Synthesis of W-modified CeO$_2$/ZrO$_2$ catalysts for selective catalytic reduction of NO with NH$_3$†

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In this paper, a series of tungsten–zirconium mixed binary oxides (denoted as W$_x$ZrO$_y$) were synthesized via co-precipitation as supports to prepare Ce$_{0.4}$/W$_x$ZrO$_y$ catalysts through an impregnation method. The promoting effect of W doping in ZrO$_2$ on selective catalytic reduction (SCR) performance of Ce$_{0.4}$/ZrO$_2$ catalysts was investigated. The results demonstrated that addition of W in ZrO$_2$ could remarkably enhance the catalytic performance of Ce$_{0.4}$/ZrO$_2$ catalysts in a broad temperature range. Especially when the W/Zr molar ratio was 0.1, the Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst exhibited the widest active temperature window of 226–446 °C (NO$_x$ conversion rate > 80%) and its N$_2$ selectivity was almost 100% in the temperature of 150–450 °C. Moreover, the Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst also exhibited good SO$_2$ tolerance, which could maintain more than 94% of NO$_x$ conversion efficiency after being exposed to a 100 ppm SO$_2$ atmosphere for 18 h. Various characterization results manifested that a proper amount of W doping in ZrO$_2$ was not only beneficial to enlarge the specific surface area of the catalyst, but also inhibited the growth of fluorite structure CeO$_2$, which were in favor of CeO$_2$ dispersion on the support. The presence of W was conducive to the growth of a stable tetragonal phase crystal of ZrO$_2$ support, and a part of W and Zr combined to form W–Zr–O$_x$ solid super acid. Both of them resulted in abundant Lewis acid sites and Brønsted acid sites, enhancing the total surface acidity, thus significantly improving NH$_3$ species adsorption on the surface of the Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst. Furthermore, the promoting effect of adding W on SCR performance was also related to the improved redox capability, higher Ce$^{3+}$/Ce$^{4+}$ ratio and abundant surface chemisorbed oxygen species. The in situ DRIFTS results indicated that nitrate species adsorbed on the surface of the Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst could react with NH$_3$ due to the activation of W. Therefore, the reaction pathway over the Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst followed both Eley–Rideal (E–R) and Langmuir–Hinshelwood (L–H) mechanisms at 250 °C.

1. Introduction

Selective catalytic reduction of nitrogen oxides with NH$_3$ (NH$_3$-SCR) has been widely employed for NOX abatement applications in stationary and mobile sources. 1,2 During the past decades, V$_2$O$_5$–WO$_3$ (or MoO$_3$)/TiO$_2$ had been considered the most pervasive and efficient SCR catalysts. 3 However, these catalysts still suffer from some inevitable shortcomings in practical application, such as a narrow operation temperature window (300–400 °C), toxicity of vanadium pentoxide and low N$_2$ selectivity at high temperatures. 4 Given these disadvantages, great efforts have been made to develop environmentally friendly catalysts with a wide temperature window and high N$_2$ selectivity.

In recent years, some non-toxic SCR catalysts such as MnO$_x$, Fe$_2$O$_3$, CuO and CeO$_2$, have been extensively investigated in order to substitute vanadium-based catalysts. 5–8 Among them, cerium-based NH$_3$-SCR catalysts have attracted a lot of researchers’ interest due to their high oxygen storage/release capacity and remarkable redox properties, which are significant to the oxidation of NO$_x$ and the acceleration of NH$_3$-SCR reactions. 9 However, pure CeO$_2$ catalysts exhibit poor thermal stability and are easy to sinter at high temperature. In addition, the high active surface oxygen of a pure CeO$_2$ catalyst results in NH$_3$ oxidation on the catalyst surface, especially at high temperature, leading to a decrease in SCR activity. 9,10 It is generally believed that acid sites are beneficial to suppress NH$_3$ oxidation and promoting NH$_3$ adsorption on the catalyst surface. Therefore, it should be feasible to enhance acid sites to improve NO$_x$ conversion and N$_2$ selectivity of a CeO$_2$ catalyst. 11,12

Zirconia (ZrO$_2$) is an acid-based amphoteric oxide with excellent redox capability and high refractory property. Previous studies reported that the addition of ZrO$_2$ to CeO$_2$ led to an improvement on thermal stability and oxygen storage capacity. 12–14 ZrO$_2$-supported CeO$_2$ catalysts exhibited good oxygen
storage capacity and highly refractory property at the same time. It can utilize the large surface area of ZrO₂ to promote the dispersion of CeO₂ on catalyst surface. Previous studies showed that CeO₂/ZrO₂ catalysts possessed excellent NH₃-SCR activity at medium temperature.¹⁴,¹⁵ Nonetheless, the low-temperature activity and SO₂ tolerance of CeO₂/ZrO₂ catalyst are still not very satisfactory, which hinders their industrial application.

As an important additive in traditional V-based catalysts, WO₃ has been recognized as an excellent “chemical” and “structural” promoter to improve SCR performance obviously.¹⁶ Previous studies have shown that the addition of WO₃ could enhance the adsorption and activation of NH₃ by increasing the surface acidity of the catalysts, which was beneficial to the improvement of NH₂-SCR activity.¹⁷,¹⁸ Recently, Fang et al. prepared WO₃/Ce₀.₆₅Zr₀.₃₅O₂ catalyst by co-precipitation and impregnation method, it could obtain an excellent NH₂-SCR performance at 250–450 °C.¹⁹ Vähileikki et al. have proven that the WO₃/Ce₀.₆₅Zr₀.₃₅O₂ catalyst exhibited high SO₂ and H₂O resistance in the temperature range of 300–500 °C.²⁰ In these studies, WO₃ was usually used as a surface modifier to modify the catalyst surface. However, there are few reports about the incorporation of W into ZrO₂ to form binary metal oxide support for NH₂-SCR. Chen et al. reported that, the addition of W in ZrO₂ could enhance the total acidity and redox properties by forming W–Zr–O₅, which would greatly promote the SCR performance.²¹,²² The authors considered that W–Zr–O₅ solid super acid could be used as SCR support with a high surface area, which might enhance the catalytic activity of Ce/Zr catalysts greatly.

