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Effect of Zr Modification on NH₃-SCR Reaction Performance of Cu-Ce/SAPO-34 Catalysts

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Abstract: Molecular sieve catalysts containing transition metals have been attracting attention for their potential applications in various fields, including environmental and industrial catalysis. A Cu-Ce-Zr/SAPO-34 series of molecular sieve catalysts were prepared by the impregnation method, and the effect of Zr introduction on the selective catalytic reduction of NO by Cu-Ce/SAPO-34 molecular sieve catalysts was explored. Through various characterization methods, the physical and chemical properties of the catalysts were analyzed, and the denitration mechanism of the molecular sieve catalyst was discussed. This study found that the total acid content of the acid sites on the catalyst surface decreased with the introduction of Zr, leading to a decrease in the denitration efficiency of the catalyst. At 350–400 °C, the denitration efficiency of the 4Cu-4Ce-4Zr/SAPO-34 catalyst was over 80%, and at 400–500 °C, it was over 99%. Moreover, excessive metal Zr could destroy its CHA structure and decrease the denitration efficiency of the catalyst. This study analyzed the reaction mechanism of NH₃-SCR of Zr-modified polymetallic zeolites and the effect of Zr modification on the NH₃-SCR reaction results. This study contributes to the understanding of the performance of molecular sieve catalysts containing transition metals. Reliable conclusions were obtained, which offer data support for future research in the field of NH₃-SCR.

Keywords: Cu-Ce-Zr/SAPO-34; molecular sieve catalyst; selective catalytic reduction; modification



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1. Introduction

Nitrogen oxides (NO_x) are currently the main atmospheric pollutants in the world. They not only endanger the natural environment but also affect human social production and living activities, and they even endanger human health. Selective catalytic reduction (SCR) technology is currently a mature denitration technology, which is widely used in thermal power plants, waste incineration furnaces, boiler facilities, diesel engines, gas turbines, and other scenarios. The core of SCR technology is the catalyst, which is the main factor of catalyst performance. The main factors affecting catalyst performance include the catalyst carrier, auxiliary pharmacy, active components, precursors, and the preparation method [1–4].

In terms of the selection of active components, researchers have conducted deep explorations of metal oxides such as Cu, Fe, and Mn and have found that they all show advantages under various working conditions. Researchers [5] found that, under the same support and preparation method, the denitration efficiency of catalysts followed the following order: Cu-Fe-based > Cu-based > Fe-based, that is, bimetallic oxide catalysts are superior to single-metal-oxide ones, and Cu-based catalysts are superior to Fe-based catalysts. According to Yan's research [6], under the same conditions, the denitration

efficiency of catalysts followed the following order: Cu–Mn > Cu > Mn; when the reaction conditions were higher than 200 °C, the order was: Cu > Cu–Mn > Mn, indicating that Cu catalysts are superior to Mn catalysts, and bimetallic oxide catalysts are superior to single-metal-oxide catalysts at a temperature lower than 200 °C. In conclusion, it was proposed to select Cu as the active component of the catalyst. In terms of the carrier, most mainstream researchers choose zeolite molecular sieves, active carbon, TiO₂, etc., as the carrier of catalysts. Zeolite molecular sieves are widely used in various fields because of their porosity, selective adsorption of molecules through channels, large specific surface area, and the fact that they are excellent catalyst carriers. As reported in the literature in [7], the denitrification performance of Cu Mn/SAPO-34 is generally better than that of Cu Mn/ZSM-5; Kouadio Brou Albert pointed out that [8] Cu/SAPO-34 catalysts have a wide active temperature window, excellent hydrothermal stability, and resistance to alkali metal and alkaline earth metal poisoning. According to the actual conditions of the laboratory, an SAPO-34 molecular sieve was proposed to be used as the catalyst carrier.

To obtain a superior denitration performance and a wider range of applications, SCR denitration catalysts are mostly bimetallic or even polymetallic in order to obtain the physical and chemical properties of various metals. Many scholars [9,10] have found that doping with metal Ce has a positive effect on the denitration ability of Cu-based molecular sieve catalysts. Ce can improve the thermal stability of the catalyst, improve the distribution of active substances on the catalyst surface, and enhance the redox performance of the catalyst. Therefore, Ce was proposed to be used as a metal in a multi-metal-oxide catalyst. According to Zhang's research [11], Zr can increase the oxygen vacancy concentration of Cu–Ce metal oxide catalysts, enhance their oxidation–reduction capacity, and improve the catalysts' adsorption capacity for NO_x. However, it will slightly reduce their denitration performance. Some scholars [12] found that doping with Zr can inhibit the aggregation of Cu on the catalyst surface, promote the dispersion of Cu, increase the concentration of Cu species on the catalyst surface, and improve the resistance to Ca poisoning. However, there is still no consensus on the reasons as to why Zr doping leads to a decline in the catalyst denitration performance, nor is there a consensus on the reasons behind the advantages and disadvantages of Zr participating in denitration reactions and their mechanisms. Therefore, Zr was selected as the last metal of the polymetallic oxide catalyst.

In previous research, it was found that a 4Cu-4Ce/SAPO-34 (the mass fraction of Cu and Ce being 4%) bimetallic oxide catalyst had the best performance in all aspects. On this basis, Zr was added to the catalyst and the influence of different Zr loading amounts on the denitration performance of the catalyst was explored to obtain the best Zr loading. The physical and chemical properties of the catalyst were studied through XRD, SEM, NH₃-TPD, in situ DRIFTS, XPS, and other characterization techniques. The possible NH₃-SCR reaction path of Cu-Ce-Zr/SAPO-34 was proposed.

