不同 Mn/(Mn+Ce) 质量比对整体式 $\text{MnO}_x\text{-CeO}_2/\text{WO}_3\text{-ZrO}_2$ 催化剂 $\text{NH}_3\text{-SCR}$ 性能的影响

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摘要: 制备了一系列不同 Mn/(Mn+Ce) 质量比的 $\text{MnO}_x\text{-CeO}_2/\text{WO}_3\text{-ZrO}_2$ 整体式催化剂用于富氧条件下的 NH_3 选择性催化还原 NO_x ($\text{NH}_3\text{-SCR}$), 并采用 N_2 吸脱附、储氧量、X 射线衍射、X 光电子能谱、 NH_3/NO 程序升温脱附以及 H_2 程序升温还原等手段对催化剂进行表征。结果表明, 当 Mn/(Mn+Ce) 质量比为 0.5 时, 整体式催化剂具有较好的 $\text{NH}_3\text{-SCR}$ 性能, 在空速 10000 h^{-1} 和 $173\sim 355\text{ }^\circ\text{C}$ 条件反应下, NO_x 转化率达 90% 以上。这是由于该 $\text{MnO}_x\text{-CeO}_2/\text{WO}_3\text{-ZrO}_2$ 催化剂具有更高的 NO 氧化活性、更高的表面 Ce 和 Mn 原子浓度以及 Ce^{3+}/Ce 值较低的 NH_3 和 NO 脱附温度以及优异的氧化还原性能所致。

关键词: 锰; 铈; 氨选择性催化还原; 氮氧化物; 质量比

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Influence of Mn/(Mn+Ce) Ratio of $\text{MnO}_x\text{-CeO}_2/\text{WO}_3\text{-ZrO}_2$ Monolith Catalyst on Selective Catalytic Reduction of NO_x with Ammonia

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Abstract: A series of monolith $\text{MnO}_x\text{-CeO}_2/\text{WO}_3\text{-ZrO}_2$ catalysts with different mass ratios of Mn/(Mn+Ce) were prepared and used for the selective catalytic reduction (SCR) of NO_x with NH_3 in the presence of excess O_2 . The catalysts were characterized by N_2 adsorption, oxygen storage capacity, X-ray diffraction, X-ray photoelectron spectroscopy, NH_3/NO temperature-programmed desorption, and H_2 temperature-programmed reduction. The best catalyst had the mass ratio of Mn/(Mn+Ce) = 0.5. It gave 90% NO_x conversion in the range of $173\sim 355\text{ }^\circ\text{C}$ at the gas hourly space velocity of 10000 h^{-1} , and characterization results showed that a higher oxidation activity of NO to NO_2 , more surface Ce and Mn with a larger $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio, lower NH_3 and NO desorption temperatures, and excellent redox ability were together responsible for its best $\text{NH}_3\text{-SCR}$ performance.

Key words: manganese; cerium; selective catalytic reduction of ammonia; nitrogen oxide; mass ratio

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Automobiles and fossil fuel combustion generate nitrogen oxides (NO_x), which are air pollutants with adverse effects,

including photochemical smog, acid rain, ozone depletion, greenhouse effects, and causing respiratory diseases [1].

Many countries limit NO_x emission. The selective catalytic reduction of NO_x with ammonia (NH_3 -SCR) in the presence of excess O_2 is a technology widely used to remove NO_x from coal-fired power plants and automobiles [2]. V_2O_5 - WO_3 (MoO_3)/ TiO_2 is the most common commercial catalyst but it has high catalytic activity and SO_2 tolerance only in a narrow reaction window of 300–400 °C [3,4]. Consequently, a SCR catalyst with an excellent low temperature performance and a wide reaction window is still needed for desulfurization equipment and electrostatic precipitators.

MnO_x is the active component often used to promote low temperature SCR activity [5–10]. CeO_2 is an additive component to enhance the oxidization of NO to NO_2 in the NH_3 -SCR reaction because it can store and release oxygen by the Ce^{3+} - Ce^{4+} redox pair [11–13]. Many works have reported on the catalytic performance of the synergism between MnO_x and CeO_2 [14–17]. Qi et al. [15–18] investigated the relationship between the mole fraction of MnO_x and CeO_2 on MnO_x - CeO_2 powder catalysts, and reported that the catalyst with the $\text{Mn}/(\text{Mn}+\text{Ce})$ mole fraction of 0.4 possessed the best NH_3 -SCR catalytic activity. However, the ratio is different for $\text{Mn}/(\text{Mn}+\text{Ce})$ loaded on different carriers. So the studying of the effect of $\text{Mn}/(\text{Mn}+\text{Ce})$ ratio on other carriers is significant.

In our previous work, we investigated the influence of different WO_3 contents of MnO_x - CeO_2 / WO_3 - ZrO_2 monolith catalysts on the NH_3 -SCR reaction [19], and showed that the catalyst with 10 wt% WO_3 for WO_3 - ZrO_2 gave excellent NH_3 -SCR performance in a broad reaction temperature window. In order to further investigate the effect of the active components on the SCR of NO_x with NH_3 , in this work, a series of MnO_x - CeO_2 /10 wt% WO_3 - ZrO_2 catalysts with different $\text{Mn}/(\text{Mn}+\text{Ce})$ mass ratios were prepared. Their activities for the NH_3 -SCR reaction were investigated together with their characterization.

