is reduced to Cu$^{0}$. Among them, peak A was located near 250 °C, which could be attributed to the reduction of Cu$^{2+}$ to Cu$^{+}$ in the 8MRs cage and cage and D6Rs; the reduction peak near 385 °C should be the reduction of Cu$^{x}$O to Cu$^{0}$; and the reduction peaks of Cu species at temperatures higher than 500 °C are generally Cu$^{+}$→Cu$^{0}$; therefore, peaks C and D should be classified as the reduction of Cu$^{+}$ to Cu$^{0}$.\textsuperscript{28−30} With the increase in the Zr loading, the moving forward peak C could be clearly observed in the spectra. Pure ZrO$_2$ is reduced around 421−425 °C. Therefore, we believed that this might be due to the reduction of Zr species of the catalyst.\textsuperscript{19} The Cu$^{2+}$ reduction peak of Cu$^{-}$S at low temperatures (∼250 °C) was not obvious; however, the reduction peak of Cu$^{2+}$ near 250 °C was significantly enhanced by the introduction of Zr. This might be because the Zr species promoted the Cu$^{2+}$ reduction within the 8MRs cage and D6Rs, which improved the redox ability of the Cu active center; this

![Figure 2. XRD patterns of the catalyst.](image2)

![Figure 3. NH$_3$-TPD profiles for Cu$^{-}$S and Zr-modified catalysts.](image3)

| sample          | $S_{\text{BET}}$ (m$^2$ g$^{-1}$)$^a$ | $V_{\text{micro}}$ (cm$^3$ g$^{-1}$)$^b$ | $V_{\text{pore}}$ (cm$^3$ g$^{-1}$)$^c$ | $D_{\text{pore}}$ (nm)$^d$ | Cu (wt %) | Zr (wt %) |
|-----------------|--------------------------------------|----------------------------------------|----------------------------------------|--------------------------|-----------|-----------|
| H-SSZ-13        | 752.22                               | 0.279                                  | 0.322                                  | 1.7115                   | —         | —         |
| Cu$^{-}$S       | 720.56                               | 0.264                                  | 0.299                                  | 1.6577                   | 2.34      |           |
| Zr$_{0.1}$Cu$^{-}$S | 695.11                               | 0.253                                  | 0.288                                  | 1.7759                   | 2.20      | 0.28      |
| Zr$_{0.2}$Cu$^{-}$S | 704.52                               | 0.262                                  | 0.286                                  | 1.6221                   | 2.15      | 0.50      |
| Zr$_{0.4}$Cu$^{-}$S | 647.52                               | 0.265                                  | 0.298                                  | 1.8974                   | 2.11      | 0.99      |
| Zr$_{0.6}$Cu$^{-}$S | 628.70                               | 0.217                                  | 0.443                                  | 2.9466                   | 2.32      | 1.53      |
| Zr$_{0.8}$Cu$^{-}$S | 594.83                               | 0.256                                  | 0.283                                  | 1.6275                   | 2.21      | 1.80      |
| Zr$_{1.0}$Cu$^{-}$S | 519.77                               | 0.191                                  | 0.223                                  | 1.7128                   | 2.26      | 2.33      |

$^a$Multi-point BET specific surface area. $^b$t-Plot method microporous volume. $^c$Highest single-point adsorption total pore volume. $^dD = 4V/A$ by BET.
change was beneficial to the NH$_3$-SCR reaction at low temperatures.

### 3.6. Copper and Zirconium Species

The XPS measurement was carried out to assess the effect of the Zr doping on the valence and surface content of Cu species. XPS profiles of Cu–S and Zr$_{0.2}$Cu–S are shown in Figure 5. The valence state and content of Cu species present could be determined by the magnitude of the Cu 2p binding energy.

Under X-rays, the inner and valence electrons of the Cu element were excited, and the 2p shell energy level of Cu was divided into 2p$_{3/2}$ and 2p$_{1/2}$. The peaks of Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ appeared near the binding energy of 933 eV and 952.7 eV, respectively. The binding energy of 932.9 eV located near 933 eV and the main peak near 952.7 eV could be assigned to Cu$^{+}$.\textsuperscript{31,32} The satellite peaks with binding energies of 934.8 and 936.7 eV appeared near the main peak at 932.9 eV, which could be ascribed to Cu$^{2+}$ (Cu–O–Si–O) coordinated with oxygen in the zeolite framework and octahedrally coordinated Cu$^{2+}$, respectively.\textsuperscript{18,29} The shake-up peak near 943.5 eV could be assigned to the presence of Cu$^{2+}$.\textsuperscript{31} The low peak at 955.4 eV was the accompanying peak at 952.7 eV and the shake-up satellite peak at 962.5 eV could be classified as Cu$^{2+}$.\textsuperscript{34} It could be seen from the profile that the doping of Zr changed the distribution of Cu active species on the catalyst surface, and an increase in the Cu$^{+}$ and Cu$^{2+}$ peak integral area could be observed. XPS results showed that the Cu content on the sample surface increased from 2.7 to 2.89%. The migration of Cu active sites to the catalyst surface was beneficial to the surface SCR reaction. The integration of each peak area was calculated to obtain the content of each Cu species on the catalyst sample surface, as shown in Figure 6.