2. Materials and Methods

2.1. Preparation of Catalysts

The 4Cu-4Ce-xZr/SAPO-34 catalyst (x being the mass fraction of metal Zr in the catalyst) with different Zr loading amounts was prepared by the immersion method. Copper nitrate, cerium nitrate, and zirconium nitrate were mixed together in correct proportions. Then, the SAPO-34 molecular sieve was placed in a muffle furnace at 400 °C for 2 h to remove impurities and water. The mass fraction of fixed Cu and Ce was 4%, while the mass fraction of Zr was changed between 0%, 2%, 4%, 6%, and 8%, respectively. Five portions of impregnating solution were prepared with the corresponding proportion. The SAPO-34 carrier was fully dissolved in the impregnating solution according to the corresponding mass. It was heated and stirred with a magnetic stirrer for 5 h to form a paste. An ultrasonic oscillator was used to vibrate the mixture for 40 min so that the active substance could fully adhere to the carrier surface. Then, it was dried at a constant temperature of 110 °C in a constant-temperature blast-drying oven overnight. The five obtained samples were fully ground to a powder and then put into a muffle furnace for

roasting at 450 °C for 2 h. After being ground again, they were bagged for standby and were recorded as 4Cu-4Ce-xZr/SAPO-34 (where x was the mass fraction of metal Zr in the catalyst).

2.2. Experimental Conditions and Equipment

2.2.1. Catalytic Activity Test

The denitration performance of the catalyst samples was tested using a VDRT-200SCR catalyst evaluation device (Quzhou Ward Instrument Co., Ltd., Quzhou, China). The test required 200 mg of the catalyst. The simulated flue gas consisted of 0.1% NH₃, 0.1% NO, and 1% O₂. N₂ was used as a balance gas. The evaluation device was equipped with a mass flow meter, which could accurately control the gas flow. The simulated flue gas flow was 200 mL/min, the space velocity was 22,000 h⁻¹, and the temperature range was 100–500 °C. The temperature was increased by 50 °C within 5 min, kept constant for 30 min, then increased by 50 °C within 5 min, and this cycle was repeated. The volume concentration of NO_x after the reaction was recorded. The NO_x concentration in the reaction tail gas was detected using a German Testo 350 Pro flue gas analyzer. The following formula was used to calculate the denitration efficiency η :

$$\eta = (\text{NO}_{x,in} - \text{NO}_{x,out}) / \text{NO}_{x,in} \times 100\%$$

where NO_{x,in} represents the volume concentration of NO_x before the reaction and NO_{x,out} is the volume concentration of NO_x after the reaction.

2.2.2. Characterization of the Catalyst

The crystal phase composition of the catalyst was characterized by an X-ray diffractometer (DX-2700B, Dandong Haoyuan Instrument Co., Ltd., Dandong, China). The scanning angle was 6–70°, and the scanning rate was 2°/min. Field emission scanning electron microscopy (JSM-7800F, Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan) was used to test the surface micromorphology and element distribution of the catalyst samples. A TP-5076TPD/TPR dynamic adsorption instrument from Tianjin Xianquan was used to conduct the temperature-programmed adsorption (NH₃-TPD) experiment on the catalyst to test the acidity of the catalyst. Fourier transform infrared absorption spectroscopy (IRT racer-100, Shimadzu Corporation, Kyoto, Japan) was used to determine the surface functional groups of the catalyst samples and the types of acidic sites of the catalyst samples.

3. Results and Discussion

3.1. NH₃-SCR Catalytic Activity

Figure 1 shows the test results of the catalyst denitration performance. In the temperature range of 150–500 °C, the NO_x conversion increased with increasing the temperature. In the temperature range of 200–350 °C, the increase in the denitration performance of the catalyst was the most obvious. 4Cu-4Ce/SAPO-34 showed the most excellent denitration performance in the temperature range of 200–500 °C, which was consistent with the conclusion that metal Zr reduced the overall denitration performance of the catalyst to a certain extent [11]. At temperatures below 200 °C, the denitration performance of the 4Cu-4Ce-4Zr/SAPO-34 catalyst was better than that of 4Cu-4Ce/SAPO-34, and we inferred that an appropriate Zr doping could improve the low-temperature activity of the denitration catalyst. Among all the trimetallic catalysts, the 4Cu-4Ce-4Zr/SAPO-34 catalyst had the best denitration performance. In the range of 350–500 °C, the denitration efficiency was above 80%. In the range of 400–500 °C, the denitration efficiency was more than 99%. The reason why the Zr reduced the denitration efficiency of the catalyst and the reason for the better denitration performance of the 4Cu-4Ce-4Zr/SAPO-34 catalyst need to be further explored.

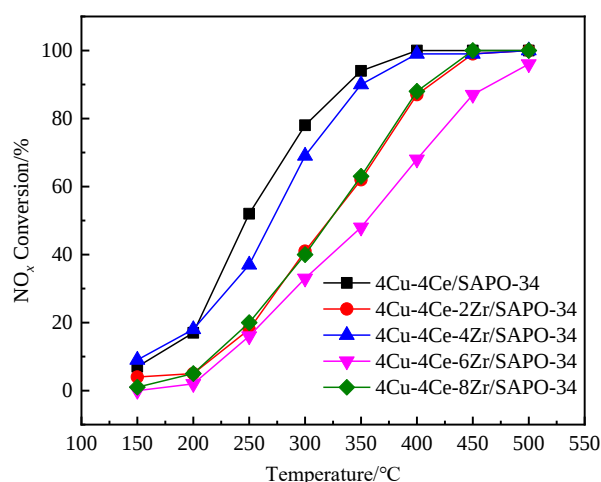


Figure 1. NO_x conversion of catalysts with different Zr loadings.