1 Experimental

1.1 Carrier preparation

The 10 wt% WO_3 - ZrO_2 carrier was prepared by the co-precipitation method from ammonium metatungstate (AR grade, 99%, Anda, Jiangyan, China) and zirconyl nitrate hydrate (AR grade, 99%, Yutai, Shangdong, China) using the appropriate mass ratio. The precursors were mixed in an aqueous solution and a buffer solution of ammonia solution (3 mol/L) and ammonia-carbonate aqueous solution (3 mol/L) were added dropwise until the pH value reached approximately 9. The precipitate obtained was dried at 70 °C for 24 h, and then calcined at 550 °C for 3 h in air to get the 10 wt% WO_3 - ZrO_2 .

1.2 Catalyst preparation

The prepared 10 wt% WO_3 - ZrO_2 carrier was used with $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (AR grade, 99%, Kemiou, Tianjin, China) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (AR grade, 99%, Jinshan, Chengdu, China) as the precursors of MnO_x and CeO_2 , respectively. MnO_x - CeO_2 / WO_3 - ZrO_2 catalysts with different $\text{Mn}/(\text{Mn}+\text{Ce})$ mass ratios (Mn and Ce denoted the metal oxides) were prepared by the incipient wetness impregnation method. The catalyst was calcined at 550 °C for 3 h in air. Some water was added to the prepared catalyst powder and this was mixed to form a uniform slurry that was coated on honeycomb cordierites (cylinder, diameter: 11 mm, length: 26 mm, bulk: 2.5 cm³, 62 cell/cm², Corning Ltd., USA). Then the cordierites were purged with air and dried, followed by calcination at 550 °C for 3 h in air. Finally, the monolithic catalyst was obtained with a loading of about 160 g/L. The composition of the catalysts are listed in Table 1.

Table 1 Compositions of catalysts

Sample	MnO_x (wt%)	CeO_2 (wt%)	$\text{Mn}/(\text{Mn}+\text{Ce})$	WO_3 (wt%)	ZrO_2 (wt%)
WO_3 - ZrO_2	0	0	—	10	90
Cat-1	4	16	0.2	8 (10) ^a	72 (90) ^b
Cat-2	6	14	0.3	8 (10) ^a	72 (90) ^b
Cat-3	8	12	0.4	8 (10) ^a	72 (90) ^b
Cat-4	10	10	0.5	8 (10) ^a	72 (90) ^b
Cat-5	12	8	0.6	8 (10) ^a	72 (90) ^b
Cat-6	20	0	—	8 (10) ^a	72 (90) ^b
Cat-7	0	20	—	8 (10) ^a	72 (90) ^b

^a WO_3 (wt%) content on the WO_3 - ZrO_2 carrier.

^b ZrO_2 (wt%) content on the WO_3 - ZrO_2 carrier.

1.3 Catalytic activity measurements

The catalytic activity measurements were carried out on a fixed bed quartz flow reactor. Reactant gases were regulated by mass flow controllers. The concentration of the simulated gases were: 0.1% NO , 0.1% NH_3 , 5% O_2 , balance Ar. The gas hourly space velocity (GHSV) was 10000 h⁻¹ and the total flow rate was 420 ml/min. The NO and NO_2 concentrations in the inlet and outlet gases were continually analyzed by a chemiluminescent NO/NO_x analyzer (Model 42i-HL, High Level, Thermo Electron Corporation). N_2O concentration was detected by FT-IR (Antaris IGS, Nicolet). To avoid any influence caused by ammonia, the outlet stream was passed through an ammonia trap containing phosphoric acid solution before it was sent to the chemiluminescent analyzer. The data were recorded after the reaction was stabilized for 0.5 h.

NO_x conversion and N_2 selectivity ($S(\text{N}_2)$) were calcu-

lated as:

$$\text{NO}_x \text{ conversion} = \frac{([\text{NO}_x]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}})}{[\text{NO}_x]_{\text{inlet}}} \times 100\% \quad (1)$$

$$S(\text{N}_2) = \frac{(1 - (2[\text{N}_2\text{O}]_{\text{outlet}} + [\text{NO}_2]_{\text{outlet}}))}{([\text{NO}_x]_{\text{inlet}} + [\text{NH}_3]_{\text{inlet}})} \times 100\% \quad (2)$$

A separate NO oxidation activity was measured when NH₃ was not supplied. The data was recorded after the reaction was stabilized for 0.5 h. The NO₂ ratio was obtained by

$$\text{NO}_2 \text{ ratio} = \frac{[\text{NO}_2]_{\text{outlet}}}{[\text{NO}_x]_{\text{outlet}}} \times 100\% \quad (3)$$

In the above three equations, NO_x represents NO and NO₂.

1.4 Characterization of supports and catalysts

1.4.1 N₂ adsorption

The surface area, pore size, and pore volume of the carriers and catalysts were measured with the Brunauer-Emmett-Teller (BET) method by N₂ adsorption at -196 °C on a Quanachrome automated surface area and pore size analyzer (Autosorb SI). The samples were pretreated at 300 °C for 3 h prior to the measurement.

1.4.2 Oxygen storage capacity (OSC)

Total oxygen storage capacity (OSC) was measured with a microreactor. Prior to measurement, the sample (200 mg) was treated at 500 °C under H₂ flow (40 ml/min) for 1 h and cooled to 200 °C under N₂ flow (20 ml/min). Then pulses of oxygen were injected until the breakthrough point. The OSC was evaluated by the oxygen consumption. The detector was a thermal conductivity detector.