The XPS profiles of Cu$^{+}$ and Cu$^{2+}$ content on the catalyst surface.

The charge transfer between Cu and Zr on the surface of the zeolite leads to the higher binding energy of Zr 3d$_{5/2}$ in the catalyst than that of metallic Zr (180.0 eV). The element Zr was present as Zr$^{4+}$ on the surface of the molecular sieve.\textsuperscript{35,36} The Zr doping could regulate the valence state of Cu elements on the catalyst surface with a 10% increase in Cu$^{+}$ and a 10% decrease in Cu$^{2+}$. The redox interaction between Cu$^{+}$ and Cu$^{2+}$ was crucial in the SCR reaction. According to the report,\textsuperscript{34} simulations showed that O$_2$ adsorbs on Cu$^{+}$ to form Cu$^{+}$–O$_2$/H$^+$ species. Cu$^{+}$–O$_2$/H$^+$ could provide a reaction site for NO oxidation to NO$_2$ and react spontaneously with gas-phase NO to form Cu$^{2+}$–OH–NO$_2$, followed by NO$_2$ release to form Cu$^{2+}$–OH. Abundant Cu$^{+}$ played an important role in
promoting the fast SCR reaction by regulating the NO and NO$_2$ ratio of the SCR reaction. Generally, the fast-SCR reaction mainly occurred at low temperatures, and the NH$_3$-SCR activity experimental results also showed that the doping of a moderate amount of Zr could enhance the NO conversion efficiency at low temperatures.

3.7. In Situ DRIFTS Study at Low Temperatures. 3.7.1. NH$_3$ Adsorption Experiment. The acid sites on the surface of the Zr$_{0.2}$Cu$-S$ catalyst could be characterized by in situ DRIFTS NH$_3$ adsorption experiments, and the sample pretreatment method is described in Section 2.3. After pretreatment, the samples were cooled to 150 °C for background scanning, and then, the NH$_3$ gas flow with Ar as balance gas was adjusted to 100 mL min$^{-1}$. The NH$_3$ adsorption spectra of Zr$_{0.2}$Cu$-S$ at 2, 5, 10, 20, 30, and 40 min are shown in Figure 8a.

Generally, IR adsorption features of high wavenumber (>3000 cm$^{-1}$) were N–H stretching vibrations, and the low wavenumber features (<1700 cm$^{-1}$) were from N–H bending vibrations. The spectra showed the adsorption peaks at 3353, 3272, 1625, 1438, and 1260 cm$^{-1}$. According to previous reports, bands at 3353, 1625, and 1260 cm$^{-1}$ could be assigned to N–H stretching and bending vibrations of adsorbed NH$_3$ on Lewis acid sites. The bands at 3272 and 1438 cm$^{-1}$ were from Al–O–NH$_4^+$ stretching and bending vibrations of NH$_3$ adsorption on the Brønsted acid sites. Negative peaks could be observed at the bands of 3739 and 3662 cm$^{-1}$. The former could be attributed to the depletion of OH of surface terminal Si–OH groups, and the latter was from NH$_3$ adsorption onto bridging hydroxyl groups. The presence of Brønsted acid sites and abundant Lewis acid sites on the catalyst surface was beneficial to the adsorption of NH$_3$. While the Brønsted acid sites mainly played an important role in the SCR reaction at high temperatures and the Lewis acid sites facilitated the SCR reaction at low temperatures, the catalyst showed superior NH$_3$-SCR activity at low temperatures.

3.7.2. Reaction between NO + O$_2$ and Pre-adsorbed of NH$_3$ at Low Temperatures. In order to understand the reaction between NO + O$_2$ and pre-adsorbed NH$_3$, and the possible reaction paths, after the saturation of NH$_3$ adsorption, a 15 min Ar purge was carried out to remove extra NH$_3$ in
tubes and the reactor. After that, the gas flow was changed to NO + O₂ with Ar as the balance gas. Infrared signals were collected at 2, 5, 10, 20, 30, and 40 min, and the spectra of the reaction between NO + O₂ and pre-adsorbed NH₃ are shown in Figure 8b.

The spectra did not show a downturn of NH₃ adsorption peaks, probably due to the reaction between adsorbed NH₃ species and NO + O₂ being too fast to be observed at 150 °C (the signals collected after 2 min), which could also suggest the excellent NO conversion efficiency of the catalyst at low temperatures. The recovery of surface hydroxyl (Si−OH) and bridging hydroxyl (Al−OH−Si) species located at the bands of 3662 and 3739 cm⁻¹ could be observed in the spectra, indicating that NH₃ at the sites was desorbed by Ar purging or adsorbed NH₃ species had been involved in the reaction. The bands at 1573, 1596, and 1625 cm⁻¹ can be attributed to the formation of nitrate species with different coordination. The increasing peak at 1625 cm⁻¹ should be assigned to nitrate adsorbed on metal ion exchange zeolites, and bridged nitrate also appears near this wavenumber. The increasing band of 1360 cm⁻¹ with time was attributed to the generation of monodentate nitrate species. In summary, at a low temperature of 150 °C, coordinated NH₃ could participate in the SCR reaction with gaseous NO + O₂, and the reaction follows the E−R mechanism.

