Effect of Bimetal Element Doping on the Low-Temperature Activity of Manganese-Based Catalysts for NH₃-SCR

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A series of novel Mn₆Zr₁₋ₓCox denitriﬁcation catalysts were prepared by the co-precipitation method. The effect of co-modiﬁcation of MnOₓ catalyst by zirconium and cobalt on the performance of NH₃-SCR was studied by doping transition metal cobalt into the Mn₆Zr₁ catalyst. The ternary oxide catalyst Mn₆Zr₀.₃Co₀.₇ can reach about 90% of NOₓ conversion in a reaction temperature range of 100–275°C, and the best NOₓ conversion can reach up to 99%. In addition, the sulfur resistance and water resistance of the Mn₆Zr₀.₃Co₀.₇ catalyst were also tested. When the concentration of SO₂ is 200ppm, the NOₓ conversion of catalyst Mn₆Zr₀.₃Co₀.₇ is still above 90%. 5 Vol% H₂O has little effect on catalyst NOₓ conversion. The results showed that the Mn₆Zr₀.₃Co₀.₇ catalyst has excellent resistance to sulfur and water. Meanwhile, the catalyst was systematically characterized. The results showed that the addition of zirconium and cobalt changes the surface morphology of the catalyst. The speciﬁc surface area, pore size, and volume of the catalyst were increased, and the reduction temperature of the catalyst was decreased. In conclusion, the doping of zirconium and cobalt successfully improves the NH₃-SCR activity of the catalyst.

Keywords: NH₃-SCR, sulfur resistance, nitrogen oxide, metal modiﬁcation, low temperature

HIGHLIGHTS

- The ternary oxide catalyst Mn₆Zr₀.₃Co₀.₇ catalyst was prepared by the co-precipitation method.
- The NOₓ conversion of the Mn₆Zr₀.₃Co₀.₇ catalyst is above 90% at 100–275°C.
- The Mn₆Zr₀.₃Co₀.₇ catalyst has excellent resistance to H₂O and SO₂.
- The Mn₆Zr₀.₃Co₀.₇ catalyst has a large speciﬁc surface area and pore diameter.
- The reaction mechanism of the Mn₆Zr₀.₃Co₀.₇ catalyst was investigated.

INTRODUCTION

With continuous exploitation and utilization of fossil fuels, serious pollution has been caused to the atmosphere, among which nitrogen oxide (NOₓ) is one of the most important pollutants. Therefore, the removal of NOₓ is particularly important. At present, the most effective method for NOₓ removal is selective catalytic reduction of NOₓ with NH₃ (NH₃-SCR) (Zhang et al., 2015; Hu et al., 2017). In
recent years, commercial SCR catalysts including V₂O₅/TiO₂-WO₃ and V₂O₅/TiO₂-MoO₃ had excellent deoxidation activity. However, because of the narrow operating temperature window, the activity of the catalyst is poor at low temperatures, and it can only work at high temperatures (350–450°C). In this way, the denitration device can only be installed at the front end of the desulfurization device, while the presence of SO₂ in the flue gas can lead to V₂O₅/TiO₂ catalyst inactivation (Shi et al., 2011; Hu et al., 2018). Therefore, the denitification device can only be installed downstream of the desulfurization device, but this cannot meet the optimal reaction temperature of the V₂O₅/TiO₂ catalyst (Jin et al., 2022). At the same time, the V₂O₅/TiO₂ catalyst may also cause vanadium poisoning (Kwon et al., 2016; Hu et al., 2018). To sum up, it is particularly important to develop a kind of low-temperature and high-activity catalyst.

At present, the most widely studied catalysts are transition metal catalysts, zeolite catalysts, and rare earth metal catalysts. Among transition metal catalysts, manganese oxide (MnOₓ) catalysts have attracted much attention due to their excellent low-temperature SCR performance. However, the working temperature window of pure MnOₓ catalyst is narrow, and when there is SO₂ and H₂O in the flue gas, the MnOₓ catalyst will be inactivated, which seriously affects the denitrification activity. Therefore, it is necessary to widen the temperature window of the MnOₓ catalyst and improve the water and sulfur resistance. The Mn-Ce binary oxide catalyst prepared by the solvothermal method has abundant chemisorption oxygen and active sites and shows excellent low-temperature activity and significant sulfur resistance (Chen et al., 2021). Tang prepared Mn-Fe-Ce0.1 ternary oxide catalyst by the co-precipitation method, which has a large specific surface area and strong surface acidity, which is conducive to enhance the SCR denitration activity of the catalyst and improving the resistance to SO₂ and H₂O (Tang et al., 2020). In addition, MnAlOₓ (Zhou et al., 2019), Fe-Mn/Al₂O₃ (Wang et al., 2016), and Mn/TiWO₃ (Chen et al., 2016a) have excellent SCR activity and water and sulfur resistance. Therefore, the introduction of one or more metal elements in the MnOₓ catalyst can enhance the phsyicochemical properties of MnOₓ catalyst so that the prepared catalyst has excellent denitification performance.

