Effect of Ion-Exchange Sequences on Catalytic Performance of Cerium-Modified Cu-SSZ-13 Catalysts for NH$_3$-SCR

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Abstract: Cerium-modified Cu-SSZ-13 catalysts were prepared by an aqueous ion-exchange method, and Ce and Cu were incorporated through different ion-exchange sequences. The results of NH$_3$-SCR activity evaluations displayed that Cu1(CeCu)2 catalyst presented excellent catalytic activity, and over 90% NO$_x$ conversion was obtained across the temperature range of 200–500 °C. The characterization results showed that the ion-exchange sequence of Cu and Ce species influenced the crystallinity of the zeolites and the coordination of Al. A small amount of Ce could participate in the reduction process and change the location and coordination environment of copper ions. Furthermore, Ce-modified Cu-SSZ-13 catalysts possessed more acidic sites due to their containing replacement of Ce and movement of Cu in the preparation process. The cooperation of strong redox abilities and NH$_3$ storage capacity led to the increase of active adsorbed species adsorption and resulted in better activity of Cu1(CeCu)2.

Keywords: cerium; Cu-SSZ-13; ion-exchange sequences; SCR; drifts

1. Introduction

With the rapid development of the economy, environmental issues—especially nitrogen oxides (NO$_x$) emitted from diesel vehicles—are getting growing attention. There is evidence that states that diesel vehicles accounted for about 10% of automobiles producing nearly 90% of NO$_x$ emitted from automobiles in China. To achieve ultra-low exhaust emission levels, China will implement the China VI Standards to control NO$_x$ pollutants emitted from diesel-fueled, heavy-duty vehicles. In exhaust aftertreatment system of diesel vehicles, the selective catalytic reduction of NO$_x$ with NH$_3$ (NH$_3$-SCR) has high efficiency and is currently considered as the most preeminent technology for NO$_x$ removal. Among all catalysts, Cu-SSZ-13 with small-pore structure has been proven to be the most promising catalyst in the NH$_3$-SCR reaction [1–4].

As we know, the complicated and changeable cold-start and low-load conditions of diesel vehicles make it more challenging for Cu-SSZ-13 catalyst in a wide variety of temperatures (200–600 °C). Also, Cu-SSZ-13 catalyst must have excellent hydrothermal stability, because the SCR unit is located in the high-temperature environment, due to the regeneration of the upstream diesel particle filter (DPF) (above 650 °C) [1]. Recently, several rare earth modified Cu-SSZ-13 catalysts have been widely reported resulting from their easy operability, outstanding de-NO$_x$ efficiency, and high improvement on hydrothermal stability. Usui et al. [5] demonstrated that introduction of a small amount of Ce by wet and solid-state ion-exchange routes could improve SCR activities over a broad temperature...
range, because it enabled abundant Brønsted acidity sites and stabilized the framework of SSZ-13. The results of Zhao et al. [6] also confirmed that rare earth ions (Ce\(^{3+}\), La\(^{3+}\), Sm\(^{3+}\), Y\(^{3+}\), Yb\(^{3+}\)) that modified Al-rich Cu-SSZ-13 catalysts had no significant impact on low-temperature NO conversions in the fresh catalyst but displayed enhancement of low temperature activity after hydrothermal aging when compared with Cu-SSZ-13. Similarly, Wang et al. [7] reported that Ce or Sm could be introduced into Cu-SSZ-13 by ion exchanged preparation procedures, and the counterparts were investigated in detail. They found that the coexistence of Ce or Sm could exhibit higher hydrothermal stability due to its preventing the framework Al from hydrolysis. Nevertheless, only few research works focused on using different ion-exchange sequences of rare earth and copper ions to modify SSZ-13 zeolite and investigating its NH\(_3\)-SCR performance.

In this study, we prepared Ce-modified Cu-SSZ-13 catalysts by an aqueous ion-exchange method and investigated the effect of different ion-exchange sequences of Cu and Ce on the SCR activity and hydrothermal stability of catalysts. XRD, \(N_2\) adsorption-desorption, as well as \(^{29}\)Si and \(^{27}\)Al NMR were carried out to investigate the textural and structural properties of the Ce-modified Cu-SSZ-13 catalysts. Besides, \(H_2\)-TPR and NH\(_3\)-TPD were used to explore the variation of reduction property and surface acidity.