3.7.3. NO + O₂ Adsorption Experiments. The sample pretreatment method is described in Section 2.3. After pretreatment, the sample was cooled to 150 °C for background scanning, and then, the NO + O₂ gas flow with Ar as the balance gas was adjusted to 100 mL min⁻¹. The NO + O₂ adsorption spectra of Zr₀.2Cu−S at 2, 5, 10, 20, 30, and 40 min are shown in Figure 8c.

The increasing peak signal range of 1500−1300 cm⁻¹ was from nitrate species (asymmetric stretching vibration of NO₂⁻), which were considered to be nitrate species from the NO₂ adsorbed onto metal sites. The bands at 1628, 1597, 1571, and 1504 cm⁻¹ were attributed to adsorbed NO₂⁻ (Cu−NO₂⁻), bridged nitrate, bidentate nitrate, and monodentate nitrate species, respectively. This demonstrated that NO could be converted to NO₂ and adsorbed on the catalyst surface under aerobic conditions at 150 °C. The adsorption state approached saturated after 10 min, indicating that the catalyst had a strong adsorption capacity for NO₂.

3.7.4. Reaction between NH₃ and Pre-adsorbed of NO + O₂ at Low Temperatures. In order to understand the reaction between NH₃ and pre-adsorbed NO + O₂, and the possible reaction paths, after the saturation of NO + O₂ adsorption, a 15 min Ar purge was carried out to remove extra NO + O₂ in tubes and the reactor. After that, the gas flow was changed to NH₃ with Ar as the balance gas. Infrared signals were collected at 2, 5, 10, 20, 30, and 40 min, and the spectra of reaction between NO + O₂ and pre-adsorbed NH₃ are shown in Figure 8d.

NH₃ could be adsorbed at 1260 and 1438 cm⁻¹, but no clear peaks were observed in the spectra. There was a visible decreasing trend of adsorbed NO₂ and bridged nitrate species at the bands of 1628 and 1597 cm⁻¹ at a low temperature of 150 °C, indicating that the adsorbed NO₂⁻ (Cu−NO₂⁻) and bridged nitrate Cu−O−NO species reacted with coordinated NH₃ and the reaction following the L−H mechanism. No obvious change was observed at the bands of 1571 and 1504 cm⁻¹. However, compared with the pre-adsorbed NO + O₂ spectra, it was found that the original nitrate species on the site were consumed. We considered that the reaction rate was too fast to be observed, where the bidentate nitrate and monodentate nitrate species were already consumed by gaseous NH₃ within 2 min. This also could verify the excellent NO conversion efficiency of the catalyst at low temperatures. In conclusion, the SCR reaction of the catalyst at a low temperature of 150 °C followed both L−H and E−R mechanisms, and the abundant adsorption sites and superior low-temperature activity promoted the SCR reaction at low temperatures.

4. CONCLUSIONS

Cu-SSZ-13 was prepared using the ion-exchange method, and Zr was introduced into Cu-SSZ-13 using the impregnation method to obtain Zr-modified Cu-SSZ-13 catalysts with different Zr contents.

(1) Among a series of catalysts, Zr₀.2Cu−S significantly broadened the active temperature range of the Cu-SSZ-13 catalyst, with NO conversion efficiency close to 100% in the temperature range of 200−400 °C and still over 80% at 450 °C.

(2) Cu and Zr elements could be well dispersed on the catalyst surface, and the structure of the zeolite was not destroyed, with a decrease in specific surface area.

(3) The doping of Zr improved the distribution of Cu species on the catalyst surface, and the interaction between Zr and Cu could regulate the proportion of Cu²⁺ and Cu⁺ on the zeolite surface to increase the Cu⁺. Abundant Cu⁺ could provide the conditions for fast SCR reaction at low temperatures. H₂-TPR also showed that the catalyst demonstrated excellent reduction performance at low temperatures.

(4) NH₃-TPD and in situ DRIFTS studies showed that there were Brønsted acid sites and abundant Lewis acid sites on the surface of Zr₀.2Cu−S, which could provide more adsorption sites for NH₃. The Lewis acid sites were beneficial to the SCR reaction at low temperatures, and the catalyst also showed excellent NO conversion efficiency at low temperatures.

(5) The transient reactions between NH₃ and NO + O₂ showed that the SCR reactions occurring on the catalyst surface at a low temperature of 150 °C follow both L−H and E−R mechanisms, which were also vital for the superior low-temperature activity of the catalyst.

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Notes

The authors declare no competing financial interest. Credit authorship contribution statement: Huiyong Du: ideas, supervision, and validation. Shuo Yang: experiment, data curation, and writing original draft. Ke Li and Qian Shen: experiment equipment and experimental guidance. Min Li: validation. Xuetao Wang: experimental guidance and validation. Chenyang Fan: validation and funding acquisition.

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