Zirconium additives can improve the dispersity and activity of the catalyst and the sulfur resistance of the catalyst (Kantcheva et al., 2011). Ali synthesized the CuₓCeₐ₃₋ₓZrₓ₀.₅ oxide catalyst by the citric acid method, which showed excellent SCR activity, N₂ selectivity, and water and sulfur resistance (Ali et al., 2017). Doped zirconium into the Cr₂O₃ catalyst by the co-precipitation method, which changed the surface performance of chromium oxide catalyst, improved the acid position of the CrZrOₓ catalyst, the concentration of surface adsorbed oxygen Oₓ and Cr⁶⁺, and improved the SCR performance of the catalyst (Guo et al., 2021). In addition, Hu reported the influence of Co₃O₄ doping on NH₃-SCR reaction in manganese-based catalyst, which greatly improved the redox capacity of the catalyst and proposed the reaction mechanism (Hu et al., 2015). Gao added cobalt to MnOₓ through complexation esterification, and the catalyst showed good activity and improved the resistance of MnOₓ to SO₂ Gao et al. (2018). Zhang found that MnCo₃₋ₓO₄ nanocages prepared by self-assembly have higher N₂ selectivity, wider operating temperature range, and better SO₂ tolerance compared with nanoparticles (Zhang et al., 2014). Therefore, the doping of zirconium and cobalt in manganese catalysts is of great research value.

In view of the reported effect of zirconium and cobalt on improving the catalytic activity and sulfur resistance of manganese-based catalysts, bimetal elements of zirconium and cobalt were added to the manganese-based catalysts simultaneously in the hope of preparing a more efficient denitrification catalyst. In this study, a series of related MnₓZr₁₋ₓCoₓ bilayer oxides catalysts were prepared by the co-precipitation method. The effects of cobalt-doped MnₓZr₁ bilayer oxides on the activity and resistance to SO₂ and H₂O were studied. In addition, the denitifiction activity was tested in a fixed-bed reactor. The physicochemical properties of catalysts were investigated by conducting a series of related experiments and characterization, such as temperature-programmed technology, SEM, XRD, BET, XPS, H2-TPR, NH3-TPD, and In Situ DRIFTs.
EXPERIMENTAL

Materials
All samples were synthesized by the co-precipitation method with Mn(NO$_3$)$_2$·4H$_2$O (99.0%, Macklin, Shanghai), Zr(NO$_3$)$_4$·5H$_2$O (≥99.0%, Macklin, Shanghai), and Co(NO$_3$)$_2$·6H$_2$O (≥99.0%, Macklin, Shanghai). NaOH (≥96.0%, Macklin, Shanghai) was used to regulate pH. (NH$_4$)$_2$CO$_3$ (≥40.0%, MACKLIN, Shanghai) was used as the precipitator. In this study, none of the reagents used needs to be further purified.

Catalyst Preparation
A series of Mn$_6$Zr$_{1-x}$Co$_x$ catalysts were prepared by the co-precipitation method. Specifically, the corresponding precursor material was weighed, in which Mn: (Zr + Co) = 6:1, and the ratio of Zr: Co was 1:9, 3:7, 5:5, 7:3, and 9:1 (all ratios were molar ratios). Then, the mixed solution was put into five 300-ml beakers according to the proportion and marked with 1#, 2#, 3#, 4#, and 5#. Also, 100 ml of deionized water was added to each of the five beakers. The mixed solution was heated at 30°C in a water bath for 30 min and mixed with a magnetic stirrer at 500 r/min. 50 ml 0.5 mol·L$^{-1}$ (NH$_4$)$_2$CO$_3$ solution was gradually dropped into the abovementioned solution with full stirring for 2 h. Also, 100 ml of deionized water was added to each of the five beakers. The mixed solution was pleased at 30°C in a water bath for 30 min and mixed with a magnetic stirrer at 500 r/min. 50 ml 0.5 mol·L$^{-1}$ NaOH solution was gradually added to the obtained solution to keep at pH = 9. The abovementioned solutions were aged at room temperature for 24 h, and then the supernatant was removed from the beaker and the sediment was collected. The sediment was washed with deionized water until neutral pH = 7. The washed sediments were dried at 105°C by using vacuum drying oven overnight to get the primary product. The primary products were calcined at 400°C for 3 h in a muffle furnace. Finally, solids were crushed and screened to 40–60 mesh to obtain the final experimental catalyst. Samples 1#, 2#, 3#, 4#, and 5# were Mn$_6$Zr$_{0.1}$Co$_{0.9}$, Mn$_6$Zr$_{0.3}$Co$_{0.7}$, Mn$_6$Zr$_{0.5}$Co$_{0.5}$, Mn$_6$Zr$_{0.7}$Co$_{0.3}$, and Mn$_6$Zr$_{0.9}$Co$_{0.1}$, respectively.