1.4.3 X-ray diffraction

Powder X-ray diffraction (XRD) experiments were performed on a Japan Science D/max-rA diffractometer using Cu K_α (λ = 0.15406 nm) radiation. The tube voltage and current were 40 kV and 100 mA, respectively. The XRD powder diffractogram was recorded at 0.03°/s intervals in the range of 20°–80°. The crystalline phases were identified using reference data from the International Center Diffraction Data (ICDD).

1.4.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) data were obtained by a British Kratos XSAM-800 electron spectrometer using 13 kV high voltage and 20 mA electron current using Mg K_α radiation. The C 1s peak (284.8 eV) was used for the calibration of the binding energy values. The pressure in the

analytical chamber was about 1 × 10⁻⁹ Pa.

1.4.5 Temperature-programmed desorption with NH₃/NO

Temperature-programmed desorption experiments of NH₃ or NO (NH₃/NO-TPD) were carried out on a fixed bed quartz reactor. A sample mass of 80 mg and a gas flow rate of 30 ml/min were used. The experiment included four stages: (1) degasification of the sample in Ar at 400 °C for 1 h, (2) adsorption of 2% NH₃ (or 2% NO) at 80 °C for 1 h, (3) isothermal desorption in Ar at 80 °C until no NH₃ (or NO) was detected, and (4) temperature programmed desorption in Ar (TPD stage) at 10 °C/min up to 500 °C. The detector was a thermal conductivity detector.

1.4.6 Temperature-programmed reduction with H₂

Temperature-programmed reduction with H₂ (H₂-TPR) experiments were carried out on a self-assembled experimental equipment with a thermal conductivity detector. All samples (100 mg) were pretreated in a quartz tubular microreactor in a flow of pure N₂ at 500 °C for 1 h, and then cooled to room temperature. The reduction was carried out in a flow of 5% H₂-95% N₂ from room temperature to 750 °C with a heating rate of 10 °C/min.

2 Results and discussion

2.1 Catalytic performance test

2.1.1 Catalytic activity

The activities of the MnO_x-CeO₂/WO₃-ZrO₂ catalysts with different Mn/(Mn+Ce) mass ratios at GHSV=10000 h⁻¹ are shown in Fig. 1. The NO_x conversion curves had a volcano shape, which showed that the NH₃-SCR reaction has an activity temperature window. Combining Fig. 1 with Table 2 showed that the activity temperature window of ΔT₉₀ (temperature range at which NO_x conversion exceeded 90%) was shifted to lower temperature, and the light-off temperature T₅₀ (temperature at which NO_x conversion was 50%) gradually decreased with the increase of the Mn/(Mn+Ce) mass ratio until 0.5 (Cat-4). However the T₅₀ of Cat-5 with the Mn/(Mn+Ce) mass ratio of 0.6 rose to 128 °C. The trend of T₉₀ (temperature at which NO_x conversion was 90%) was in agreement with the trend of T₅₀, which indicated that the total activity first increased and then decreased with increasing Mn/(Mn+Ce) mass ratio with a maximum at 0.5. Moreover, Table 2 showed that the differences between T₉₀ and T₅₀ (ΔT = T₉₀ - T₅₀) of the four catalysts with Mn/(Mn+Ce) ≤ 0.5 were all about 70 °C, which

Fig. 1. NO_x conversion of carrier and $\text{MnO}_x\text{-CeO}_2/\text{WO}_3\text{-ZrO}_2$ catalysts with different $\text{Mn}/(\text{Mn}+\text{Ce})$ mass ratios.

Table 2 Comparison of $\text{MnO}_x\text{-CeO}_2/\text{WO}_3\text{-ZrO}_2$ catalysts with different $\text{Mn}/(\text{Mn}+\text{Ce})$ mass ratios

Sample	$T_{50}/^\circ\text{C}$	$T_{90}/^\circ\text{C}$	$\Delta T (T_{90}-T_{50})/^\circ\text{C}$	$\Delta T_{90}/^\circ\text{C}$
Cat-1	182	254	72	254–346 (92)
Cat-2	151	220	69	220–294 (74)
Cat-3	139	207	68	207–317 (110)
Cat-4	103	173	70	173–355 (182)
Cat-5	128	250	122	250–317 (67)
Cat-6	149	212	63	212–376 (164)
Cat-7	218	267	49	267–477 (210)

showed that these catalysts possess a similar temperature behavior. However, the ΔT of Cat-5 was 122 °C. The results indicated that the $\text{Mn}/(\text{Mn}+\text{Ce})$ mass ratio played a key role in the catalytic performance, and it affected T_{50} , T_{90} , ΔT_{90} , ΔT and maximum NO_x conversion. In addition, Cat-4 exhibited high H_2O and SO_2 tolerance, which was shown in our previous work [19]. So Cat-4 with the mass ratio of $\text{Mn}/(\text{Mn}+\text{Ce}) = 0.5$ has the best catalytic performance of the five catalysts.

The comparison of the NO_x conversion between the carrier and catalysts are presented in Fig. 1. The 10% $\text{WO}_3\text{-ZrO}_2$ carrier had some activity and gave 10% NO_x conversion below 350 °C, and the NO_x conversion increased with temperature and reached 40% at 500 °C. From Fig. 1, it can be clearly seen that the activity of the carrier was remarkably increased when 20% MnO_x (Cat-6) and 20% CeO_2 (Cat-7) were impregnated onto the carrier, respectively. The T_{50} of Cat-6 was 149 °C. Cat-7 had the highest T_{50} , which was 218 °C, and it reached T_{90} fastest while ΔT was only 49 °C. Comparing Cat-4 with Cat-6 and Cat-7, the low temperature performance of Cat-4 was better than the two catalysts with a single active component. From the above results, it can be concluded that MnO_x and CeO_2 to-

gether as active components improved the low temperature catalytic reduction NO_x performance. N_2 selectivity often decreased with increased temperature for catalysts with manganese oxides [11]. In this work, the N_2 selectivity of Cat-4 also followed this rule, while the generated amount of N_2O was considerably enhanced by increasing temperature. The results are shown Fig. 2. It can be seen that the N_2 selectivity of Cat-4 was over 90% below 375 °C.