In this work, we focused on the effects of W doping in ZrO₂ on SCR performance of Ce/ZrO₂ catalyst. A series of Ce/WZrO₂ catalysts were prepared by successive co-precipitation and impregnation methods. Catalytic performance tests showed that Ce/WZrO₂ catalysts exhibited a much higher NOx removal efficiency than that of Ce/ZrO₂ catalyst. Further, the effects of W doping in ZrO₂ were investigated in detail by using N₂ physisorption, XRD, Raman, SEM, TEM, XPS, H₂–TPR, NH₃–TPD and in situ DRIFTS. Finally, the possible reaction mechanisms were also discussed to gain insights into the effect of WZrO₂ solid super acid support on SCR reaction pathways.

2. Experimental

2.1 Catalyst preparation

A series of tungsten–zirconium oxides with various molar ratios of W/Zr were prepared by using the co-precipitation method. The typical synthesis process was as follows: a proper amount of Zr(NO₃)₄·5H₂O and (NH₄)₆H₂(W₂O₇)₆·xH₂O were dissolved in deionized water. Then the mixed solution was heated to 40 °C and held for 2 h under continuous magnetic stirring. Next, ammonia solution (25 wt%) was added dropwise to the above solution with vigorous stirring to adjust the solution pH to 10. The obtained precipitate was naturally cooled down to room temperature for 5 h and then filtered, and washed with deionized water until pH changed little. Afterwards, the precipitate was washed with anhydrous ethanol, and dried at 80 °C overnight. The collected solid was calcined at 550 °C in air for 3 h, and finally grounded into a fine powder. The prepared tungsten–zirconium mixed oxides were denoted as WₓZrO₃, where x represented the molar ratio of W/Zr (x = 0.025, 0.05, 0.1, 0.2). Pristine ZrO₂ was also prepared for reference by using the precipitation method. Both Ce₀.₄/ZrO₂ and Ce₀.₄/WₓZrO₂ catalysts were prepared by the impregnation method, where 0.4 represented the molar ratio of Ce/Zr. Firstly, a certain amount of Ce(NO₃)₃·6H₂O was dissolved in deionized water. Then a desired amount of ZrO₂ or WₓZrO₂ powder was impregnated in the solution with strong stirring for 0.5 h. Next, the mixture continued to be stirred sufficiently at 80 °C in a water bath to evaporate the solvent. The solid was dried at 100 °C for 12 h, and calcined at 500 °C for 3 h in air. Finally, all catalysts were crushed and sieved to 40–60 mesh for testing.

2.2 Catalyst activity test

The SCR activity tests of these prepared catalysts were carried out in a fixed-bed quartz reactor (I.D. 6 mm) at atmospheric pressure with a catalyst dosage of 0.5 mL (40–60 mesh). SCR activity measurements were operated in a temperature range of 150–450 °C. The simulated gas consisted of 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, 100 ppm SO₂ (when used) and N₂ as balance gas with a total flow rate of 500 mL min⁻¹. The corresponding gas hourly space velocity (GHSV) was 60 000 h⁻¹. The outlet concentrations of NO, NO₂, NH₃ and N₂O were monitored by an FTIR spectrometer (Antaris IGS, ThermoFisher Scientific) equipped with a heated low-volume multiple-path gas cell (2 m) and an MCT detector cooled by liquid nitrogen. Here NOx referred to the sum of NO and NO₂. NOx conversion efficiency and N₂ selectivity were calculated as follows:

\[
\text{NOx conversion} (\%) = \left(1 - \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} - \frac{[\text{N}_2\text{O}]_{\text{out}}}{[\text{N}_2\text{O}]_{\text{in}}} + \frac{[\text{NH}_3]_{\text{in}}}{[\text{NH}_3]_{\text{out}}} \right) \times 100\% \tag{1}
\]

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

2.3 Catalyst characterization

The textural properties of the prepared samples were measured using N₂ physisorption (ASAP 2020 PLUS, Micromeritics). The powder X-ray diffraction (XRD) patterns were performed on a diffractometer (TTRAX III, Rigaku, Japan) with a Cu-Kα radiation source (λ = 0.15406 nm) under 40 kV and 30 Ma. The Raman spectra of samples were carried out at a Raman Spectrometer (RM2000, Renishaw), using an Ar ion laser (532 nm) as the excitation source. The morphology of the samples was characterized by scanning electron microscopic (SEM, Tescan Mira4). The transmission electron microscopic (TEM) images were performed on FEI Talos F200X and the chemical analysis was obtained by energy dispersive X-ray spectrometer (EDS, Oxford Ultim Max65). X-ray photoelectron spectroscopy (XPS) measurement was obtained on a surface analysis photoelectron spectrometer (ESCALAB 250Xi, ThermoFisher Scientific) using
Al Kα as a radiation source. Temperature programmed reduction with H₂ (H₂-TPR) experiments were operated on a chemisorption analyzer (Autochem II 2920, Micromeritics). Temperature programmed desorption of NH₃ (NH₃-TPD) experiments were operated on a chemisorption analyzer (Autochem II 2920, Micromeritics). In situ DRIFTS measurements were carried out by an FTIR spectrometer (Nicolet iS50, ThermoFisher Scientific) equipped with an MCT/A detector. The spectral resolution was 4 cm⁻¹ with co-addition 64 scans.