Catalytic Performance Test
The activity of the catalyst was evaluated and detected by temperature-programmed technology, as shown in Figure 1. Each test used a catalyst (0.2 g, 40–60 mesh) with a volume of about 0.5 ml, which was placed in a fixed-bed quartz reactor (diameter = 9 mm, length = 60 mm) for the NH$_3$-SCR activity evaluation test. The reaction gas of NH$_3$-SCR denitration consists of 500 ppm NO, 500 ppm NH$_3$, 5vol% O$_2$, 100–200 ppm SO$_2$ (when used), 5Vol% H$_2$O (when used), and N$_2$ as equilibrium gas. The total flow rate of the gas is 500 ml min$^{-1}$, and the gas hourly space velocity (GHSV) was about 60,000 h$^{-1}$. The reaction temperature was 100–300°C when the catalyst activity was tested. The concentrations of NO$_x$ and O$_2$ before and after the reaction were measured by a flue gas analyzer. The remaining unconverted gas is filtered with sodium hydroxide solution. Each temperature point was held for 30 min, and the data were recorded in a numerical stable state. NO$_x$ conversion and N$_2$ selectivity are calculated by the following equations, respectively:

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

$$\text{N}_2\text{ selectivity} (\%) = \left(1 - \frac{2[N_2O]_{\text{out}} + [\text{NO}]_{\text{out}} - 2[N_2O]_{\text{in}} - [\text{NO}]_{\text{in}}}{[\text{NH}_3]_{\text{in}} + [\text{NO}_x]_{\text{in}} - [\text{NH}_3]_{\text{out}} - [\text{NO}_x]_{\text{out}}} \right) \times 100\%.$$  

The SCR activity of the catalyst can also be quantitatively expressed by the first-order rate constant (k), which can be calculated by the formula of NO conversion (X) as follows (Gao et al., 2014; Jiang et al., 2020).

$$k = -\frac{F_0}{[\text{NO}]_{\text{in}}W} \ln(1 - X),$$
Ink = $-\frac{E_a}{RT} + \ln A$, \hspace{1cm} (4)

where $F_0$ is NO feeding rate; $[\text{NO}]_0$ is NO concentration at the inlet; $W$ is catalyst dosage; $E_a$ is the apparent activation energy; $T$ is the Kelvin temperature; $R$ is the gas constant; $A$ is the pre-exponential factor.

Catalyst Characterization

The X-ray diffraction (XRD) test was carried out with Cu–Kα radiation ($\lambda = 0.15418$ nm) in a 40-kV and 40-mA X-ray tube by using a Bruker D8 Advance in Germany, and the scanning range is 10–80°. A scanning electron microscope (SEM), produced by Hitachi Company Japan, was used to analyze the morphology of the catalysts. Before the test, the sample is evenly smeared on the surface of the conductive adhesive and then sprayed with gold. The $\text{N}_2$ adsorption–desorption isotherms of the catalysts were determined by using Quantachrome Instruments Quadrasorb Evo with high purity $\text{N}_2$ as the adsorbent. Before each analysis, the catalysts were degassed in a vacuum at 300°C for 3 h, and isotherms were measured at liquid nitrogen $\text{N}_2$ ($-196°C$). The speed is 6°/min. The XPS tester uses the Escalab 250XI spectrometer from Semer, Inc., operating under monochrome Al Kα radiation (1486.6 eV), 12 kV, and 15 mA ultra-high vacuum, and all binding energies were calibrated by C1s peak at 284.4 eV. Temperature programmed reduction of $\text{H}_2$ (H2-TPR) and temperature-programmed desorption of $\text{NH}_3$ (NH3-TPD) were performed on the Mac AutoChem II 2920 instrument (United States). The former was pretreated in 300°C argon at a flow rate of 20 ml/min for 1h and cooled to room temperature. The gas was converted into a mixture of 5Vol % $\text{H}_2$-$\text{N}_2$ at a flow rate of 30 ml/min. After a straight baseline, the catalyst was heated from room temperature to 800°C at a rate of 10°C/min. The latter was pretreated in 300°C argon at a flow rate of 20 ml/ min for 1h and cooled to room temperature. The samples were then exposed to a mixture of 5 vol% $\text{NH}_3$-$\text{N}_2$ for 1 h and then purified with high-purity He at a flow rate of 20 ml/min to remove the physically adsorbed $\text{NH}_3$. After the baseline was stabilized, the sample was heated from room temperature to 800°C at a rate of 10°C/min. The in situ Diffuse Reflectance Infrared Transform Spectroscopy (in situ DRIFTS) experiments were applied on a Thermo fisher Nicolet iS50 FTIR spectrometer to characterize the desorption of NO and $\text{NH}_3$ on catalytic materials.