3.2. XRD

Figure 2 shows the XRD spectrum of the prepared catalyst and SAPO-34. In the figure, it can be seen that 9.47°, 12.84°, 16.04°, 17.72°, 20.52°, 25.03°, 25.88°, and 30.58° were the characteristic peaks of the SAPO-34 molecular sieve support [13], which was a typical CHA structure with a high crystallinity. The corresponding characteristic peaks of the metal oxides were also detected in the experiment. The characteristic peaks detected at 35.3° and 38.5° were associated with CuO [14], 28.2° and 33.1° were associated with CeO₂ [15], and 33.8°, 50.7°, and 60.1° were associated with ZrO₂ [16]. Five catalysts showed the same characteristic peaks of SAPO-34, while their peaks were slightly different. Comparing the characteristic peaks of 4Cu-4Ce/SAPO-34, SAPO-34, and 4Cu-4Ce-4Zr/SAPO-34, it was found that the loading of Cu and Ce reduced the characteristic peaks of SAPO-34. After the Zr modification, the characteristic peaks of SAPO-34 were enhanced, which proved that a small amount of Zr could promote the crystallization growth of the SAPO-34 zeolite molecular sieve to a certain extent. It also enhanced the CHA skeleton structure of SAPO-34 [14]. However, the characteristic peaks of SAPO-34 of 4Cu-4Ce-6Zr/SAPO-34 and 4Cu-4Ce-8Zr/SAPO-34 almost disappeared. It was speculated that a large number of Zr oxides appeared in the channel and outer surface of the crystal, resulting in a decrease in its crystallinity, the disappearance of the characteristic peaks, and the destruction of the crystal structure [17,18]. The characteristic peaks of Cu, Ce, and Zr were not detected in the five catalysts, indicating that the above metal species were dispersed on the surface of the catalyst in an amorphous form, which was conducive to the NH₃-SCR reaction [19].

3.3. NH₃-TPD

Figure 3 shows the NH₃-TPD spectrum of the prepared catalyst. The figure shows the temperature of the acid center of ammonia desorption. Three desorption peaks were found at about 77 °C, 161.1 °C, and 371.1 °C, representing the different types of acid sites on the catalyst surface. In general, the intensity of the acid sites was proportional to the temperature of the desorption peak, and the number of acid sites was proportional to the area of the desorption peak. The desorption peaks at about 77 °C and 161.1 °C were attributed to weak acidic sites bound to NH₃, while the desorption peaks at 371.1 °C were attributed to strong acidic sites bound to NH₃ [20]. Compared with the desorption peaks of 4Cu-4Ce/SAPO-34, 4Cu-4Ce-4Zr/SAPO-34, and 4Cu-4Ce-8Zr/SAPO-34, the number of weak acid sites at 77 °C decreased, and the intensity increased with the increase in the Zr mass fraction. In addition, the number of acidic sites of 4Cu-4Ce/SAPO-34 was the largest. The number and intensity of weak acid sites at 161.1 °C increased first and then decreased, and the number and intensity of acidic sites of 4Cu-4Ce-4Zr/SAPO-34 were the largest. The catalysts with the strongest acidic sites at about 371.1 °C were 4Cu-4Ce/SAPO-34 and 4Cu-4Ce-6Zr/SAPO-34. In conclusion, the total number of acidic sites of 4Cu-4Ce/SAPO-

34 was the largest, and thus the denitration efficiency was the highest. This shows that the Zr loading reduced the total number of acidic sites of 4Cu-4Ce/SAPO-34, thus reducing the denitration efficiency. The denitration efficiency of 4Cu-4Ce-4Zr/SAPO-34 was only lower than that of 4Cu-4Ce/SAPO-34, which could be attributed to the fact that the number and intensity of weak acid sites at 161.1 °C increased due to the introduction of the appropriate amount of Zr. Similarly, the poor denitration efficiency of 4Cu-4Ce-6Zr/SAPO-34 could be attributed to the excessive metal Zr, which led to a reduction in the number of acidic sites. The type of specific acid sites at each temperature needs to be further concluded through in situ DRIFTS tests.

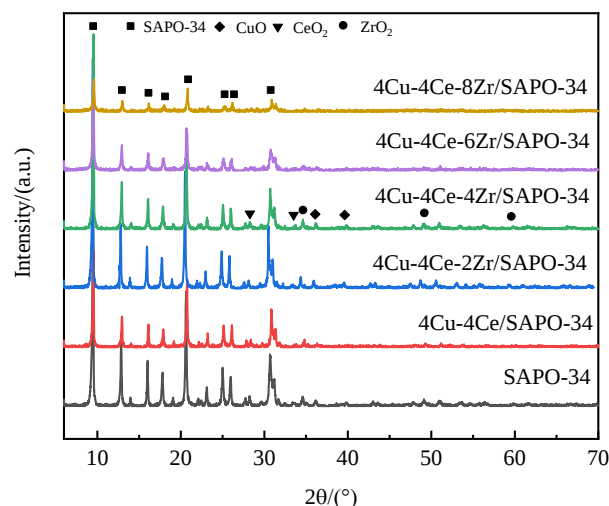


Figure 2. XRD spectra of catalysts with different Zr loadings.

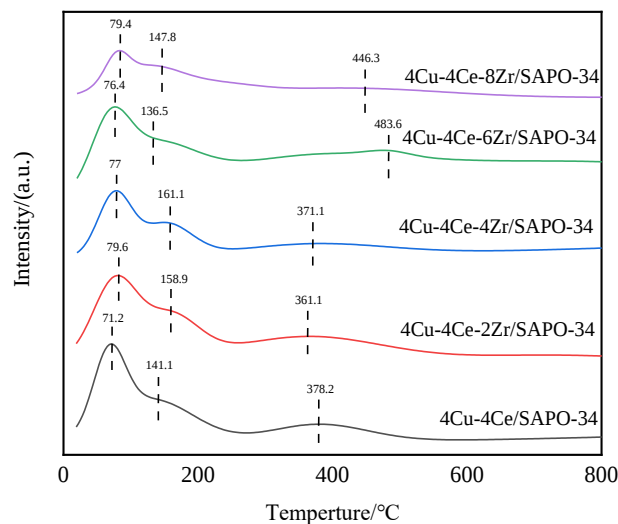


Figure 3. NH₃-TPD spectra of catalysts with different Zr loadings.