Fig. 2. N_2 selectivity and N_2O concentration of Cat-4 in $\text{NH}_3\text{-SCR}$ reaction.

2.1.2 Oxidation of NO to NO_2

Figure 3 depicts the NO_2 ratio (the fraction of NO_2 in the total outlet concentration of NO_x) as a function of reaction temperature in the absence of NH_3 over Cat-1 to Cat-5 from NO partially oxidized to NO_2 in the presence of excess O_2 . The NO_2 ratio showed an increasing trend with the $\text{Mn}/(\text{Mn}+\text{Ce})$ mass ratio below 300 °C, although the curve for each catalyst was different. At above 300 °C, the NO_2 ratios for all catalysts rapidly increased with temperature

Fig. 3. Generation of NO_2 ratio on various catalysts in the absence of ammonia.

and then these became small after reaching the peak value. Cat-4 had the largest rate of increase of NO₂ and the peak maximum was at 350 °C at which NO_x conversion reached 100%. The other catalysts had the peak maximum at 400 °C. Qi et al. [11] suggested that NO can be more easily reduced to N₂ by NH₃ when there is some NO₂ than with NO alone because the overall reaction would be the “fast SCR” reaction: $2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$ when some NO was oxidized to NO₂ in the SCR reaction. There is only a little NO₂ generated by the NO oxidation reaction in Fig. 3, but the NO₂ formed can be continuously fed to the reducing agent NH₃, and would block NH₃ oxidation reaction at high temperatures [20]. Therefore, Cat-4 had the highest oxidation rate of NO to NO₂ and the lowest oxidation temperature, which contributed to its excellent NH₃-SCR activity.

2.2 Characterization

2.2.1 Textural properties of carrier and catalysts

The textural properties of the carrier and catalysts are shown in Table 3. Compared with the carrier, the surface area and pore volume of catalysts were sharply decreased after the carrier was loaded with the active components. This may be because the active components filled or partially plugged the pores of the carrier. The surface area and pore volume showed an increasing trend with the Mn/(Mn+Ce) ratio. Cat-4 had the largest surface area and pore volume of 60.0 m²/g and 0.17 ml/g, respectively. These values started to decrease with the further increase of the value of Mn/(Mn+Ce). The pore diameters of the catalysts showed improvement after the introduction of active components. However, the pore diameters of the catalysts decreased with the increase of the ratio of Mn/(Mn+Ce), except for Cat-4 that had the largest pore diameter of 11.3 nm. Cat-4 had the largest surface area, pore volume, and pore diameter, which helped the active components to disperse well on the carrier. Thereby, the active sites were increased, and the NH₃-SCR reaction performance improved. At the same time, the larger pore volume and pore diameter helped the transport of reactants and products [21,22]. Therefore, the NH₃-SCR performance of Cat-4 was improved.

Table 3 Textural properties and OSC of the carrier and catalysts

Sample	Specific surface area (m ² /g)	Pore volume (ml/g)	Average pore diameter (nm)	OSC (μmol/g)
WO ₃ -ZrO ₂	117.1	0.23	7.9	0
Cat-1	37.5	0.10	11.0	270
Cat-2	41.8	0.11	10.7	313
Cat-3	41.6	0.11	10.7	346
Cat-4	60.0	0.17	11.3	359
Cat-5	38.0	0.10	10.6	351

2.2.2 OSC of carrier and catalysts

As can be seen from Table 3, there was no OSC on the 10% WO₃-ZrO₂ carrier. The catalysts with different mass ratios of Mn/(Mn+Ce) had oxygen storage capacity. The order of the OSC was consistent with the textural properties, Cat-4 with the largest OSC at Mn/(Mn+Ce) = 0.5. Cat-4 with the largest surface area, pore volume, and pore diameter was conducive for high MnO_x-CeO₂ dispersion on the carrier, which improved the circulation and transformation of active oxygen species on the catalyst and this resulted in the largest OSC value for Cat-4. A previous study [23] has shown that the NH₃-SCR reaction mainly occurs by $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$ (5). However, the reaction will proceed by the “fast SCR” reaction: $2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$ (4) when there is NO₂ in the reaction system. The rate of reaction (4) is faster than that of reaction (5). Therefore, the reaction rate would be increased if there is NO₂ generated in the reaction system. Although the NH₃-SCR reaction is carried out in a rich oxygen environment, the proportion of generated NO_x still cannot meet the requirement of accelerating the reaction in the system [24]. Active oxygen on the catalyst surface favors the oxidation of NO to NO₂, which then promotes the NO_x conversion of the catalyst [18]. Therefore, a catalyst with a larger OSC and more surface active oxygen can increase the NH₃-SCR reaction. With respect to the textural properties and OSC results, the catalytic activities of the five catalysts were consistent with the characterization results. In particular, Cat-4 had a large OSC and the best NH₃-SCR performance.