2. Results and Discussion

2.1. Catalytic Performance

Figure 1 depicted the NH\(_3\)-SCR performance of Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts with the temperature change. As shown in Figure 1a, it can be seen that Cu-SSZ-13 displayed high NO\(_x\) conversions (>90%) in the temperature range of 200–400 °C. Note that Cu\(_1\)(CeCu)\(_2\), (CeCu)\(_1\)\(_2\) and (CeCu)\(_1\)Cu\(_2\) displayed an enhancement in activity compared with Cu-SSZ-13 at low and high temperatures. In the case of the (CeCu)\(_1\)Cu\(_2\) sample, it showed the highest catalytic performance at 200 °C and nearly 100% NO\(_x\) conversion was obtained at this temperature. As compared with Cu-SSZ-13, however, the NO\(_x\) conversion of (CeCu)\(_1\)Cu\(_2\) decreased from 71 to 64% at 550 °C and 59 to 52% at 600 °C. For (CeCu)\(_1\)\(_2\) and Cu\(_1\)(CeCu)\(_2\), the low-temperature SCR activity (200 °C) and high-temperature activity (>400 °C) were enhanced significantly compared to the NO\(_x\) conversions obtained with the Cu-SSZ-13 catalyst. Figure 1b revealed the SCR activity of these four catalysts after hydrothermal aging with 10% \(H_2O\) at 850 °C for 10 h under the GHSV of 60,000 h\(^{-1}\). It can be seen that the NO\(_x\) conversion of all catalysts decreased to different degrees, but the activity of Cu\(_1\)(CeCu)\(_2\) and (CeCu)\(_1\)Cu\(_2\) was obviously higher than that of Cu-SSZ-13 at high temperature (450–600 °C). Therefore, it was clear that introduction of Ce ions in Cu-SSZ-13 had significant impact on the activity, and Cu\(_1\)(CeCu)\(_2\) was selected as the optimum catalyst due to its excellent NH\(_3\)-SCR performance, and over 90% NO\(_x\) conversion of fresh catalyst was obtained across the temperature range of 200–500 °C.

2.2. Textural Properties

The XRD patterns of Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts were shown in Figure 2. It could be seen that all catalysts exhibited a typical chabazite (CHA) crystal structure with characteristic 2\(\theta\) degrees at 9.6°, 13.0°, 16.1°, 18.1°, 20.7°, 25.2°, 26.3° and 31.0° (PDF data file 52-0784) [8,9]. No noticeable diffraction peaks assigned to Cu species and Ce species were observed indicating that those should be present in the form of isolated ions or highly dispersed on the zeolite crystals [10–12]. There was no obvious difference in diffraction peak position between the catalysts, suggesting the introduced Ce species did not change the CHA structure. The peak intensity had been reported to correlate with the crystallinity of the zeolites [13,14]. As the pattern shown, the intensity of the characteristic peaks of Cu-SSZ-13 and Cu\(_1\)(CeCu)\(_2\) at 9.6° was much higher than that of (CeCu)\(_1\)\(_2\) and (CeCu)\(_1\)Cu\(_2\) samples, an effect that might be related to the ion-exchange sequence of the cerium species. As reported by Usui [5], the cerium species in the Cu-SSZ-13 should be present in the form of isolated ions as long as the cerium loading was less than 3 wt.%,
and over 3 wt.% cerium species located at extra ion-exchange sites should not affect the crystallographic features of the zeolite catalyst. This was associated with our observation (Figure 2 and Table 1) and also illustrated that Ce cations in Cu1(CeCu)2, (CeCu)12, and (CeCu)1Cu2 were located at the ion-exchange sites in double six-ring (D6R) or CHA cage.

Figure 1. NH3-SCR performance of fresh (a) and aged (b) Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts.

![Figure 1](image1.png)

Figure 2. XRD profiles of Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts.