3.4. SEM

Figure 4 shows SEM photos of some of the prepared catalysts. SEM characterization is mainly used to explore the crystal state, microstructure, and adhesion state of active components on catalyst surfaces. As shown in Figure 4, all the catalysts presented a cube state related to the CHA structure of SAPO-34. The grain size was about 4 μm. The surface of the 4Cu-4Ce/SAPO-34(a) catalyst was covered with randomly shaped materials, and it was speculated that Cu and Ce oxides were attached to the crystal surface after interaction [21]. The XRD results showed that the characteristic peaks of the 4Cu-4Ce-2Zr/SAPO-34(b) and 4Cu-4Ce-4Zr/SAPO-34(c) samples were high, that is, both the crystallinity and strength were high. Compared with the SEM photos, it was found that the

4Cu-4Ce-2Zr/SAPO-34(b) and 4Cu-4Ce-4Zr/SAPO-34(c) cubes had complete structures and flat surfaces, and each particle was in an independent state, which confirmed the conclusion of the XRD analysis. For the 4Cu-4Ce-6Zr/SAPO-34(d) catalyst, it was found that most of cubic structures were damaged, the surface was rough, and most of the particles were bonded together after being damaged, which was consistent with the conclusion that the XRD results showed that the characteristic peaks disappeared, the crystallization decreased, and the grain structure was damaged.

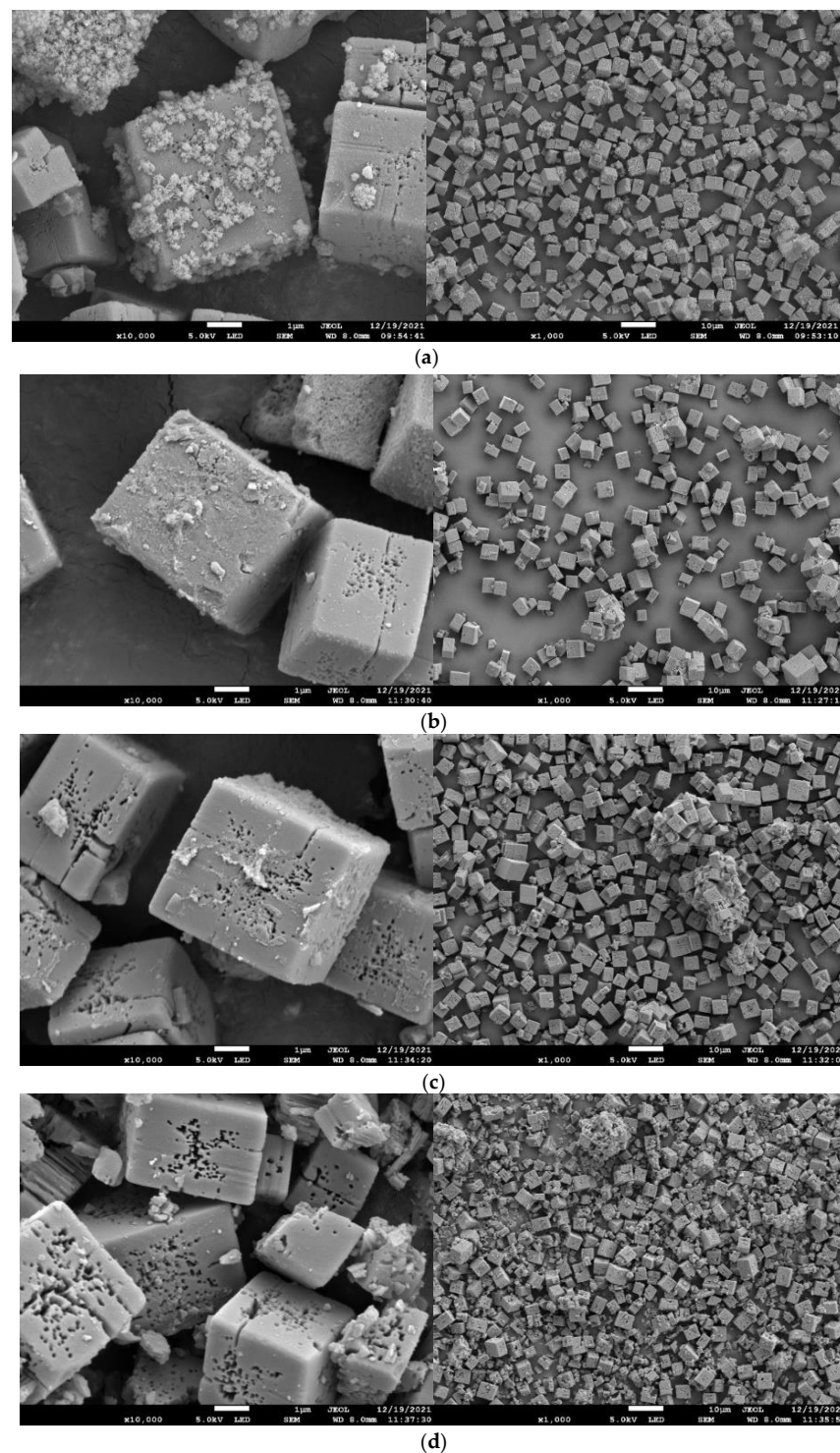


Figure 4. SEM images of 4Cu-4Ce/SAPO-34 (a), 4Cu-4Ce-2Zr/SAPO-34 (b), 4Cu-4Ce-4Zr/SAPO-34 (c), and 4Cu-4Ce-6Zr/SAPO-34 (d) (the magnifications is 10,000 and 1000 times).

3.5. In Situ DRIFTS Measurements

To ascertain the types of acidic sites on the surface of the 4Cu-4Ce-4Zr/SAPO-34 catalyst and the paths of the NH_3 -SCR denitration reaction, samples of the 4Cu-4Ce-4Zr/SAPO-34 catalyst were measured and analyzed by in situ DRIFTS measurements.