EVALUATION OF CATALYST ACTIVITY

Catalytic Activity for NH3-SCR

All samples were tested for the catalytic performance of NH3-SCR and the results are shown in Figure 2A. The NOx conversion of all catalysts increased first and then decreased with the increase of reaction temperature. When the reaction temperature is 125–250°C, the NOx conversion of the Mn6Zr1 catalyst is more than 90%, showing excellent catalytic activity. The effect of Co/Zr ratios on NH3-SCR performance of Mn6Zr1-xCo x catalysts is shown in Figure 2A. It is worth noting that the NOx conversion first declines and then enhances with the increase of Co ratio. Among these catalysts, the Mn6Zr0.3Co0.7 catalyst exhibits optimal NH3-SCR activity with the NOx conversion being above 90% in the range of 100–275°C and 99% in the range of 150–225°C. However, the Mn6Zr0.5Co0.5 catalyst shows the worst NH3-SCR activity. These findings indicate that the high same Co/Zr content does not improve the catalytic performance of NOx conversion. This may be because the combination of zirconium and cobalt can change the physical and chemical properties of the catalyst surface, thus affecting the adsorption, redox, and surface reaction of active molecules on the catalyst surface. Meanwhile, the $\text{N}_2$ selectivity of all catalysts was tested, as shown in Figure 2B. The selectivity of $\text{N}_2$ decreases with the increase of reaction temperature, which may be related to the formation of $\text{N}_2\text{O}$ on the catalyst. When the Mn6Zr1 catalyst is doped with cobalt, the selectivity of $\text{N}_2$ is obviously improved. At 100–200°C, the $\text{N}_2$ selectivity of the Mn6Zr0.3Co0.7 catalyst is above 80%, and the optimum $\text{N}_2$ selectivity is 96%. In conclusion, cobalt doping in the Mn6Zr1...
catalyst significantly enhances its catalytic activity, widens the temperature window, and improves the selectivity of N₂.

**SO₂ and H₂O Tolerance Resistance of Catalyst**

In order to simulate the flue gas atmosphere under the actual conditions, the denitrification efficiency of the catalyst was tested under the conditions containing SO₂ or H₂O, which were all measured at the optimum reaction temperature. The NOₓ conversion in the SO₂ atmosphere is shown in Figure 3A. The Mn₆Zr₁ catalyst has significantly higher sulfur resistance than the Mn₆Zr₁ catalyst. The NOₓ conversion of the Mn₆Zr₀.₃Co₀.₇ catalyst stabilized at 95% after 4 h when 100 ppm SO₂ was injected into the simulated flue gas. The NOₓ conversion of the Mn₆Zr₀.₃Co₀.₇ catalyst remains above 90% when 200 ppm SO₂ is added. The results indicated that cobalt doping in the Mn₆Zr₁ catalyst significantly improved its resistance to sulfur. The main reason may be that cobalt doping into the Mn₆Zr₁ catalyst increases the active sites on the catalyst surface and changes the physicochemical properties and redox performance of the catalyst. In addition, the NOₓ conversion of two kinds of catalyst did not recover to the initial NOₓ conversion after the SO₂ was turned off, mainly because SO₂ and NH₃ reaction formation sulfate or metal oxides are difficult to decompose under low-temperature, which covers some active sites on the catalyst and acid sites, and the activity cannot recover to the original SCR catalysts (Jia et al., 2018). At the same time, the water tolerance test of the catalyst was measured under the condition of 5Vol% H₂O, and the results are shown in Figure 3B. The results showed that when 5Vol% H₂O is added to the simulated gas, the NOₓ conversion of the two catalysts decreases and the conversion of the catalysts is basically stable after 8 h. The conversion of the Mn₆Zr₀.₃Co₀.₇ catalyst is stable at 95% and that of Mn₆Zr₁ catalyst is stable at 92%. The Mn₆Zr₀.₃Co₀.₇ catalyst showed the best water resistance, indicating that the doping of cobalt also improved the water resistance of the Mn₆Zr₁ catalyst. The NOₓ conversion of the Mn₆Zr₀.₃Co₀.₇ catalyst recovered up to 99% of the initial value after the water vapor was turned off, indicating that the catalyst is reversible.