3. Results and discussion

3.1 SCR performance

The catalytic performance of the prepared catalysts for NH₃-SCR of NOₓ in the temperature range of 150–450 °C was tested, and the results were displayed in Fig. 1. It could be seen from Fig. 1(a) that W-doped ZrO₂ supports imposed significant impacts on SCR catalytic activities of Ce₀.₄/ZrO₂ catalysts. Without W doping, Ce₀.₄/ZrO₂ catalyst showed rather poor SCR activity in the whole temperature region with the maximum NOₓ conversion of only about 56% at 370 °C, which was in accordance with our previous study.¹⁵ In contrast, Ce₀.₄/WₓZrOₓ catalysts exhibited much better catalytic activity in the test temperature range. With the increase of W/Zr molar ratio from 0.025 to 0.1, the promotional effect of W on SCR activity was observed over W-containing catalysts with dramatically increasing NOₓ conversion and broadened operation temperature windows. However, further increasing W/Zr molar ratio to 0.2, SCR performance of Ce₀.₄/W₀.₂ZrOₓ catalysts deteriorated obviously in the whole operating temperature, and NOₓ conversion efficiency was only 41% at 226 °C. After all, Ce₀.₄/W₀.₁ZrOₓ catalyst possessed the largest active temperature window (NOₓ conversion rate > 80%) of 226–446 °C under GHSV of 60 000 h⁻¹. Fig. 1(b) showed the N₂ selectivity of Ce₀.₄/ZrO₂ and Ce₀.₄/WₓZrOₓ catalysts. It could be seen that N₂ selectivity over Ce₀.₄/ZrO₂ catalyst began to decline slowly when the reaction temperature was above 375 °C, and reduced to 95% at 450 °C. In contrast, all Ce₀.₄/WₓZrOₓ catalysts exhibited superior N₂ selectivity. It was close to 100% in the whole temperature range. The above results demonstrated that the doping of W in ZrO₂ supports could remarkably improve NH₃-SCR performance of Ce/Zr catalysts. Since the comprehensive performance of Ce₀.₄/W₀.₁ZrOₓ catalyst was obviously better than other catalysts, comparative investigations between Ce₀.₄/ZrO₂ and Ce₀.₄/W₀.₁ZrOₓ catalysts were conducted to elucidate the effect of W–Zr binary metal oxide support on NH₃-SCR performance.

It is well known that the common catalysts (vanadium-based) would gradually sinter and the catalytic performance decreased seriously after the SCR reactions. Therefore, the thermostability of catalyst was an important factor that must be considered in the practical application. To investigate the thermostability, Ce₀.₄/W₀.₁ZrOₓ catalyst was cycled two times SCR reactions (as shown in Fig. S1†). It could be seen that there was no significant difference in the catalytic performance between two cycles. In addition, XRD, H₂-TPR and NH₃-TPD techniques were used for the fresh Ce₀.₄/W₀.₁ZrOₓ and the used Ce₀.₄/W₀.₁ZrOₓ (₂nd cycle) catalysts to investigate the effect of SCR reaction process on the structure, redox and surface acidity over Ce₀.₄/W₀.₁ZrOₓ catalyst (as shown in Fig. S2–S4†). These results demonstrated that the Ce₀.₄/W₀.₁ZrOₓ catalysts structure, redox and surface acidity were not significantly different before and after the SCR reactions. In other words, Ce₀.₄/W₀.₁ZrOₓ catalyst exhibited excellent thermostability and its
catalytic performance remained high even after treatment at high temperature.

Considering that the flue gas usually contained a certain concentration of SO2 in practical cases, which would impose a significant impact on the deactivation of NH3-SCR catalysts. Hence, the effect of SO2 on NOx conversion over Ce0.4/W0.1ZrO2 catalyst as a function of time was carried out at 300 °C, and the result was shown in Fig. 1(c). As 100 ppm SO2 was introduced in the feeding gas, NOx conversion efficiency of Ce0.4/W0.1ZrO2 catalyst began to decrease slowly, and reduced to 94% within the first 1 h. After stopping SO2 injection, NOx conversion kept still stable at ~94%. The result indicated that Ce0.4/W0.1ZrO2 catalyst had an excellent tolerance to SO2 at 300 °C, and the slight deactivation due to SO2 poisoning was not irreversible.

3.2 Structural and textural characteristics

3.2.1 BET. N2 adsorption–desorption isotherms of the prepared samples were collected to understand the textural properties of Ce0.4/ZrO2 and Ce0.4/WmZrO2 catalysts. It could be seen from Fig. 2 that all samples exhibited type-IV isotherms according to IUPAS, suggesting the presence of mesoporous materials. The BET surface area, pore size and pore volume of Ce0.4/ZrO2 and Ce0.4/WmZrO2 catalysts were presented in Table 1. The specific surface area of Ce0.4/ZrO2 catalyst was 46.1 m2 g−1. With W/Zr molar ratio increasing from 0.025 to 0.1, the specific surface area over Ce0.4/WmZrO2 catalysts increased from 42.9 to 57.9 m2 g−1. It implied that a proper amount of W doping had an improving effect on specific surface area of Ce0.4/ZrO2 catalyst. Nevertheless, when further increasing W/Zr molar ratio from 0.1 to 0.2, the specific surface area of Ce0.4/W0.2ZrO2 catalyst decreased sharply from 57.9 to 29.4 m2 g−1. It may be due to the excessive W causing the aggregation of active species (CeO2) on the surface of Ce0.4/W0.2ZrO2 catalyst. Generally, the increase of the specific surface area could provide more reaction sites, thus improving SCR catalytic activity.14–26 Although BET surface area of Ce0.4/W0.025ZrO2 (42.9 m2 g−1) and Ce0.4/W0.1ZrO2 (29.4 m2 g−1) catalysts was lower than that of Ce0.4/ZrO2 (46.1 m2 g−1) catalyst, they exhibited much better higher NH3-SCR activity, indicating that the BET surface area might not play a key role in SCR reactions.