3.5.1. NH_3 Adsorption Experiment

Figure 5 shows the in situ DRIFTS spectra of NH_3 adsorbed onto the 4Cu-4Ce-4Zr/SAPO-34 catalyst. The test temperature was 100°C , and the characteristic curves of the samples at 3, 6, 10, 20, 30, and 40 min were recorded. In Figure 5, it can be seen that the characteristic peaks appeared at 1097, 1128, 1400, 1458, 1508, 1651, 2360, 3034, and 3117 cm^{-1} . The adsorption peak at 3117 cm^{-1} in the N-H stretching vibration area was attributed to the symmetric vibrations of NH_3 in the Lewis acid coordination state [22], the peak at 3034 cm^{-1} was attributed to the Brønsted acid site with the deformation vibrations of NH_4^+ in an ionic state adsorbed on the peak [23], the peak at 2360 cm^{-1} was attributed to the N-N stretching vibrations of surface N_2 molecules [24], and the peak at 1651 cm^{-1} was attributed to the symmetric bending vibrations of N-H bonds in covalently adsorbed NH_3 in the Lewis acid sites. The peaks at 1458 and 1400 cm^{-1} were classified as the deformed vibrations of NH_4^+ in the ionic state on the Brønsted acid site [25,26], and the peaks at 1508, 1128, and 1097 cm^{-1} were regarded as the symmetric vibrations of NH_3 coordinated by the Lewis acid site [27]. According to the conclusions of the NH_3 -TPD analysis, the majority of the weak acid sites were considered to be weak Lewis acid sites, and the quantity of strong acid sites was less than that of Brønsted acid sites. In general, there were both Lewis acid sites and Brønsted acid sites on the surface of the 4Cu-4Ce-4Zr/SAPO-34 catalyst. Lewis acid sites were dominant due to their large amount, which played an important role in the NH_3 -SCR activity of 4Cu-4Ce-4Zr/SAPO-34.

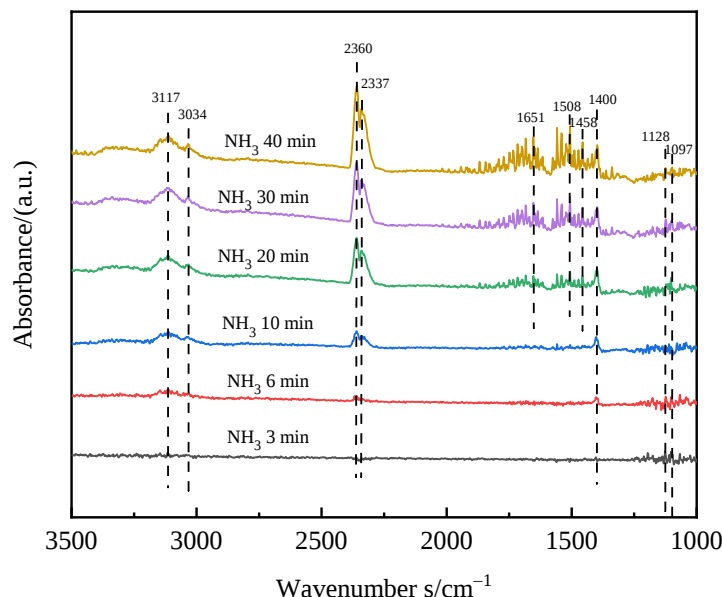


Figure 5. In situ DRIFTS of NH_3 adsorbed on the 4Cu-4Ce-4Zr/SAPO-34 catalyst.

3.5.2. Transient Reaction of $\text{NO}+\text{O}_2$ after NH_3 Adsorption Saturation

After NH_3 was saturated for 40 min, $\text{NO}+\text{O}_2$ was introduced for transient reaction, and the samples were scanned at 3, 6, 10, 20, and 30 min to analyze the change in the curve. As shown in Figure 6, with the introduction of $\text{NO}+\text{O}_2$, the characteristic peaks of Lewis acid at 3117 and 3034 cm^{-1} disappeared, and the N-N extension vibration at 2360 cm^{-1} was enhanced, which may be due to the reaction between adsorbed NH_3 and gaseous $\text{NO}+\text{O}_2$, resulting in the formation of N_2 , which enhanced the characteristic peak at 2360 cm^{-1} attributed to N_2 . the rest of the characteristic peaks did not change significantly, but new

characteristic peaks were formed at 1383 cm^{-1} and 1265 cm^{-1} , among which the adsorption species at 1265 cm^{-1} belonged to the bridged nitrate species [26,28], and the adsorption peak at 1383 cm^{-1} was the strongest and belonged to the $\text{CIS-N}_2\text{O}_2^{2-}$ species [29,30], indicating that new nitrate species were generated on the catalyst surface. In general, the characteristic peaks of Lewis acid disappear, which proved that the adsorbed NH_3 reacted with gaseous $\text{NO}+\text{O}_2$. This process followed the E-R mechanism, while the characteristic peaks of Brønsted acid did not change significantly. Therefore, the weak Lewis acid site played a leading role in the reaction process.

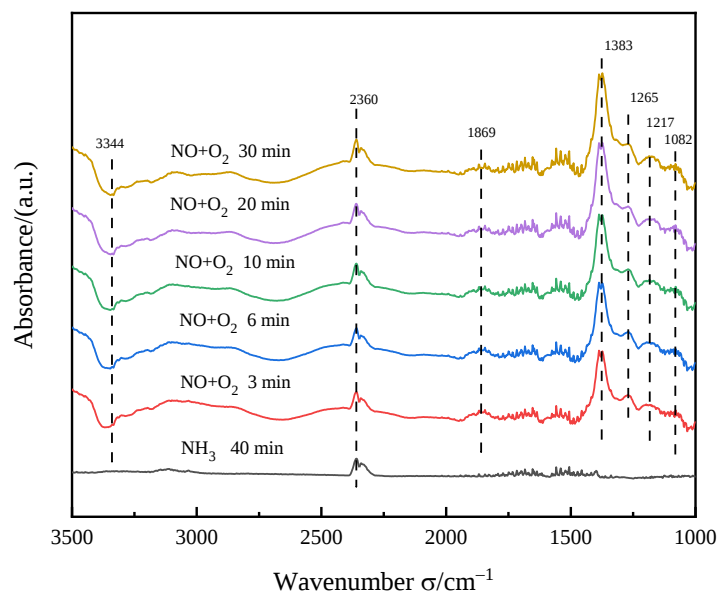


Figure 6. In situ DRIFTS of $\text{NO}+\text{O}_2$ reacting with pre-adsorbed NH_3 over the 4Cu-4Ce-4Zr/SAPO-34 catalyst.