**CHARACTERIZATION ANALYSIS OF CATALYSTS**

**Crystal Structure Analysis**

In order to understand the crystal structure of the catalysts, all the catalysts were characterized by XRD, and the results are shown in Figure 4. It can be seen that MnO₂(PDF#12-0141) and Mn₃O₄(PDF#04-0732) species exist on the Mn₆Zr₁ catalyst. The diffraction peaks of Mn₆Zr₀.₃Co₀.₇ series catalysts decrease gradually with the decrease of doping cobalt content x. This indicates that MnOₓ species are highly dispersed and form a microcrystalline structure on the Mn₆Zr₀.₃Coₓ catalyst, which contributes to the improvement of catalyst activity (Gong et al., 2020). In addition,
when $\Theta = 55^\circ$, there is a wide diffraction peak, which can be understood as the mixed oxide of MnO$_2$ and Mn$_3$O$_4$. The wide peak structure is conducive to the adsorption, desorption, and redox reaction on the catalyst surface (Tang et al., 2007). It is worth noting that the phases of ZrO$_2$ and CoO$_x$ were not detected on all the catalysts, indicating that the phases related to them are likely to be introduced into the lattice of MnO$_x$ to form a solid solution (Azalim et al., 2011).

Crystal Morphology Analysis

Figure 5 shows the SEM morphology of CoO$_x$, Mn$_6$Zr$_1$, and Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalysts. As shown in Figure 5A, the morphology of CoO$_x$ is an irregular block structure. As shown in Figure 5B,C the Mn$_6$Zr$_1$ catalyst present a cubic structure. It was found that the surface morphology of the original catalyst changed significantly after doping cobalt. As can be seen from Figures 5D,E, the morphology of the Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalyst changes into a spherical structure with a diameter of 26 μm. In addition, Figure 5F clearly shows that the surface of Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalyst forms a villous structure of about 1 μm. Such villi increase the specific surface area of the catalyst and the active sites on the surface. In the SCR denitration process, the reaction molecules can be captured better, thus promoting the denitration activity of the catalyst.

Specific Surface Area and Pore Structure Analysis

Figure 6 shows the N$_2$ adsorption isotherms and pore size distribution of Mn$_6$Zr$_1$, Mn$_6$Zr$_{0.3}$Co$_{0.7}$, and CoO$_x$.

| Samples       | Surface area (m$^2$/g) | Pore volume (cm$^3$/g) | Average pore diameter (nm) |
|---------------|------------------------|------------------------|-----------------------------|
| Mn$_6$Zr$_1$  | 153                    | 0.28                   | 2.5                         |
| CoO$_x$       | 109.3                  | 0.28                   | 6.7                         |
| Mn$_6$Zr$_{0.3}$Co$_{0.7}$ | 155.6             | 0.29                   | 3.7                         |

**TABLE 1 | Surface areas, pore-volume, and average pore diameter of the samples.**
Mn₆Zr₀.₃Co₀.₇ at liquid nitrogen temperature. The specific surface area, pore volume, and pore diameter of the three catalysts are shown in Table 1. In Figure 6A, the shapes of all isotherms can be regarded as type IV isotherms, which are characteristic of mesoporous materials (Jia et al., 2017). All the isotherms of the samples have lagged rings which can be attributed to type H3. When P/P₀ relative pressure is low, N₂ adsorption increases sharply, indicating the presence of narrow micropores in the catalyst (Huang et al., 2021). Figure 6B shows the pore size distribution of the catalyst. The results showed that the peak of the three catalysts at 2 nm belongs to micropore aggregation, and the wide peak at 3–7 nm belongs to mesoporous distribution. It shows that the samples are mainly mesoporous, supplemented by microporous. There are many intermediate holes in the catalyst, which are conducive to the removal of NOₓ, thus showing good catalytic activity. Table 1 shows that the specific surface area, pore volume, and pore size of the Mn₆Zr₀.₃Co₀.₇ catalyst are increased to 156 m²/g, 0.29 cm³/g, and 3.7 nm, respectively, after the addition of cobalt. The results are consistent with SEM analysis of the Mn₆Zr₀.₃Co₀.₇ catalyst. The increase of specific surface area is conducive to the dispersion of the active substance and the contact between the active site and the reactants, and the larger pore size can promote the rapid passage of the reactive gas, thus improving the NH₃-SCR activity of the catalyst (Zhai et al., 2021).