2.2.3 Structure of the catalyst

XRD experiments were carried out in order to study the structural properties of the catalysts. The results are given in Fig. 4. All the catalysts were mainly present as the tetragonal ZrO₂ phase after calcination at 550 °C with XRD peaks at 30.3°, 35.3°, 50.5°, 60.2°, and 74.5°. The five catalysts with different mass ratios of Mn/(Mn+Ce) showed cubic Ce_{0.75}Zr_{0.25}O₂ crystals that had peaks at $2\theta = 28.8^\circ$, 48.0° , and 57.0° . There was a small shift, which was negligible, in these three diffraction peaks with increasing Mn/(Mn+Ce) mass ratio. However, the intensity of the peaks gradually decreased and the crystalline phase became blurred, which indicated that the crystallites of the Ce_{0.75}Zr_{0.25}O₂ solid solution became smaller because of the decrease of CeO₂ loading. In addition, no MnO_x phase was observed with the catalysts containing Mn, which may be due to the fact that Mn was well incorporated into the matrix of ZrO₂ [25] or that MnO_x existed as an amorphous phase or was highly dispersed [6,26]. For Cat-6, only one diffraction peak of the monoclinic ZrO₂ phase was observed at 28.4° . Moreover,

Fig. 4. XRD diffraction patterns for the different catalysts.

there was no diffraction peak for MnO_x , suggesting that MnO_x mainly exists as an amorphous structure. For Cat-7, the diffractogram of CeO_2 showed three diffraction peaks of the cubic fluorite-like structure located at 28.5° , 47.4° , and 56.3° . Based on the above analysis, there was only one diffraction peak attributed to the monoclinic ZrO_2 phase when MnO_x was the only one active component, and there were cubic fluorite-like CeO_2 phases with the three characteristic peaks when CeO_2 was the single active component. Therefore, the co-existence of MnO_x and CeO_2 promoted the formation of the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ solid solution.

In order to further characterize the state of Zr, a peak shift of the XRD patterns in the 2θ range of 29° – 32° for tetragonal ZrO_2 was examined. This is shown in Fig. 4(b). With increasing $\text{Mn}/(\text{Mn}+\text{Ce})$ mass ratio, the diffraction peak attributed to tetragonal ZrO_2 was shifted higher to 30.23° for Cat-2, 30.34° for Cat-3, 30.45° for Cat-4, and 30.34° for Cat-5. This is listed in Table 4. Cat-4 with $\text{Mn}/(\text{Mn}+\text{Ce}) = 0.5$ has the highest 2θ of the five catalysts, indicating that the structural matrix of ZrO_2 has been altered by Mn and some manganese species has entered the tetragonal lattice to generate the MnZrO_x solid solution [27]. Since the radius of Mn^{4+} (0.060 nm) and Mn^{3+} (0.066 nm) are smaller than those of Ce^{4+} (0.092 nm) and Ce^{3+} (0.103 nm), manganese cations more easily enter the ZrO_2 lattice (the radius of Zr^{4+} is 0.079 nm) [25] than ceria cations, and the incorporation of manganese cations into tetragonal ZrO_2 led to the decrease of the lattice parameters [27]. The cell volume V_{cell} of the different catalysts was calculated from the formula: $V_{\text{cell}} = a \times b \times c$, in which, a , b , and c are the cell parameters. The values are listed in Table 4. As shown in Table 4, Cat-4 had the smallest V_{cell} of 0.0656 nm^3 and the highest value of 2θ of 30.45° , which was consistent with the above analysis. Combining with Table 3, we can also see that the textural properties are in good agreement with the structural properties. The order of the average particle size of zirconia for the

different catalysts, calculated from the diffraction peak at 30.3° of the (101) crystal plane was opposite to that of their surface area (in Table 3), which means that Cat-4 had the smallest crystal and the largest surface area. On further increasing the mass ratio of $\text{Mn}/(\text{Mn}+\text{Ce})$, the additional Mn cannot be incorporated into the matrix of ZrO_2 and the additional manganese blocked the pore network of the WO_3 - ZrO_2 carrier, which resulted in the decrease of 2θ , average particle size and surface area of tetragonal ZrO_2 and V_{cell} increases, so that the dispersion of MnO_x on the catalyst surface was reduced [26]. Therefore, it can be concluded that Mn incorporated into the matrix of ZrO_2 promoted the dispersion of MnO_x on the catalyst surface, and the appropriate mass ratio of $\text{Mn}/(\text{Mn}+\text{Ce})$ helped the dispersion of MnO_x on the catalysts, which plays a significant role in reducing NO_x to N_2 .

Table 4 Structural properties of tetragonal ZrO_2

Sample	$2\theta/$ ($^\circ$)	$a = b$ (nm)	c (nm)	V_{cell} (nm^3)	Zirconia particle size d_{ZrO_2} (nm)
Cat-1	30.31	0.3598	0.5137	0.0665	13.8
Cat-2	30.23	0.3605	0.5149	0.0669	13.4
Cat-3	30.34	0.3592	0.5142	0.0664	12.7
Cat-4	30.45	0.3600	0.5061	0.0656	11.7
Cat-5	30.34	0.3592	0.5136	0.0663	12.4
Cat-6	30.43	0.3590	0.5168	0.0666	12.7
Cat-7	30.32	0.3595	0.5127	0.0662	12.7