3.2.2 XRD and Raman results. The XRD patterns of ZrO2, W0.1ZrO2, Ce0.4/ZrO2 and Ce0.4/W0.1ZrO2 samples were illustrated in Fig. 3. It could be seen from Fig. 3(a) that pristine ZrO2 exhibited characteristic peaks of monoclinic and tetragonal phases (PDF-ICDD 50-1089), respectively.14,15 After the introduction of W, no characteristic diffraction peaks of monoclinic phase ZrO2 could be found in the curve of W0.1ZrO2 sample. It suggested that the addition of W in ZrO2 support was conducive to the formation of a stable tetragonal phase crystal and inhibited the formation of the monoclinic phase. Previous studies proved that the tetragonal phase surface exhibited stronger acidity than that of the monoclinic phase.27 It was beneficial to promote the adsorption of NH3 species on catalyst surface, thus enhancing SCR reactions. However, no obvious WO3 phase was detected in XRD pattern over W0.1ZrO2 sample, suggesting that W was uniformly dispersed on the surface of support or entered into the ZrO2 lattice. In order to further confirm the above results, W0.1ZrO2 sample was tested by TEM and EDS. As showed in Fig. S5† the TEM pattern of W0.1ZrO2 sample only observed the lattice of ZrO2 and did not detect the lattice belonging to WO3. EDS scan mapping results showed that the W species were well dispersed on the support, as presented in Fig. S6†. Besides, compared to ZrO2, the peak at

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**Table 1** BET surface area and pore structure results of prepared catalysts

| Catalysts | $S_{BET}$ (m² g⁻¹) | Pore diameter (nm) | Pore volume (cm³ g⁻¹) |
|-----------|---------------------|-------------------|---------------------|
| Ce0.4/ZrO2 | 46.1 | 11.2 | 0.14 |
| Ce0.4/W0.025ZrO2 | 42.9 | 9.1 | 0.11 |
| Ce0.4/W0.05ZrO2 | 51.7 | 8.1 | 0.10 |
| Ce0.4/W0.1ZrO2 | 57.9 | 6.5 | 0.09 |
| Ce0.4/W0.2ZrO2 | 29.4 | 9.7 | 0.07 |
As to Ce0.4/W0.1ZrO2 were detected. Corresponding to the characteristic peaks of monoclinic phase than that of Zr4+ (0.79 ˚A), W6+ was easier to enter into the ZrO2 lattice, leading to the cell volume (Vcell = abc) over ZrO2 sample from 67.01 ˚A³ decreased to 66.79 ˚A³. This result showed that W had entered the lattice of ZrO2 to form W–ZrO2 solid super acid. 31,38 Therefore, the introduction of W species might exist in two forms: amorphous tungsten oxide and W–ZrO2 solid super acid.

After impregnation of CeO2, the crystal structures of ZrO2 and W0.1ZrO2 in Ce0.4/ZrO2 and Ce0.4/W0.1ZrO2 catalysts were the same as to their single supports, as shown in Fig. 3(a). Some diffraction peaks located at 28.6, 33.1, 47.4 and 56.4° could be identified over Ce0.4/ZrO2 catalyst, which was attributed to (111), (200), (220) and (311) planes of fluorite structure CeO2 (PDF-ICDD 34-0394). As to Ce0.4/W0.1ZrO2 catalyst, the characteristic peaks corresponding to the crystalline phases of CeO2 could also be detected, but the peak intensities became much weaker compared to those of Ce0.4/ZrO2 catalyst. This phenomenon indicated that the existence of W species could suppress the formation of fluorite structure CeO2, leading to a decrease in the crystallite size. It was beneficial to obtain a highly-dispersed state of ceria oxide active species over W0.1ZrO2 support, thus enhancing NH3–SCR activity. Besides, the difference in BET surface area between Ce0.4/ZrO2 and W-containing samples could be interpreted by the crystal phase. From the XRD result, it could be seen that the introduction of W could inhibit the ZrO2 phase transformation from a tetragonal phase to a denser monoclinic phase. 29,30 Moreover, an appropriate amount of W led to high dispersion of active species on catalyst surface. It was conducive to the increase of surface area for W-containing samples.

Raman characterization results were presented in Fig. 4. For pristine ZrO2 sample, the band at 98, 187, 333, 380, 473, 560 and 613 cm⁻¹ were assigned to the Raman-active modes for monoclinic phase of ZrO2, and other bands at 143, 315 and 641 cm⁻¹ were assigned to the tetragonal ZrO2. 13 As to W0.1ZrO2 sample, the peaks at 147, 284, 315, 457 and 645 cm⁻¹ were typically characteristic peaks of tetragonal ZrO2, and no Raman bands corresponding to the characteristic peaks of monoclinic phase were detected. 15 Note that, two Raman bands corresponded to tetragonal phase over W0.1ZrO2 sample had been shifted to 147 and 645 cm⁻¹ respectively, which might be attributed to a strong interaction between W and Zr in the form of W–ZrO2 solid super acid. This result was well in accordance with the above XRD results.