**Analysis of Surface Element Composition**

The surface elemental states of Mn₆Zr₁ and Mn₆Zr₀.₃Co₀.₇ catalysts were characterized by XPS technology. The XPS analysis results are shown in Figure 7 and Table 2. The XPS

| Catalysts | Mn 2p | O 1s | Co 2p |
|-----------|-------|------|-------|
|           | Mn³⁺/Mn | Mn⁴⁺/Mn | O₁s/(O₁s+O₁β) | Co³⁺/Co | Co³⁺/Co²⁺ |
| Mn₆Zr₁    | 34.32% | 46.54% | 47.94% | 0 | 0 |
| Mn₆Zr₀.₃Co₀.₇ | 31.04% | 50.13% | 48.16% | 57% | 133% |
spectra of Mn 2p showed two main peaks including Mn2p3/2 and Mn2p1/2. Through peak fitting deconvolution, the three characteristic peaks of Mn4+, Mn3+, and Mn2+ in Mn2P3/2 on the Mn6Zr1 catalyst are 643.1, 641.7, and 640.6 eV, respectively. Mn2p3/2 is divided into the three characteristic peaks of 643.2, 641.9, and 640.7 eV on the Mn6Zr0.3Co0.7 catalyst corresponding to the binding energies of Mn4+, Mn3+, and Mn2+, respectively (Chen et al., 2020; Pan et al., 2020). As can be seen from Table 2, when the Co element is doped in the Mn6Zr1 catalyst, the Mn4+/Mn ratio in the Mn6Zr0.3Co0.7 catalyst is significantly higher than that obtained by Mn6Zr1. One possible reason is the interaction of cobalt and zirconium with manganese oxides. The ratio of Mn4+/Mn in the Mn6Zr0.3Co0.7 catalyst is larger than that of Mn3+/Mn, indicating that Mn4+ is dominant. In addition, the Mn4+ has the strongest catalytic activity in the NH3-SCR reaction. This is one of the important reasons for the excellent activity of the Mn6Zr0.3Co0.7 catalyst (Chen et al., 2016b).

Figure 7B shows the XPS spectra of O1s of the two catalysts. The O1s peaks of both catalysts were composed of two fitting peaks of 529.5–529.8 eV and 531.1–531.4 eV, respectively. The former is attributed to lattice oxygen, denoted as Oα. The latter is attributed to adsorbed oxygen, denoted as Oβ (Boningari et al., 2015). Table 2 shows that the Oα/(Oα+Oβ) value of the Mn6Zr0.3Co0.7 catalyst is 48.16%, which is higher than that of Mn6Zr1 (47.97%). It can be seen that the adsorbed oxygen on the surface of Mn6Zr1 is more abundant. Since the mobility of chemisorbed oxygen is higher than that of lattice oxygen, chemisorbed oxygen is generally more active than lattice oxygen (Fan et al., 2018). Therefore, a higher Oα/(Oα+Oβ) ratio is favorable for low-temperature NH3-SCR reaction and capable of promoting the oxidation of NO to NO2, thus accelerating the “Fast SCR” reaction (Zhang et al., 2018; Wu et al., 2021).

Figure 7C is the XPS spectrum of Zr3d. The binding energies of Mn6Zr1 and Mn6Zr0.3Co0.7 catalysts at Zr3d3/2 are 181.9 and 181.7 eV, respectively. The binding energy of Zr3d3/2 on pure ZrO2 is 182.1 eV (Fang et al., 2018). The binding energy Mn6Zr0.3Co0.7 is significantly lower than that of the two other catalysts. A lower binding energy means more active elements, which will ultimately improve the catalytic reaction (Fang et al., 2017).

The XPS spectrum of Co2p is shown in Figure 7D. It can be seen that Co2p3/2 is fitted into three peaks. The peak at 780.3 eV can be attributed to Co3+. The peak at 781.8 eV can be attributed to Co2+, and the other peak belongs to the satellite peak with a peak of 786.5 eV (Wang et al., 2019). According to the literature, Co3+ plays an important role in NH3-SCR reaction. More Co3+ species on the catalyst surface, the better the redox performance of the catalyst (Meng et al., 2013). As can be seen from Table 2, the values of Co3+/Co and Co3+/Co2+ indicate that there are a large number of Co3+ species on the surface of the Mn6Zr0.3Co0.7 catalyst, and Co3+ occupies a dominant position, which well proves the reason for the excellent catalyst activity.