2.2.4 XPS analysis

To investigate the influence of different $\text{Mn}/(\text{Mn}+\text{Ce})$ mass ratio on the surface electronic properties, the five catalysts were characterized by XPS. The XPS results of the Ce 3d peak for the catalysts are presented in Fig. 5(a). The Ce 3d_{3/2} and Ce 3d_{5/2} states contribution were denoted by “u” and “v”, respectively. The labels u, u2, and u3 showed the photoelectron peaks of Ce^{4+} 3d_{3/2} and v, v2, and v3

Fig. 5. XPS spectra for Ce 3d (a), Mn 2p (b), and O 1s (c) for the five catalysts.

showed the photoelectron peaks of Ce⁴⁺ 3d_{5/2} [28]. The other two peaks, u1 and v1, were attributed to Ce³⁺ 3d_{3/2} and 3d_{5/2}. According to the XPS patterns in Fig. 5(a), the characteristic peaks of Ce⁴⁺ (u3 and v) were stronger than those of Ce³⁺ (u1 and v1), which showed that the dominating valance state of Ce was Ce⁴⁺ for the five catalysts, and Ce³⁺ as the secondary valance state played a key role in creating charge imbalance, vacancies and unsaturated chemical bonds on the catalyst surface [29]. The binding energies (BE) of the characteristic peaks of Ce⁴⁺ 3d_{5/2} (v) and Ce³⁺ 3d_{5/2} (v1) are listed in Table 5. With the increase of the Mn/(Mn+Ce) mass ratio, there was a little difference that was within the error range for the BE value (about 822.5 eV) of Ce⁴⁺ 3d_{5/2} of all catalysts except for Cat-1, which was located at 822.9 eV. This may be due to the fact that Cat-1 had the largest loading of CeO_x (16 wt%) and has a strong interaction between Ce and the carrier [14]. For Ce³⁺ 3d_{5/2} (v1), there was an increasing trend of BE with increased Mn/(Mn+Ce), but the trend was not obvious. However, for Cat-4, the BE suddenly decreased about 1 eV to 885.7 eV when the mass ratio of Mn/(Mn+Ce) reached 0.5, indicating that Cat-4 possessed the highest electron density for Ce³⁺ 3d_{5/2} among all the catalysts. This is beneficial because Ce³⁺ can lose one electron to be oxidized to Ce⁴⁺, which improves the mobility of the active oxygen between Ce³⁺ and Ce⁴⁺ [14]. From Fig. 5(a), it can be seen that the total peak area of Ce 3d was reduced with increasing Mn/(Mn+Ce) mass ratio, which then suddenly increased at the mass Mn/(Mn+Ce) ratio of 0.5. This then decreased with a higher Mn/(Mn+Ce). This is in good agreement with the result of the surface atomic concentration of Ce in the catalysts listed in Table 6. Cat-1 with the largest CeO₂ loading (16 wt%) had more surface atomic concentration of Ce (3.2%), but the surface atomic concentration of Ce was abruptly increased to 4.0% for Cat-4. The relative content of Ce³⁺/Ce on the various catalyst surfaces was calculated from the sum of the areas for Ce³⁺ (u1 and

v1) divided by the sum of the areas of total cerium (the series u and v). This is listed in Table 5. The order of the value of Ce³⁺/Ce with the change of Mn/(Mn+Ce) was the same as that of the surface atomic concentration of Ce. A previous paper [30] reported that the increase of the Ce³⁺ content enhanced lattice oxygen defects on the catalyst surface. In addition, more Ce³⁺/Ce can promote the oxidation of NO to NO₂ because of the charge imbalance, vacancies and unsaturated chemical bonds on the catalyst surface [29,31]. It is generally regarded that the NH₃-SCR reaction at low temperature would be considerably enhanced when some NO is oxidized to NO₂ to give the “fast SCR” reaction: 2NH₃ + NO + NO₂ → 2N₂ + 3H₂O (4) [32]. Cat-4 has the most surface atomic concentration of Ce (4.0%) and the largest value of Ce³⁺/Ce (20.7%), which is one reason for its best catalytic activity.

As shown in Fig. 5(b), Tables 5 and 6, the peak intensities and sharpening of the Mn 2p peak was remarkably increased with the Mn/(Mn+Ce) mass ratio until 0.5, so Cat-4 has the most surface atomic concentration of Mn. For all the catalysts, there were two peaks of Mn 2p_{3/2} and Mn 2p_{1/2}. The BE of Mn 2p_{3/2} was located at 641.9 eV, except for Cat-1 at 641.7 eV and Cat-5 at 642.3 eV, suggesting that Mn⁴⁺ was the mainly valance state of Mn in these catalysts [33]. It also can be seen that the largest surface atomic concentration of Ce and Mn promoted the

Table 5 Binding energies of the characteristic peaks for different elements in the samples

Sample	Binding energy (eV)					
	Ce ⁴⁺ 3d _{5/2}	Ce ³⁺ 3d _{5/2}	Mn 2p _{3/2}	O _{latt}	O _{ads}	O _{sur}
Cat-1	822.9	886.3	641.7	529.3	530.7	532.1
Cat-2	882.3	886.4	641.9	529.5	530.8	532.1
Cat-3	882.5	886.7	642.0	529.5	530.8	532.1
Cat-4	882.5	885.7	641.9	529.3	530.7	532.2
Cat-5	822.6	866.6	642.3	529.8	531.1	532.4

Table 6 Surface atomic concentration of different elements in the catalysts

Sample	Surface atomic concentration (%)						
	Ce	Ce ³⁺ /Ce	Mn	O	O _{latt}	O _{ads}	O _{sur}
Cat-1	3.2	14.6	3.6	81.8	24.2	40.6	17.0
Cat-2	2.5	14.1	3.5	84.3	26.5	39.7	18.1
Cat-3	2.0	14.0	3.8	86.7	19.0	41.6	26.1
Cat-4	4.0	20.7	3.8	84.3	20.2	43.9	20.2
Cat-5	2.4	14.5	2.9	86.7	22.6	46.7	17.4

synergism between Mn and Ce because Ce can provide oxygen to Mn to enhance the valence and oxidation ability of Mn [34], and consequently, the activity for the SCR reaction was improved.