![Figure 2](image2.png)

Table 1. Elemental compositions and textural properties over Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts.

| Samples          | CuO (%)  | CeO2 (ppm) | Langmuir Surface Area (m²/g) | VT (mL/g) |
|------------------|----------|------------|-----------------------------|-----------|
| Cu-SSZ-13        | 1.90     | -          | 793.7                       | 0.2789    |
| Cu1(CeCu)2       | 1.83     | 120        | 763.3                       | 0.2695    |
| (CeCu)12         | 2.04     | 130        | 768.6                       | 0.2730    |
| (CeCu)1Cu2       | 1.84     | 60         | 803.1                       | 0.2779    |

a Calculated by ICP. b VT is the t-Plot micropore volume.

Figure 3 presented N2 adsorption-desorption isotherms and pore width distribution curves over Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts. All samples showed typical type I isotherms according to the BDDT classification, which was consistent with the microporous materials [15,16]. Although the DFT model pore size distribution showed that Cu-SSZ-13, Cu1(CeCu)2, (CeCu)12, and (CeCu)1Cu2 catalysts had only a narrow visible
Table 1. Elemental compositions and textural properties over Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts.

| Catalyst                  | Cu (%)  | Ce (ppm) | Langmuir Surface Area | Total Pore Volume |
|---------------------------|---------|----------|-----------------------|-------------------|
| Cu1(CeCu)2               | 1.83    | 120      | 763.3                 | 0.2695            |
| (CeCu)1Cu2               | 1.84    | 60       | 803.1                 | 0.2779            |
| Cu-SSZ-13                | 1.90    | -        | 793.7                 | 0.2789            |
| (CeCu)12                 | 2.04    | 130      | 768.6                 | 0.2730            |

Figure 3. N₂ adsorption-desorption isotherms (a) and pore width distribution curves (b) of the catalysts.

2.3. NMR Measurements

As displayed in Figure 4, solid state NMR measurements were used to monitor the effects of ion-exchange sequence of Cu and Ce species on Al and Si atoms in the framework of SSZ-13. From $^{27}$Al NMR spectra (Figure 4a), one resonance feature at a chemical shift of 54 ppm in all these samples was corresponded to tetrahedral Al in the zeolite framework. Meanwhile, a small amount of extra-framework octahedral Al atoms near 5 ppm was observed in the curves of all the catalysts. Apparently, the intensity of the panels over Cu1(CeCu)2, (CeCu)12, and (CeCu)1Cu2 catalysts decreased significantly compared to Cu-SSZ-13, signifying that the introduction of Ce had a great effect on the coordination of Al in molecular sieve. It should be noted that there was a slightly more distorted over Cu-SSZ-13 considering its broader signal because the degree of distortion of the tetrahedral Al was in accordance with the signal width [17,18]. Apparently, the introduction of Ce led the zeolite body to relax and decreased this type of distortion since the signal had narrowed down instead of broadening. However, it was clearly shown that slight skeleton dealumination took place on Ce-modified Cu-SSZ-13 catalysts during the calcination process because of the weak signal intensities. This finding was not consistent with the result of XRD. In the $^{29}$Si NMR spectra (Figure 4b), the dominant peak at around 115 ppm was assigned to the presence of tetrahedral Si species (Si(OSi)$_4$) in the framework, and another weaker feature at 109 ppm was attributed to tetrahedral Si with three Si and one Al neighbor (Si(OSi)$_3$(OAl)) [17–19]. As we know, dealumination would cause the intensity of the 109 ppm signal to decrease [18]. However, it was worth pointing out that intensities for both signals decreased or increased at the same time after the introduction of Ce. Thus, this phenomenon was not a strong indication of the existence of dealumination.