3.5.3. $\text{NO}+\text{O}_2$ Adsorption Experiment

Figure 7 shows the in situ DRIFTS spectra of $\text{NO}+\text{O}_2$ adsorption on the 4Cu-4Ce-4Zr/SAPO-34 catalyst. The experimental temperature was kept at $150\text{ }^\circ\text{C}$, the characteristic curves of the samples were recorded at 3, 6, 10, 20, 30, and 40 min, and characteristic peaks appeared at 1244 , 1384 , 2268 , 2397 , and 3109 cm^{-1} . The characteristic peak at 1384 cm^{-1} was the strongest, which was classified as belonging to a $\text{CIS-N}_2\text{O}_2^{2-}$ species, the peak at 1244 cm^{-1} was considered to be due to a bridging nitrate species [31,32], and the characteristic peaks at 2268 and 2397 cm^{-1} were mainly composed of NOH^+ and HNO_2^+ and were formed by NO adsorption on the catalyst surface [33]. The peak at 3109 cm^{-1} was the hydroxyl vibration peak formed by the oxygen in the mixed gas and the H bond in the molecular sieve framework. The in situ DRIFTS spectrum of $\text{NO}+\text{O}_2$ adsorption on the 4Cu-4Ce-4Zr/SAPO-34 catalyst hardly changed with time, indicating that the adsorption of NO onto the 4Cu-4Ce-4Zr/SAPO-34 catalyst reached a saturated state at the beginning, and this may be related to metallic Zr.

Figure 8 shows the in situ DRIFTS spectra of 4Cu-4Ce/SAPO-34 and 4Cu-4Ce-4Zr/SAPO-34 after adsorbing $\text{NO}+\text{O}_2$ for 40 min up to saturation. Compared with 4Cu-4Ce/SAPO-34, 4Cu-4Ce-4Zr/SAPO-34 had more adsorption peaks and higher peaks, indicating that there were more nitrate species adsorbed onto the surface of 4Cu-4Ce-4Zr/SAPO-34, which proved that metal Zr could enhance the adsorption capacity of the catalyst for NO_x [11,34], which facilitated the reaction with NH_3 -SCR.

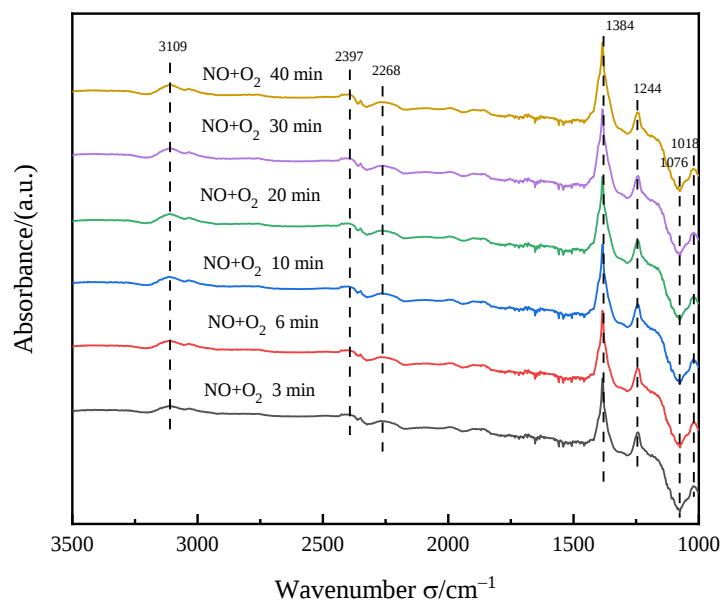


Figure 7. In situ DRIFTS of NO+O₂ adsorbed over the 4Cu-4Ce-4Zr/SAPO-34 catalyst.

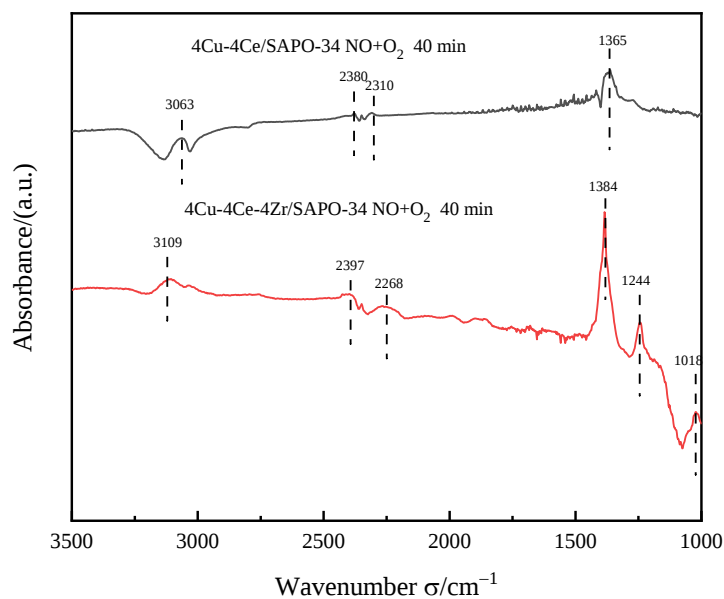


Figure 8. In situ DRIFTS of NO+O₂ adsorbed over the 4Cu-4Ce-4Zr/SAPO-34 and 4Cu-4Ce/SAPO-34 catalyst.

3.5.4. Transient Reaction of NH₃ after NO+O₂ Adsorption Saturation

NO+O₂ was adsorbed on the surface of the 4Cu-4Ce-4Zr/SAPO-34 catalyst for 40 min. After the adsorption was saturated, a transient reaction experiment of NH₃ was carried out. The sample was scanned at 3, 6, 10, 20, and 30 min to analyze its changes. Figure 9 shows the characteristic reaction curve of the above experiment. It can be seen that after NH₃ was introduced, the bridging nitrate characteristic peak at 1244 cm⁻¹ and the monodentate nitrate characteristic peak at 1384 cm⁻¹ did not change significantly. However, new characteristic peaks were formed at 1624 and 3334 cm⁻¹, and the characteristic peak at 1624 cm⁻¹ was attributed to weakly adsorbed NO₂ [35]. It was speculated that the introduction of NH₃ might enhance the conversion and adsorption of NO. The characteristic peak at 3334 cm⁻¹ was considered to be due to the NH₃ species adsorbed on the Lewis acid site [36,37]. During the reaction process, the main characteristic peaks of the nitrate species formed on the catalyst surface did not change significantly, and new NH₃ adsorption species were formed,

but both of them did not change significantly after they became stable, indicating that no obvious reaction occurred between the adsorbed NO and NH₃, that is, the process did not follow the L-H mechanism.