### Table 2: Cell parameter, cell volume and crystallite size of prepared samples

| Samples          | 2θ° | a   | b   | c   | Vcell/Å³ | Crystallite size/Å |
|------------------|-----|-----|-----|-----|----------|-------------------|
| ZrO2             | 52.24 | 3.600 | 5.168 | 67.01 | 79       |
| W0.1ZrO2         | 50.43 | 3.601 | 5.150 | 66.79 | 34       |
| Ce0.4/ZrO2       | 50.11 | 3.599 | 5.157 | 66.84 | 85       |
| Ce0.4/W0.1ZrO2   | 50.34 | 3.602 | 5.146 | 66.79 | 45       |

Fig. 4: Raman results of ZrO2 and W0.1ZrO2 samples.

Fig. 5: SEM images of ZrO2 (a), W0.1ZrO2 (b), Ce0.4/ZrO2 (c) and Ce0.4/W0.1ZrO2 (d).

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3.2.4 XPS. The XPS spectra of Ce 3d, O 1s, Zr 3d and W 4f over Ce0.4/ZrO2 and Ce0.4/W0.1ZrOx catalysts were shown in Fig. 6, these absorbed peaks were calibrated against the C 1s peak standardized at 284.8 eV.\(^{21}\) As shown in Fig. 6(a), the XPS spectra of Ce were fitted into 8 sub-peaks, in which two sub-bands marked in red represent 3d\(^{10}\)4f\(^2\) state of Ce\(^{3+}\), and the other ones marked in blue correspond to 3d\(^{10}\)4f\(^0\) state of Ce\(^{4+}\).\(^{32,33}\) The Ce\(^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})\) ratios were calculated as the integral areas of the corresponding curves, and the results were listed in Table 3. Compared to Ce0.4/ZrO2 catalyst, the ratio of Ce\(^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})\) at the surface of Ce0.4/W0.1ZrO\(_x\) catalyst increased from 12.6% to 16.5%. The increase of Ce\(^{3+}\) content might be due to the interaction between cerium and the neighboring W atoms.\(^{34}\) Since the existence of Ce\(^{3+}\) species could induce a charge imbalance and unsaturated chemical bonds on the catalyst surface, it was conducive to improve redox properties and surface active oxygen content.\(^{32,33}\) As there were abundant Ce\(^{3+}\) species at the surface of Ce0.4/W0.1ZrO\(_x\) catalyst, it was reasonable to obtain an enhancement effect on NO oxidation into NO\(_2\), thus facilitating the fast SCR reaction in denitrification process.

The O 1s XPS information of Ce0.4/ZrO2 and Ce0.4/W0.1ZrO\(_x\) catalysts was presented in Fig. 6(b). Two kinds of surface oxygen species were identified by performing a peak-fitting deconvolution. The peaks at a lower binding energy of 529.0–531.0 eV were assigned to surface lattice oxygen (donated as O\(_b\)), and the peaks at a higher binding energy of 531.0–533.0 eV were attributed to the surface chemisorbed oxygen (donated as O\(_a\)).\(^7\) Previous studies pointed out that, surface chemisorbed oxygen (O\(_a\)) was highly active in NO oxidation and NH\(_3\) activation process due to its higher mobility than lattice oxygen (O\(_b\)).\(^{34}\) The O\(_a)/(O_a + O_b)\) ratios of Ce0.4/ZrO2 and Ce0.4/W0.1ZrO\(_x\) catalysts were calculated by the area integral of O\(_a\) and O\(_b\) curves. As shown in Table 3, the O\(_a)/(O_a + O_b)\) ratio in Ce0.4/ZrO2 catalyst (12.6%) was much lower than that of Ce0.4/W0.1ZrO\(_x\) catalyst (16.5%). It was possible that the addition of W species resulted in the formation of low-valence state metal cations, thus producing a great deal of oxygen vacancies, charge unbalance and unsaturated chemical bonds on the surface of Ce0.4/ W0.1ZrO\(_x\) catalyst.\(^{17,18}\) This was also in favor of boosting NO oxidation to NO\(_2\), promoting SCR reactions proceeding through a ‘fast SCR’ route.

Fig. 6(c) presented the Zr 3d XPS spectra of Ce0.4/ZrO2 and Ce0.4/W0.1ZrO\(_x\) catalysts. There were two peaks at binding energy of 184.0–185.0 eV (Zr 3d\(_{3/2}\)) and 181.5–182.5 eV (Zr 3d\(_{5/2}\)), which corresponded to Zr\(^{4+}\) species.\(^{35}\) Apparently, the peak intensities of Zr\(^{4+}\) for Ce0.4/ZrO2 catalyst were much higher than those for Ce0.4/W0.1ZrO\(_x\) catalyst. Moreover, the peaks of Zr\(^{4+}\) for Ce0.4/ZrO2 catalyst had been shifted to higher binding energy values. It was possibly due to the introduction of W, which

Table 3 XPS data of Ce0.4/ZrO2 and Ce0.4/W0.1ZrO\(_x\) catalysts

| Samples         | Surface atom concentration (%) | The relative molar ratio (%) |
|-----------------|--------------------------------|----------------------------|
|                 | Ce    | Zr    | O    | W    | Ce\(^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})\) | O\(_a/(O_a + O_b)\) |
| Ce0.4/ZrO2      | 17.9  | 6.8   | 75.3 | —    | 12.6                                      | 41.7                     |
| Ce0.4/W0.1ZrO\(_x\) | 21.6  | 1.6   | 75.9 | 0.9  | 16.5                                      | 51.6                     |
resulted in W–Zr–O solid super acid at catalyst surface, arising a change in the electron density and lattice spacing of ZrO2. The results were in accordance with the XRD and Raman results.