2.4. H₂-TPR Measurements

The H₂-TPR profiles over the Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts were presented in Figure 5. Obviously, all the catalysts exhibited different reduction behaviors, indicating the presence of different Cu and Ce species in the catalysts. For Cu-SSZ-13, the original TPR curve from 170 to 670 °C could be accurately divided into four peaks after peak fitting process on the basis of the Gaussian deconvolution, and each peak corresponded with the reduction of one kind of Cu species. According to literature [20], the peak over
Cu-SSZ-13 appearing at 256 °C was assigned to the reduction of isolated Cu$^{2+}$ ions in the CHA cage. The peak around 368 °C, which was the strongest one in intensity among these H$_2$ peaks, represented the reduction of Cu$^{2+}$ ions on the D6R. This was consistent with the earlier report that the ion-exchange sites on the D6R were first saturated by Cu$^{2+}$ ions and then coordinated to the CHA cage, and the former required a higher temperature compared to that on other sites because of its highly stable nature in the CHA-type zeolite structure [21]. The high-temperature peak around 406 °C could be attributed to the reduction of Cu$^{+}$ to Cu$^{0}$. In addition, the peak located at about 539 °C corresponded to the reduction of highly stable Cu$^{+}$ ions to Cu$^{0}$ [20,21]. We observed, however, that Ce/Cu-SSZ-13 catalysts exhibited different reducibility properties that depended on the ion-exchange sequence of Cu and Ce species. It was noted that almost all the reduction temperatures of (CeCu)12 and (CeCu)1Cu2 samples shifted to much lower values with respect to Cu-SSZ-13, while a slight difference in the peak temperature between the Cu1(CeCu)2 and Cu-SSZ-13 samples was in fact observed. From this result, we could first conclude that the stability of the zeolite structure of Cu-SSZ-13 and Cu1(CeCu)2 was better than that of (CeCu)12 and (CeCu)1Cu2. Remarkably, with the introduction of Ce to the Cu-SSZ-13 catalysts, a clear increase in the amount of reduction of metal ion on D6R and CHA cage was observed. Also, there was quite a significant increase when computing the total H$_2$ consumption (shown in Table 2), indicating that the location and coordination environment of copper ions might change, and cerium ions also participated in the reduction process. Besides, comparing the peak concentrations of the reduction of metal ion species could give information about the reducibility of the four samples (Table 2). We further investigated that the ion-exchange sequence of Cu and Ce species influenced the coordination between Cu and Al atoms of the zeolite framework. In particular, the fraction of first peak attributed to [Cu(OH)]$^+$ in CHA cage in (CeCu)1Cu2 (10.5%) was significantly lower than that of Cu-SSZ-13 (21.8%). On the other hand, as proposed by Usui and coworkers [5], the introduction of Ce in Cu-SSZ-13 should be located in the CHA cage because of the relatively large ionic radius of Ce (1.1 Å). Therefore, it was reasonable to assume that a portion of Ce cations was introduced into CHA cages and replaced the unstable Cu$^{2+}$ ions upon the ion exchange of SSZ-13 in cerium nitrate solutions. On the contrary, we noticed that Ce-modified samples contained higher fractions of more stable Cu$^{2+}$ in D6R, the reduction peak of that, however, was shifted to a lower temperature in (CeCu)12 (347 °C) and (CeCu)1Cu2 (327 °C) compared to ~360 °C for Cu-SSZ-13. Consequently, the ion-exchange sequence of Cu and Ce species influenced the reduction of the catalysts, and the improvement of redox properties over Ce-modified Cu-SSZ-13 samples would be beneficial for the low temperature catalytic reactivity [22]. This was in agreement with the results of the NH$_3$-SCR performance.

Figure 4. Solid state $^{27}$Al (a) and $^{29}$Si (b) MAS NMR spectra of Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts.
Table 2. Quantitative analysis of the TPR and TPD profiles of Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts.

| Samples         | H₂ Total Consumption (cm³/g) | Acidity (cm³/g) | Peak Concentration from H₂-TPR (%) | X /Cu-SSZ-13 from NH₃-TPD (%) |
|-----------------|------------------------------|-----------------|-----------------------------------|------------------------------|
|                 |                              |                 | Peak 1 | Peak 2 | Peak 2 | Peak 3 |
| Cu-SSZ-13       | 44.9                         | 32.7            | 21.8   | 49.7   | -      | -      |
| Cu1(CeCu)2      | 51.0                         | 35.5            | 18.2   | 57.3   | 5.9    | 3.1    |
| (CeCu)12        | 62.8                         | 39.1            | 23.7   | 53.9   | 15.2   | 2.6    |
| (CeCu)1Cu2      | 76.1                         | 47.8            | 10.5   | 59.3   | 12.4   | 1.8    |

a Peak 1 was the green peak, and peak 2 was the blue peak in Figure 5. b X represented Cu1(CeCu)2, (CeCu)12 or (CeCu)1Cu2; Peak 2 and peak 3 were the blue and magenta peak in Figure 6, respectively.