Temperature Programming Testing

The surface acidity of the catalyst is also very important in NH3-SCR reactions. The surface acidity of the catalyst was investigated by using NH3-TPD. As can be seen from Figure 8A, the desorption peaks of the two catalysts at around 100°C may be due to the physical adsorption of NH3 at the weak acid site, and part of NH4+ ions are adsorbed by the Brønsted acid site. The desorption peaks at 239 and 242°C are the chemical adsorption of NH3 at the weak acid site (Liu et al., 2012; Jia et al., 2017). There is a desorption peak at 239 and 242°C are the chemical adsorption of NH3 at the medium acid site and the latter belongs to the strong acid site (Fang et al., 2013). As is known to all, the desorption peak area of NH4+ on the catalyst surface but also increased the amount of acid, which was conducive to the adsorption of NH3 and promoted the SCR reaction.

![Figure 8](image-url)
H$_2$-TPR was used to evaluate the redox performance of each catalyst and the interaction between the support and the active component. The redox capacity of the sample depended on the initial reduction temperature. In Figure 8B, both Mn$_6$Zr$_1$ and Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalysts have two reduction peaks. Studies had showed that all manganese-based catalysts follow MnO$_2$ $\rightarrow$ Mn$_3$O$_4$ $\rightarrow$ Mn$_2$O$_3$ $\rightarrow$ MnO (Thirupathi and Smirniotis, 2011; France et al., 2017). Both catalysts show reduction peaks at 200–300°C and 300–500°C. The former can be attributed to the reduction of Mn$^{4+}$ $\rightarrow$ Mn$^{3+}$ and Co$^{3+}$ $\rightarrow$ Co$^{2+}$, while the latter can be attributed to the reduction of Mn$^{3+}$ $\rightarrow$ Mn$^{2+}$ and Co$^{2+}$ $\rightarrow$ Co (Jiang and Song, 2013; Sun et al., 2018). The peak of the Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalyst in the temperature range of 500–700°C can be attributed to the reduction of CoO (Lamonier et al., 2007). In addition, the reduction peak temperature of the Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalyst is significantly lower than that of the Mn$_6$Zr$_1$ catalyst, which may be due to the formation of more surface oxygen vacancies in SCR reaction, which is conducive to the enhancement of oxygen fluidity or activation of reactants (Boningari et al., 2015). This indicates that the doping of cobalt enhances the redox capacity of the catalyst, which well-explains the reason why the Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalyst has a good low-temperature denitrification activity.

**Kinetic Analysis**

The SCR activity differences of Mn$_6$Zr$_1$ and Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalysts were further investigated by kinetic experiments. According to the Arrhenius formula, the apparent activation energy $E_a$ of NO$_x$ conversion can be obtained by the slope of the Lnk curve along with 1/T, as shown in Figure 10. It can be seen that the apparent activation energy $E_a$ of Mn$_6$Zr$_1$ and Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalysts is 22.53 kJ/mol and 5.41 kJ/mol, respectively. The results showed that zirconium doping significantly reduced the apparent activation energy of the catalyst. According to existing pieces of literature, the lower the activation energy of the catalyst, the higher the catalytic SCR activity (Wu et al., 2020).

**In situ DRIFT Analysis**

The adsorption reaction of NH$_3$ and NO$_x$ on the Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalyst is the key to the SCR process. Therefore, in situ DRIFT spectra were carried out, and the results are shown in Figure 9. At 200°C, the Mn$_6$Zr$_{0.3}$Co$_{0.7}$ sample was pre-adsorbed with NH$_3$ for 60min and then purged with N$_2$ for 30 min. After removing the physically adsorbed ammonia, the Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalyst was exposed to the mixture of NO + O$_2$. The peaks at 1622 cm$^{-1}$ and 1170 cm$^{-1}$ were observed after NH$_3$ adsorption, which was due to the coordination state of NH$_3$ at the Lewis acid site on the catalyst surface (Han et al., 2019; Xiong et al., 2020). The characteristic peaks at 1450 cm$^{-1}$ and 1420 cm$^{-1}$ are attributed to the stretching vibration of NH$_4^+$ at the Brønsted acid sites (Zhang et al., 2021; Ge et al., 2022). Lewis and Brønsted acid sites coexist on the Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalyst surface. In addition, a characteristic peak of coordination NH$_3$ appeared at 1215 cm$^{-1}$ (Han et al., 2019). The band at 1070 cm$^{-1}$ belongs to the active intermediate species NH$_2$. With the introduction of NO + O$_2$, the intensity of characteristic peaks of NH$_4^+$, coordination NH$_3$, and amide (-NH$_2$) gradually decreased and disappeared rapidly. Bridging nitrates (1629 cm$^{-1}$, 1599 cm$^{-1}$, and 1230 cm$^{-1}$), bridged bidentate nitrate (1270 cm$^{-1}$), and nitrates (998 cm$^{-1}$) were formed (Han et al., 2019; Gong et al., 2020). All coordination NH$_3$, NH$_4^+$, and -NH$_2$ are involved in the reaction. The removal of NO by NH$_3$-SCR on the Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalyst follows L-H and E-R mechanisms according to the change of the characteristic peak of the in situ drift spectrum.