Fig. 6(d) presented the XPS spectra of W 4f over Ce0.4/W0.1ZrOx catalyst. Spectrum deconvoluted into two doublets showed two chemical states of W on the surface of Ce0.4/W0.1ZrOx catalyst. The spectral peaks at 35.7 and 37.8 eV corresponded to W 4f7/2 and W 4f5/2 respectively, which were attributed to W6+ state. Doublet with relatively low intensity (peaks at 34.1 and 36.9 eV) corresponded to W5+ state.

3.3 Redox properties

H2-TPR experiments were performed to evaluate the redox properties of Ce0.4/ZrO2 and Ce0.4/W0.1ZrOx catalysts, and the results were shown in Fig. 7 and Table 4. Two distinctive peaks at 503 and 802 °C could be observed in H2-TPR profiles of Ce0.4/ZrO2 catalyst, corresponding to the reduction of surface Ce4+ species to Ce3+ and bulk Ce4+ to Ce3+. For Ce0.4/W0.1ZrOx catalyst, there were three broad reduction peaks around 410, 520 and 792 °C, in which the first peak was assigned to the reduction of the surface Ce4+ species to Ce3+, the second one assigned to the reduction of W6+ to W5+, and the third peak assigned to the reduction of bulk Ce4+ to Ce3+. Compared with Ce0.4/ZrO2 catalyst, the peak corresponding to the reduction of surface Ce4+ to Ce3+ over Ce0.4/W0.1ZrOx catalyst had been shifted to a lower temperature (410 °C). It indicated that the surface Ce4+ species became more reducible after doping W species. Previous study reported that when host oxide (such as CeO2) was reducible, the dopant might donate extra electrons to the host cations.39 In view of this, it was very possible that W as dopant would donate electrons to adjacent Ce4+ species, resulting in a strong interaction between W and Ce, thus improving the redox properties of Ce0.4/W0.1ZrOx catalyst. Furthermore, H2 consumption amount over Ce0.4/W0.1ZrOx catalyst (2.34 mmol g−1) was much higher than that of Ce0.4/ZrO2 catalyst (1.48 mmol g−1). In other words, addition of W species in Ce0.4/ZrO2 catalyst support could greatly enhance the redox properties, which was an important factor for promoting SCR catalytic activity of Ce0.4/W0.1ZrOx catalyst at low-temperature.

3.4 Surface acidity

Surface acidity of NH3-SCR catalysts was one more critical factor in denitrification reaction. NH3-TPD experiment was performed to probe the number of acid sites in Ce0.4/ZrO2 and Ce0.4/W0.1ZrOx catalysts, and the results were presented in Fig. 8. The quantitative analysis results of total surface acidities were listed in Table 5. It could be seen from Fig. 8 that NH3-TPD profiles of both Ce0.4/ZrO2 and Ce0.4/W0.1ZrOx catalysts exhibited three desorption peaks, which were labeled as α, β and γ, respectively. The peak α was attributed to weak acid sites, the peak β was assigned to medium acid sites, and the peak γ was ascribed to strong acid sites.21,40 As shown in Fig. 8, there were only slight differences in the peak positions of weak and medium acid sites...
between these two catalysts. However, the peak position of strong acid sites over Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst shifted to a much lower temperature compared to Ce$_{0.4}$/ZrO$_2$ catalyst. It could be ascribed to the formation of W–Zr–O solid super acid at the surface of Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst. As shown in Table 5, the total acid amounts at the surface of Ce$_{0.4}$/ZrO$_2$ and Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalysts were 1.42 and 1.94 mmol g$^{-1}$, respectively. The results demonstrated that, Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst possessed a superior total acidity over Ce$_{0.4}$/ZrO$_2$ and Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst. The doping W in ZrO$_2$ support effectively improved the surface acidity of Ce$_{0.4}$/ZrO$_2$ catalyst, which was beneficial to adsorb more NH$_3$ species, thus enhancing SCR performance.

3.5 In situ DRIFTS

3.5.1 NH$_3$ adsorption. NH$_3$-TPD experiment could determine the total amount of acid sites, but it failed to distinguish the acid sites (Brønsted acid sites and Lewis acid sites) and the adsorbed NH$_3$ species on catalyst surface. Here steady-state in situ DRIFTS experiments of NH$_3$ adsorption were carried out to ascertain the nature of acid sites and acquire more information about the surface acidity.

Fig. 9 showed the in situ DRIFTS spectra of NH$_3$ adsorption over Ce$_{0.4}$/ZrO$_2$ and Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalysts at different temperatures (100–350 °C). For Ce$_{0.4}$/ZrO$_2$ catalyst, after NH$_3$ adsorption, several bands were detected in the range of 1000–1800 cm$^{-1}$. The bands peaked at 1542 cm$^{-1}$ and 1152 cm$^{-1}$ were assigned to asymmetric and symmetric N–H bending vibrations of N–H bonds in coordinated NH$_3$ linked to Lewis acid sites. The band peaked at 1358 cm$^{-1}$ could be ascribed to the amide (–NH$_2$) species. Obviously, there was no obvious band corresponding to Brønsted acid sites in the in situ DRIFTS spectra of NH$_3$ adsorption over Ce$_{0.4}$/ZrO$_2$ catalyst.

For Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst, the in situ DRIFTS spectra of NH$_3$ adsorption over Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst were quite different from those for Ce$_{0.4}$/ZrO$_2$ catalyst. The NH$_3$ species adsorbed on Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst surface (1152 and 1542 cm$^{-1}$) were attributed to coordinated NH$_3$ on Lewis acid sites. But several new bands could also be detected: the bands peaked at 1354 cm$^{-1}$ and 1232 cm$^{-1}$ were assigned to asymmetric and symmetric bending vibrations of N–H bonds in coordinated NH$_3$ linked to Lewis acid sites, and the band peaked at 1431 cm$^{-1}$ was attributed to NH$_4^+$ species on Brønsted acid sites.