Figure 5. H₂-TPR profiles of Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts.

Figure 6. NH₃-TPD profiles of Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts.

2.5. NH₃-TPD Measurements

Through NH₃-TPD measurements, it was possible not only to determine the acidity of the catalyst but also to titrate different acid sites present in zeolite catalysts. The TPD plots of the Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts were presented in Figure 6. The Cu-SSZ-13 was characterized by three NH₃ peaks, and where the peak centered at about...
246 °C probably corresponded to NH₃ weakly adsorbed on extra-framework Al Lewis sites or loosely bound ammonia not removed during the purge step, and the NH₃ adsorption peak at around 367 °C represented acid sites in D6R, while the high-temperature (528 °C) peak could be related majorly to NH₃ desorbed from acid sites in CHA cages [7,21,23]. When the catalysts were promoted with Ce ions, the effect of co-cations on the acidity of Cu-SSZ-13 was noteworthy, as an increase in the NH₃ desorption amounts of all the Ce-modified samples was appreciable over the whole desorption temperature range. These results suggested that some new sites were created by Ce species. However, the effect of Ce on the overall NH₃ storage capacity was quite different for the Cu-SSZ-13 with varied ion-exchange sequence of Cu and Ce species. For instance, Cu1(CeCu)2/Cu-SSZ-13 equaled 5.9 for the intermediate peak and 3.1 for the high temperature peak, while the ratios were 15.2, 2.6 and 12.4, 1.8 for (CeCu)12/Cu-SSZ-13 and (CeCu)1Cu2/Cu-SSZ-13 respectively, which was clearly seen in Table 2. Obviously, there was a much larger growth trend of acid sites in CHA cage over Cu1(CeCu)2 catalyst, while the (CeCu)12 and (CeCu)1Cu2 samples maintained higher NH₃ storage capacity in D6R. These different contributions to the NH₃ storage could explain why Ce-modified Cu-SSZ-13 catalysts had different SCR performance when ion-exchange sequence of Cu and Ce species varied. Notice that (CeCu)12 also showed a weak desorption peak at around 463 °C, which might be attributed to the medium-strength acid sites. According to the early report by Wang et al. [7], the ion exchange of Ce could replace a small fraction of unstable [Cu(OH)]⁺ ions in CHA cages. Meanwhile, as reported by Gao et al. [24], the [Cu(OH)]⁺ could convert to “naked” Cu²⁺ ions and move to the sites in windows of 6MR during the dehydration procedure. Taken together with TPR results above, it was reasonable to assume that the extra desorption peak of (CeCu)12 mainly resulted from the movement of [Cu(OH)]⁺ ions. As already shown in literature by Paolucci et al. [25], [Cu(OH)]⁺ and Cu²⁺ differed in their NH₃ coordination behavior: [Cu(OH)]⁺ could be able to coordinate and store 3 NH₃, while Cu²⁺ could store up to 4 NH₃. It was understandable that the sample containing replacement of Ce and movement of Cu in the preparation process could likely form more acidic sites and thus improve the storage capacity of ammonia.

3. Materials and Methods

3.1. Catalyst Preparation

The parent H-SSZ-13 with the mole ratio of SiO₂/Al₂O₃ = 22 was directly provided by Zeolite Company. The initial H-SSZ-13 powder was ion exchanged twice in 0.05 M Cu(CH₃COO)₂ solution at ambient temperature for 6 h, and the ratio of solid to solution was 1:40. After that, the powder was filtered, washed, and calcined at 550 °C for 6 h. Finally, Cu-SSZ-13 catalyst was obtained.