**ANALYSIS OF CATALYTIC MECHANISM**

The Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalyst prepared doping zirconium and cobalt into the MnO$_x$ shows excellent denitrification ability and has a wide temperature window. The Mn$_6$Zr$_{0.3}$Co$_{0.7}$ catalyst has a large specific surface area and abundant mesopores, which provides a convenient opportunity for gas adsorption and diffusion, thus improving the
denitrification activity of the catalyst. Amorphous MnOx, ZrO2, and CoOx are formed on the surface of the Mn6Zr0.3Co0.7 catalyst, which are the main active oxides on the surface of the catalyst, promoting SCR denitration of the catalyst. The elemental valence states on the surface of the Mn6Zr0.3Co0.7 catalyst were characterized by XPS technology. The Mn4+, Oα, and Co3+ species on the surface of the Mn6Zr0.3Co0.7 catalyst increased. Mn4+ is considered to be one of the best low-temperature denitri-
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cation species. Adsorbed oxygen Oα has excellent oxygen mobility, which enables the rapid oxidation of NO to NO2, resulting in a Fast SCR reaction. Co3+ can promote the oxygen reduction performance of the catalyst. The surface acidity of the Mn6Zr0.3Co0.7 catalyst was enhanced, which made it easier for the catalyst to adsorb NH3 and activate or decompose NH3 on its surface. At the same time, the reduction experiment of the Mn6Zr0.3Co0.7 catalyst shows that the reduction temperature of the Mn6Zr0.3Co0.7 catalyst decreases, which corresponds to the excellent denitri-
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cation activity of the catalyst at low temperature. In addition, the Lewis and Bronsted acid sites were found on the surface of the Mn6Zr0.3Co0.7 catalysts.

The common NO removal process is divided into two steps: NO reacts with O2 to form NxOy, which is further reduced to N2 by adsorbed NH3. The former is closely related to reactive oxygen species, including lattice oxygen and adsorbed oxygen, while the latter participates in the cleavage of the N-H bond in NH3 adsorbed on the Lewis acid site. Migration of H or NH3 combines with a surface hydroxyl group to form NH4+ adsorbed on the Bronsted acid site. They can form intermediates NH4NO2, NH4NO3, and NH2NO. Finally, these intermediates decompose into N2 and H2O. The Mn6Zr0.3Co0.7 catalyst exhibits superior NH3-SCR denitration capacity, which is mainly attributed to the excellent physicochemical properties of the catalyst. Combining the results with references (Jiang et al., 2021; Kang et al., 2021), the reaction path of the Mn6Zr0.3Co0.7 catalyst can be described by E-R and L-H mechanisms. The whole reaction process is shown in Figure 11.

**CONCLUSION**

In this study, a series of Mn6Zr0.3Co0.7 catalysts were prepared by doping of cobalt into the Mn6Zr1 catalyst. The catalytic performance of the doped catalyst has been significantly improved in low-temperature denitri-
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cation performance, sulfur resistance, and water resistance. To be specific, the NOx conversion of the Mn6Zr0.3Co0.7 catalyst is above 90% in the reaction temperature range of 100–275°C, and the best NOx conversion is up to 99%. Under 200 ppm SO2, the NOx conversion still remains above 90%. Under 5Vol% H2O, the NOx conversion basically remains at about 95%. According to the analysis of the characterization results, the Mn6Zr0.3Co0.7 catalyst has a large specific surface area, pore size, pore volume, and strong redox performance, which are the main reasons for the excellent catalytic activity.

**DATA AVAILABILITY STATEMENT**

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

**AUTHOR CONTRIBUTIONS**

HL: conceptualization, methodology, validation, formal analysis, resources, investigation, writing—original draft, writing—review and editing, and visualization. SZ: conceptualization, methodology, formal analysis, resources, writing—original draft, and writing—review and editing. AZ: conceptualization, methodology, formal analysis, writing—original draft, writing—review and editing, and supervision. XZ: conceptualization, methodology, formal analysis, resources, writing—original draft, and supervision. ZS: conceptualization, methodology, formal analysis, writing—original draft, and supervision. CY: conceptualization, methodology, formal analysis, resources. QZ: conceptualization, methodology, formal analysis, and resources.

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