Compared to Ce$_{0.4}$/ZrO$_2$ catalyst, much more NH$_3$ could be adsorbed on the surface of Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst, which was in accordance with NH$_3$-TPD results. This result suggested that the introduction of W species tremendously increased the amount of both Brønsted acid sites and Lewis acid sites on catalyst surface, thus significantly improving the adsorption of NH$_3$ species, which played a key role in NH$_3$-SCR process. Although the introduction of W species could also be detected: the bands peaked at 1585 cm$^{-1}$ and 1190, 1232 cm$^{-1}$ were assigned to asymmetric and symmetric bending vibrations of N–H bonds in coordinated NH$_3$ linked to Lewis acid sites, and the band peaked at 1431 cm$^{-1}$ was attributed to NH$_4^+$ species on Brønsted acid sites.

3.5.2 NO + O$_2$ co-adsorption. The in situ DRIFTS experiments of NO + O$_2$ co-adsorption over Ce$_{0.4}$/ZrO$_2$ and Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalysts were also performed to probe NO$_2$ species adsorbed on catalyst surface at different temperatures. As shown in Fig. 10(a), for Ce$_{0.4}$/ZrO$_2$ catalyst, the intensity of band at 1190 cm$^{-1}$ decreased quickly with temperature increasing from 100 to 150 °C. Meanwhile, some new bands peaked at 1244, 1278, 1354 1533 and 1562 cm$^{-1}$ appeared obviously. The bands peaked at 1354 and 1383 cm$^{-1}$ could be assigned to M–NO$_2$ nitro compounds. The bands peaked at 1244, 1533 and 1562 cm$^{-1}$ could be ascribed to bidentate nitrates. The bands peaked at 1190, 1278 and 1606 cm$^{-1}$ could be attributed to nitrosyl anion species, monodentate nitrate and gaseous NO$_2$ molecules, respectively. The results showed that, the higher the reaction temperature was, the more nitrates could be detected on the surface of Ce$_{0.4}$/ZrO$_2$ catalyst. As shown in Fig. 10(b), for Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst, several bands, bidentate nitrates (1244, 1533 and 1562 cm$^{-1}$), monodentate nitrate (1278 cm$^{-1}$) and bridged nitrate (1219 cm$^{-1}$), could also be detected after NO + O$_2$ adsorption, which could be assigned to adsorbed NO$_x$ species. The bands peaked at 1354, 1383 cm$^{-1}$ and 1606 cm$^{-1}$ were attributed to M–NO$_2$ nitro compounds and gaseous NO$_2$ molecules. Compared to in situ DRIFTS spectra of NO + O$_2$ co-adsorption over Ce$_{0.4}$/ZrO$_2$ catalysts, it was worth noting that the band intensity of adsorbed NO$_x$ species on the surface of Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst was significantly weaker. Moreover, with the increase of reaction temperature, the band intensities of adsorbed NO$_x$ species on the surface of Ce$_{0.4}$/W$_{0.1}$ZrO$_2$ catalyst became weaker gradually. The above results indicated that the introduction of W species not only resulted in more Brønsted acid sites and Lewis acid
sites formed on the surface of Ce₀.₄/W₀.₁ZrOₓ catalyst, but also reduced the thermal stability of the inactive nitrate species, leaving more active sites available for the adsorption of NH₃ species. It was conducive to improving SCR performance.

### 3.5.3 Reactions of pre-adsorbed NH₃ species with NO + O₂

**In situ** DRIFTS experiments were carried out to investigate the reactions between pre-adsorbed NH₃ species and NO + O₂ over Ce₀.₄/ZrO₂ and Ce₀.₄/W₀.₁ZrOₓ catalysts at 250°C. It could be seen from Fig. 11(a) that, after Ce₀.₄/ZrO₂ catalyst being pre-adsorbed with NH₃ and then purged with N₂, there were two weak bands peaked at 1152 cm⁻¹ and 1542 cm⁻¹ corresponding to coordinated NH₃ linked to Lewis acid sites.

After switching to NO + O₂, the coordinated NH₃ species (1152 cm⁻¹ and 1542 cm⁻¹) were consumed within 3 and 10 min, respectively, indicating that both coordinated NH₃ species adsorbed on the surface of Ce₀.₄/ZrO₂ catalyst could participate in SCR reactions. After reacting for 5 min, the bands corresponding to NO₂ molecules (1606 cm⁻¹), bidentate nitrates (1533 and 1562 cm⁻¹), monodentate nitrate (1278 cm⁻¹), bidentate nitrates (1244 cm⁻¹) began to appear.

These nitrate species formed and accumulated on the surface of Ce₀.₄/ZrO₂ catalyst due to the formation of inactive nitrate species. It resulted in less active sites for NH₃ adsorption, which was unfavorable for SCR reactions.

As shown in Fig. 11(b), after saturated adsorption of NH₃ for 30 min, several bands appeared in the spectra over Ce₀.₄/W₀.₁ZrOₓ catalyst. The bands peaked at 1152, 1232, 1542 and 1585 cm⁻¹ on Lewis acid sites were attributed to NH₃ species, while the band peaked at 1431 cm⁻¹ on Bronsted acid sites was assigned to NH₄⁺. After introduction of NO + O₂, all bands belonging to NH₃ species on Lewis acid sites and Bronsted acid sites decreased obviously in intensity. It could be seen that these NH₃ species had been completely substituted by nitrate species after 10 min. This result indicated that both coordinated NH₃ and NH₄⁺ species on Ce₀.₄/W₀.₁ZrOₓ catalyst surface could act as reducing agents to reduce NOₓ. Furthermore, the coordinated NH₃ species over Ce₀.₄/W₀.₁ZrOₓ catalyst played a dominant role in SCR reactions, and the NH₄⁺ species was also involved in SCR reactions. As the doping of W to Ce₀.₄/ZrO₂ catalyst resulted in more coordinated NH₃ and ionic NH₄⁺, both of them led to the improvement of NH₃-SCR performance.