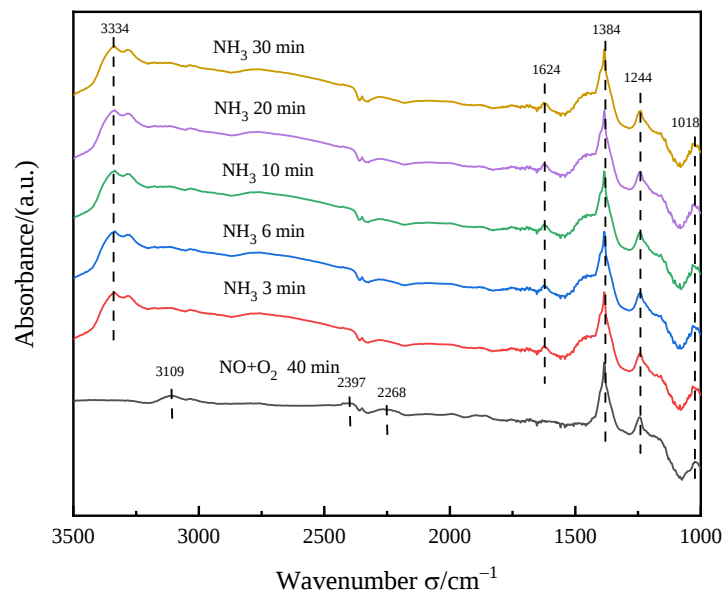


Figure 9. In situ DRIFTS of NH₃ reacting with pre-adsorbed NO+O₂ over the 4Cu-4Ce-4Zr/SAPO-34 catalyst.

3.6. XPS

Figures 10–12 show the XPS spectra of Cu 2p, Ce 3d, and Zr 3d of 4Cu-4Ce/SAPO-34 and 4Cu-4Ce-4Zr/SAPO-34 catalysts, respectively, in which the surface valence structure of the catalyst and the influence of Zr doping on the catalyst were analyzed.

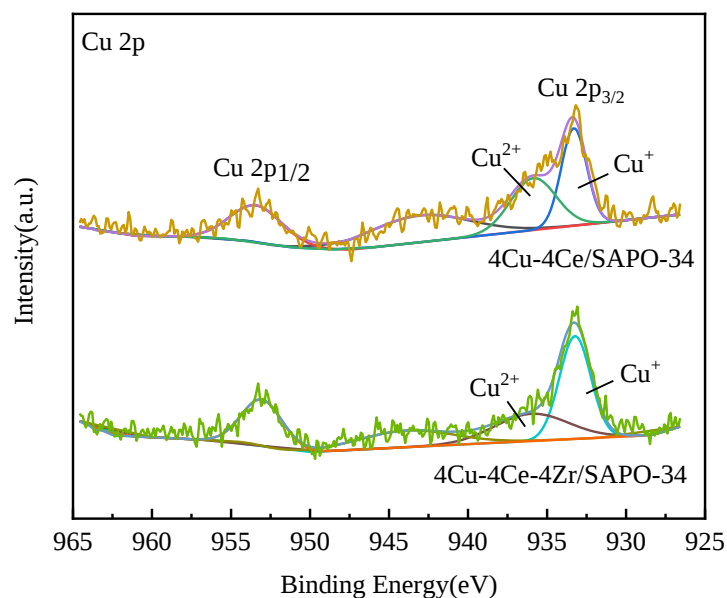


Figure 10. Cu 2p XPS spectra of 4Cu-4Ce/SAPO-34 and 4Cu-4Ce-4Zr/SAPO-34.

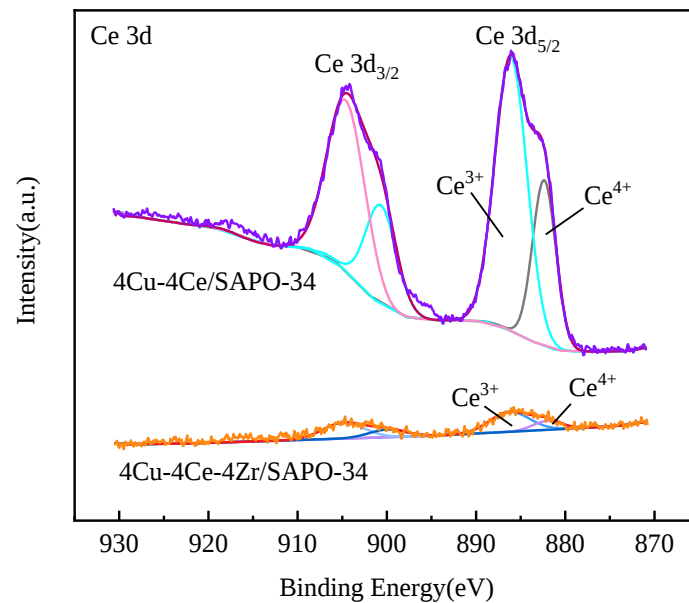


Figure 11. Ce 3d XPS spectra of 4Cu-4Ce-4Zr/SAPO-34 and 4Cu-4Ce/SAPO-34.