At the same time, the Ce-modified Cu-SSZ-13 catalysts were prepared using the same ion-exchange procedure, and the influence of Ce in the catalyst was controlled by the different exchange sequences with Cu. For the Cu1(CeCu)2 sample, the initial H-SSZ-13 powder was firstly ion exchanged in 0.05 M Cu(CH₃COO)₂ solution at ambient temperature for 6 h. After filtered, washed, and calcined, the power was added into 0.05 M Cu(CH₃COO)₂ and 0.00625 M Ce(NO₃)₃·6H₂O solution with vigorous stirring for 6 h. Then the powder was filtered, washed, and calcined at 550 °C for 6 h. The (CeCu)12 was produced using ion exchange (twice) of H-SSZ-13 with an aqueous solution of 0.05 M Cu(CH₃COO)₂ and 0.00625 M Ce(NO₃)₃·6H₂O solution at 25 °C for 6 h. Then, the zeolite slurries were filtered, washed with deionized water and calcined at 550 °C for 6 h. For the (CeCu)1Cu2 sample, H-SSZ-13 was exchanged with 0.05 M Cu(CH₃COO)₂ and Ce(NO₃)₃·6H₂O solution firstly and then 0.05 M Cu(CH₃COO)₂ solution at 25 °C for 6 h. After that, the powder was filtered, washed, and calcined at 550 °C for 6 h.

3.2. Catalyst Characterization

XRD was conducted on a Bruker D8 advance (Bruker, Karlsruhe, Baden-Wurttemberg, Germany); the diffraction angle ranged from 5 to 90 ° using Cu Kα radiation at 40 mA
and 40 kV. N₂ adsorption and desorption was conducted on a Micromeritics ASAP 2020 physical adsorption instrument (Micromeritics, Norcross, GA, USA). ²⁹Si and ²⁷Al NMR spectra were carried out on Agilent 600M (Agilent, Palo Alto, CA, USA) utilizing a 4 mm MAS probe. H₂-TPR and NH₃-TPD were performed on an AutoChemII2920 chemisorption analyzer (Micromeritics, Norcross, GA, USA), and the catalyst sample was pretreated under N₂ at 300 °C for 1 h and then cooled down to 50 °C. After that, the catalyst was heated to the required temperature at 10 °C/min in a 5% H₂/Ar or 6000 ppm NH₃/Ar at a flow rate of 50 mL/min.

3.3. Activity Evaluation
De-NOₓ tests of catalysts were conducted on a fixed-bed quartz reactor. The gas composition was composed of 200 ppm NH₃, 200 ppm NO, 5% H₂O, 10% O₂, 50 ppm C₃H₆, 4.5% CO₂, 200 ppm CO, and balance N₂. The total gas flow rate was 300 mL·min⁻¹ and the gas hourly space velocity was 250,000 h⁻¹. The concentration of NOₓ was monitored by an online flue gas analyzer. The NOₓ conversion was calculated as 
\[
\text{NO}_x\text{ conversion} = \frac{[\text{NO}_x]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}}}{[\text{NO}_x]_{\text{inlet}}} \times 100%,
\]
where NOₓ = NO + NO₂ [8].

4. Conclusions
Comparing the Cu-SSZ-13 and Ce-modified Cu-SSZ-13 catalysts synthesized via aqueous ion-exchange, and effects of Ce and Cu ion-exchange sequences on NOₓ conversion in NH₃-SCR reaction and the related physical and chemical properties were explored and analyzed in detail. The XRD as well as ²⁷Al and ²⁹Si NMR results indicated that the ion-exchange sequence of Cu and Ce species influenced the crystallinity of the zeolites and the coordination of Al. H₂-TPR demonstrated that the location and coordination environment of copper ions might change after introduction of a small amount Ce, and Ce ions also participated in the reduction process. Moreover, the improvement of redox properties over Ce-modified Cu-SSZ-13 samples would be beneficial for the low temperature catalytic reactivity. NH₃-TPD analysis confirmed that Ce-modified Cu-SSZ-13 catalysts with varied ion-exchange sequence of Cu and Ce species had different NH₃ storage performance, and the sample containing replacement of Ce and movement of Cu in the preparation process could likely form more acidic sites and thus improve the storage capacity of ammonia. The Cu₁(CeCu)₂ catalyst exchanged Cu firstly and then Ce and Cu at the same time, demonstrating excellent catalytic activity, and over 90% NOₓ conversion of fresh catalyst was obtained across the temperature range of 200–500 °C. Therefore, the cooperation of strong redox abilities and NH₃ storage capacity led to the increase of active adsorbed species adsorption and resulted in the better activity of Cu₁(CeCu)₂.

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