Figure 5(c) presents XPS measurement results of the O 1s core level of the oxygen species on the catalysts surface. The data are summarized in Tables 5 and 6. According to the literature, there are two lattice oxygen peaks of O 1s at 528.9–530 eV, one adsorbed oxygen peak at 531.9 eV and one surface oxygen peaks at 533.5 eV in pure CeO₂. For pure MnO_x, the O 1s spectrum has only one peak at 529.8 eV attributed to lattice oxygen. The peak at 531.3 eV can be assigned to adsorbed species (H₂O, CO₂, surface OH species) and active oxygen, and the peak of surface oxygen from hydroxyl species and adsorbed water species is at 533.5 eV [27]. For all five catalysts, there were three peaks,

denoted as O_{latt}, O_{ads}, and O_{sur}. The three BEs of O 1s showed a small difference that was within the error range. On the MnO_x-CeO₂/WO₃-ZrO₂ catalysts, there was a shift to higher values with increasing Mn/(Mn+Ce) ratio except for Cat-5 with the high Mn content. Simultaneously, the amount of lattice oxygen decreased with increasing Mn/(Mn+Ce) mass, while the amount of adsorbed oxygen increased. The XPS O 1s results are in agreement with the following TPR analysis, and would explain the increased intensity of the reduction peaks in H₂-TPR (given in detail in the TPR analysis). The above observation is in agreement with Arena's report that "Mn←O" electron transfer processes enable the formation of very reactive electrophilic oxygen species (O₂⁻, O₂⁼, O⁻, O[·]) [35]. These very reactive electrophilic oxygen species are active oxygen species. Adsorbed oxygen is the most active oxygen species, which plays an important role in the oxidation processes [36]. The active oxygen can be easily transferred by the oxygen in the gas phase or in the molecules adsorbed on the catalysts [37]; they can actively take part in oxidation and are responsible for the high catalytic activity of Cat-4.

2.2.5 NH₃/NO-TPD analysis

The NH₃-TPD patterns of the five catalysts are presented in Fig. 6(a). In all the catalysts, two desorption peaks in the

Fig. 6. NH₃-TPD (a) and NO-TPD (b) profiles of the catalysts and the deconvoluted peaks.

temperature range of 80–500 °C were observed. Qi et al. [17,18] have proposed that the Lewis acid sites are the main acid sites, rather than the Brønsted acid sites, on pure MnO_x , pure CeO_2 , and $\text{MnO}_x\text{-CeO}_2$ mixed oxides. In the preceding report, the quantity of Lewis acid sites was about as the same as that of strong Brønsted acid sites in $\text{WO}_3\text{-ZrO}_2$ mixed oxides measured by the co-precipitation method [38]. Thus, we assigned the TPD peaks as: the low temperature peaks were assigned to the desorption of bonds between NH_3 and Lewis acid sites or NH_4^+ and the surface hydroxyls [32], and the other broader peak was attributed to the desorption of coordinated NH_3 bonded to Brønsted acid sites of $\text{WO}_3\text{-ZrO}_2$ mixed oxides [39]. As seen from Fig. 6(a), the two peak temperatures shifted to lower temperatures on increasing the Mn/(Mn+Ce) mass ratio, suggesting that the relative strength of the acid sites became weaker. The two desorption peaks of Cat-4 were located at 195 and 271 °C, which were the lowest among the five catalysts. Both peaks were shifted to a lower temperature of more than 50 °C compared with Cat-1. The above shift of the desorption peak temperatures is in good agreement with the order of T_{50} , indicating that Cat-4 possessed better low temperature catalytic activity, as reported by Chen et al. [40].

The NO-TPD patterns of the five catalysts are presented in Fig. 6(b). It can be seen that there were also two NO desorption peaks. Several FT-IR bands attributed to bidentate nitrate and the monodentate have been investigated in the adsorption of NO on $\text{MnO}_x\text{-CeO}_2$ mixed oxides by Qi et al. [17]. Liu et al. [32] proposed that the desorption peaks of the bridging nitrate species and bidentate nitrate species were located at the high temperature from their NO_x -TPD results. Thus, the two NO desorption peaks in Fig. 6(b) were attributed to the decomposition of a bidentate nitrate species with high thermal stability. With the increase of the Mn/(Mn+Ce) mass ratio, the intensities of the main NO desorption peaks became stronger and the temperature of NO desorption peak shifted to lower temperatures with the increase of the Mn/(Mn+Ce) ratio. Cat-4 had the strongest NO desorption intensity and the lowest NO desorption temperature (277 and 366 °C) of the five catalysts. It has been demonstrated that the increase of MnO_x benefits NO oxidation to NO_2 , which then increases the generation of nitrate species at lower temperatures [32]. According to this analysis, the lower NO desorption temperature and larger peak area over Cat-4 suggested that more nitrate species took part in $\text{NH}_3\text{-SCR}$ reaction. This was beneficial for promote NO_x conversion.