### 3.5.4 Reactions of pre-adsorbed NO + O₂ with NH₃

A series of **in situ** DRIFTS experiments were performed to investigate the reactions between pre-adsorbed NO + O₂ species and NH₃ on the surface of Ce₀.₄/ZrO₂ and Ce₀.₄/W₀.₁ZrOₓ catalysts at 250°C, and the results were displayed in Fig. 12.

As shown in Fig. 12(a), after saturated pre-adsorption of NO + O₂ on the surface of Ce₀.₄/ZrO₂ catalyst, several bands, monodentate nitrate (1278 cm⁻¹), bidentate nitrates (1244, 1533 and
Though the addition of W might inhibit the adsorption of nitrate species on Ce$_{0.4}$/W$_{0.1}$/ZrO$_2$ catalyst surface (see Fig. 10), the reactions between adsorbed nitrate species and NH$_3$ could still play an important role in NH$_3$-SCR of NO$_x$.

3.5.5 Discussion on reaction mechanism. The in situ DRIFTS results showed that NH$_3$ species pre-adsorbed on the surface of Ce$_{0.4}$/ZrO$_2$ catalyst could react with NO and had been completely consumed within a short time. On the other hand, NO$_x$ species pre-adsorbed on the surface of Ce$_{0.4}$/ZrO$_2$ catalyst could not react with NH$_3$. Therefore, SCR reactions over Ce$_{0.4}$/ZrO$_2$ catalyst occurred only via Eley–Rideal (E–R) mechanism at 250 °C.

As to Ce$_{0.4}$/W$_{0.1}$/ZrO$_2$ catalyst, both Eley–Rideal (E–R) and Langmuir–Hinshelwood (L–H) mechanisms had been followed during NH$_3$-SCR reactions at 250 °C. Moreover, E–R rather than L–H mechanism was the dominant reaction pathway. The coordinated NH$_3$ species were considered the most important intermediates in E–R mechanism. Abundant Lewis acid sites had been formed on the surface of Ce$_{0.4}$/W$_{0.1}$/ZrO$_2$ catalyst due to the introduction of W, which promoted the generation of coordinated NH$_3$ species. Different from Ce$_{0.4}$/ZrO$_2$ catalyst, ionic NH$_4^+$ species on Bronsted acid sites had been formed on the surface of Ce$_{0.4}$/W$_{0.1}$/ZrO$_2$ catalyst, which could further react with NO$_x$, thus providing a supplementary pathway for N$_2$ formation. As to L–H mechanism, the addition of W species favored the activation of adsorbed NO$_x$ species, especially bridged nitrites and adsorbed NO$_x$, promoting the reactions between adsorbed NO$_x$ species and NH$_3$.

4. Conclusion

In this work, W$_m$/ZrO$_x$-supported Ce-based catalysts have been prepared, and the effects of W doping in ZrO$_2$ on NH$_3$-SCR performance over Ce$_{0.4}$/W$_m$/ZrO$_x$ catalysts have been investigated systematically. It was found that various W/Zr molar ratios imposed a distinctive impact on the SCR activity of the prepared Ce$_{0.4}$/W$_m$/ZrO$_x$ catalysts. Compared to Ce$_{0.4}$/ZrO$_2$ catalyst, the addition of W in ZrO$_2$ promoted the catalytic performance in a broad temperature range. Especially, Ce$_{0.4}$/W$_{0.1}$/ZrO$_2$ catalyst exhibited the widest active temperature window (NO$_x$ conversion rate > 80%) of 226–446 °C and nearly 100% N$_2$ selectivity. It was attributed to the enhanced redox property, W doping would lead to an increase in Ce$^{3+}$ and O$_2$ contents on the surface of Ce$_{0.4}$/W$_{0.1}$/ZrO$_2$ catalyst. Besides, Ce$_{0.4}$/W$_{0.1}$/ZrO$_2$ catalyst also had good SO$_2$ tolerance, which could maintain more than 94% of NO$_x$ conversion efficiency after being exposed to 100 ppm SO$_2$ atmosphere for 18 h. The results showed that introduction of W in ZrO$_2$ resulted in a larger specific surface area, and formed more Brønsted acid sites and Lewis acid sites at the surface of Ce$_{0.4}$/W$_{0.1}$/ZrO$_2$ catalyst, which enhanced the total surface acidity. Moreover, the thermal stability of inactive nitrite species had also been reduced significantly, leaving more active sites available for the adsorption of NH$_3$ species. It was conducive to improving SCR performance. The in situ DRIFTS results indicated that coordinated NH$_3$ and ionic NH$_4^+$ species were active intermediates, and bridging nitrites, monodentate nitrates and bidentate nitrates were involved in SCR.
reactions over Ce$_{0.4}$/W$_{0.1}$ZrO$_x$ catalyst at 250 °C. Therefore, SCR reactions occurred over Ce$_{0.4}$/W$_{0.1}$ZrO$_x$ catalyst might follow both Eley–Rideal (E–R) mechanism and Langmuir–Hinshelwood (L–H) mechanism.

**Author contributions**

Chenglong Li: conceptualization, investigation, writing—original draft, review and editing; Zhitao Han: conceptualization, validation, supervision, project administration, funding acquisition, writing, review and editing; Yuqing Hu: formal analysis, investigation, data curation; Tingjun Liu: formal analysis, investigation; Xinxian Pan: project administration and funding acquisition.

**Conflicts of interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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