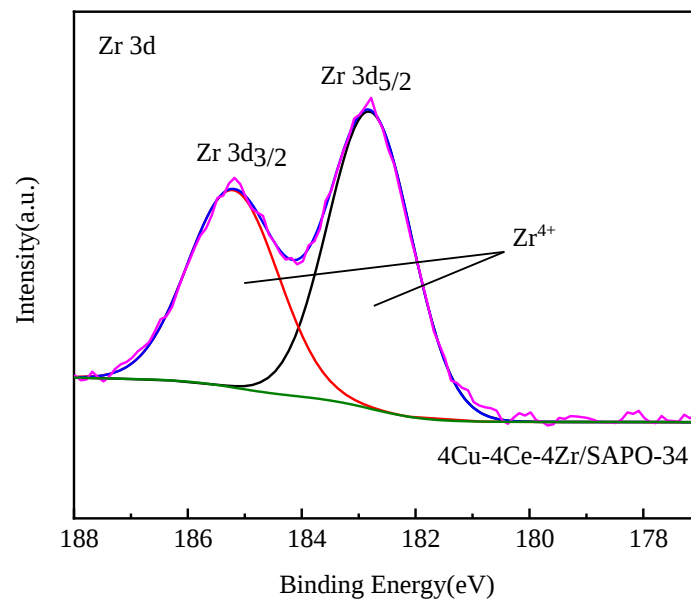


Figure 12. Zr 3d XPS spectrum of 4Cu-4Ce-4Zr/SAPO-34.

There were two characteristic peaks of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ orbits in the Cu 2p spectrum of 4Cu-4Ce/SAPO-34, as shown in Figure 10. According to the reference [38,39], Cu $2p_{3/2}$ can be resolved into two characteristic peaks. The characteristic peak with a binding energy of 933.3 eV was due to Cu⁺, and the characteristic peak with a binding energy of 935.7 eV was due to Cu²⁺. Similarly, the characteristic peak with a binding energy of 953.6 eV at Cu $2p_{1/2}$ was classified as Cu⁺, and the satellite peak with a binding energy of 943.1 eV was classified as Cu²⁺. After doping with Zr, the binding energies of the Cu⁺ characteristic peak were 933.2 eV and 953 eV, and the binding energies of the Cu²⁺ characteristic peak were 936 eV and 943.9 eV, which was similar with the characteristic peak of the binding energy of 4Cu-4Ce/SAPO-34 copper ions. As for the area of the characteristic peak, after doping with Zr, the area of the characteristic peak of Cu⁺ increased by about 15%. Cu⁺ can promote the catalytic performance of a catalyst in the low-temperature range [40,41], so the doping with Zr improved the low-temperature performance of the catalyst. The characteristic peak area of Cu²⁺ decreased by about 40%, and the total

characteristic peak area of $\text{Cu}^+ + \text{Cu}^{2+}$ decreased by about 8.3%. $\text{Cu}^+ + \text{Cu}^{2+}$ played a key role in the performance of the catalyst, which might be the reason for the decline in the catalyst performance after Zr doping.

In the Ce 3d spectrum of 4Cu-4Ce/SAPO-34, as shown in Figure 11, there were characteristic peaks of Ce 3d_{5/2} and Ce 3d_{3/2} orbits. According to reference [42,43], both Ce 3d_{5/2} and Ce 3d_{3/2} can be resolved into two characteristic peaks. The characteristic peaks with binding energies of 886.1 eV and 904.5 eV were classified as Ce^{3+} , which were caused by its photoelectron emission, while the characteristic peaks with binding energies of 882.4 eV and 900.6 eV were caused by photoelectron emission of Ce^{4+} . After doping with Zr, the binding energies of the characteristic peaks of Ce^{3+} were 886.2 eV and 904.9 eV, and those of the characteristic peaks of Ce^{4+} were 882.5 eV and 900.9 eV. The binding energies of the four characteristic peaks were slightly increased, which confirmed that Zr could increase the stability of the catalyst. The area of the characteristic peak of Ce^{3+} decreased by 90.6%, the area of the characteristic peak of Ce^{4+} decreased by about 92.3%, and the total area of the characteristic peak of $\text{Ce}^{3+} + \text{Ce}^{4+}$ decreased by about 91.1%. The transition from Ce^{4+} to Ce^{3+} enabled the Ce to have a strong redox performance and oxygen storage performance [43,44]. The addition of Zr caused a significant decrease in the total amount of $\text{Ce}^{3+} + \text{Ce}^{4+}$, which was one of the reasons for the decline in the performance of the catalyst after Zr doping.

The Zr 3d spectrum of 4Cu-4Ce-4Zr/SAPO-34 shown in Figure 12 contains the characteristic peaks of Zr 3d_{5/2} and Zr 3d_{3/2} orbits. According to the reference [45,46], the characteristic peak binding energy of the Zr 3d_{3/2} orbit was 185.18 eV, and that of the Zr 3d_{5/2} orbit was 182.78 eV. Both characteristic peaks belonged to Zr^{4+} . Therefore, it was concluded that Zr on the 4Cu-4Ce-4Zr/SAPO-34 surface only existed in the form of Zr^{4+} .

4. Conclusions

The overall denitration performance of 4Cu-4Ce-4Zr/SAPO-34 was only inferior to that of 4Cu-4Ce/SAPO-34. At 350~400 °C, the denitration efficiency was more than 80%, and at 400~500 °C, the denitration efficiency was more than 99%. Zr could improve the low-temperature performance of NH_3 -SCR below 200 °C but reduced its overall denitration performance. The main reason was that Zr could reduce the amount of Cu and Ce metal ions on the catalyst surface, thus decreasing the total acid content of the acidic sites on the catalyst surface.

An appropriate amount of Zr could increase the relative crystallinity of the molecular sieve. There was an interaction between Zr and the CHA structure of SAPO-34, which could enhance its skeleton structure. In addition, Cu, Ce, and Zr were well dispersed, but excessive Zr damage the CHA structure, leading to a decline in the catalyst's denitration performance.

There were Lewis acid sites and Brønsted acid sites on the surface of the 4Cu-4Ce-4Zr/SAPO-34 catalyst, which was dominated by Lewis acid sites. Zr could increase the amount of weak Lewis acid sites and enhance the catalyst's adsorption capacity for NO_x , which is of great significance for its NH_3 -SCR reaction performance. The reaction process only followed the E-R mechanism, not the L-H mechanism.

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