2.2.6 H_2 -TPR results

In order to investigate the influence of changing the mass ratio of Mn/(Mn+Ce) on the redox properties of the cata-

lysts, H_2 -TPR experiments were carried out. The results are given in Fig. 7. A main reduction peak with the maximum at 657 °C was observed on the 10% $\text{WO}_3\text{-ZrO}_2$ carrier, while pure ZrO_2 gave a sharp reduction peak at 673 °C. This indicated that the H_2 -TPR of $\text{WO}_3\text{-ZrO}_2$ has two reductive steps, which were associated with the reduction of Zr^{4+} to Zr^{3+} and W^{6+} to W^0 . After supporting 20% MnO_x on $\text{WO}_3\text{-ZrO}_2$ (Cat-6), the reduction temperature was shifted to low temperature and there were four reduction peaks: a shoulder peak at 350 °C attributed to the reduction of MnO_2 to Mn_2O_3 and surface absorbed oxygen species, a sharp peak at 480 °C ascribed to the reduction of Mn_2O_3 to Mn_3O_4 , another shoulder peak at 510 °C assigned to the reduction of Mn_3O_4 to MnO [41,42], and another sharp peak at 620 °C due to the reduction of both Zr^{4+} to Zr^{3+} and W^{6+} to W^0 . Only two reduction peaks were observed after supporting 20% CeO_2 on $\text{WO}_3\text{-ZrO}_2$ (Cat-7): the first at 546 °C can be considered as the reduction of reducible surface CeO_2 to Ce_2O_3 and surface absorbed oxygen species [27] and the second at 624 °C was the reduction of both Zr^{4+} to Zr^{3+} and W^{6+} to W^0 . Therefore, it can be concluded that there were several types of reduction peaks after manganese species and cerium species were together impregnated on $\text{WO}_3\text{-ZrO}_2$, which were ascribed to $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$, $\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$, $\text{Mn}_3\text{O}_4 \rightarrow$

Fig. 7. H_2 -TPR profiles of $\text{MnO}_x\text{-CeO}_2/\text{WO}_3\text{-ZrO}_2$ with different Mn/(Mn+Ce) ratios (a) and H_2 -TPR profiles of different catalysts, $\text{WO}_3\text{-ZrO}_2$, and pure ZrO_2 (b).

MnO , $\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3$, $\text{Zr}^{4+} \rightarrow \text{Zr}^{3+}$, $\text{W}^{6+} \rightarrow \text{W}^0$, and surface absorbed oxygen species in the sequence from low temperature to high temperature.

For Cat-1 with $\text{Mn}/(\text{Mn}+\text{Ce}) = 0.2$, the reduction peaks of MnO_2 to Mn_2O_3 and the surface absorbed oxygen species were located at 304 °C, the reduction peak of Mn_2O_3 to Mn_3O_4 was at 449 °C, the reduction peak of Mn_3O_4 to MnO was at 505 °C, the reduction peak of reducible surface CeO_2 to Ce_2O_3 was at 553 °C, and the reduction peaks of both Zr^{4+} to Zr^{3+} and W^{6+} to W^0 were at 633 °C. With the increase of the $\text{Mn}/(\text{Mn}+\text{Ce})$ mass ratio, the intensities of the reduction peaks became stronger and the reduction temperatures shifted to lower values, but the various reduction peaks were no longer resolved but became continuous one by one. At the mass ratio of $\text{Mn}/(\text{Mn}+\text{Ce}) = 0.5$, Cat-4 showed four peaks in the H_2 -TPR spectrum, the reduction peaks of MnO_2 to Mn_2O_3 and surface absorbed oxygen species was shifted to 290 °C, which was the lowest reduction temperature for this, and this catalyst had the largest reduction peak of MnO_2 to Mn_2O_3 among the five catalysts. In addition, the reduction peak of Mn_2O_3 to Mn_3O_4 was shifted to 440 °C and the reduction peaks of Mn_3O_4 to MnO and CeO_2 to Ce_2O_3 were merged into a sharp reduction peak at 469 °C, which indicated that the manganese species was the main reducible species in Cat-4 with 10% content of both MnO_x and CeO_2 . The reduction peaks of both Zr^{4+} to Zr^{3+} and W^{6+} to W^0 was shifted to 620 °C. The whole reduction range was shifted towards higher temperature when the mass ratio of $\text{Mn}/(\text{Mn}+\text{Ce})$ exceeded 0.5, and the main reduction peaks of the manganese species became sharper and stronger.

Cat-4 had the lowest reduction temperature and largest reduction peak of MnO_x , which illustrated that MnO_x on Cat-4 was more changed than that on the other catalysts, and the lower reduction temperature showed the higher dispersion of MnO_x [43]. The lower reduction temperature and sharper reduction peak indicated a stronger redox ability of the catalyst [44], which was one of the main reasons why Cat-4 had better low temperature SCR activity than the other catalysts. Furthermore, Cat-4 had stronger OSC ability and more surface O_{ads} concentration than the other catalysts, according to the results of OSC and the analysis of the O 1s XPS result, so there were more mobile active surface oxygen species, which increased the redox ability of Cat-4 and promoted its SCR activity.

3 Conclusions

A 10% MnO_x -10% CeO_2 /10% WO_3 - ZrO_2 monolith catalyst gave a higher activity than other catalysts with different $\text{Mn}/(\text{Mn}+\text{Ce})$ mass ratios for the SCR of NO with NH_3 in the presence of excess O_2 . Increasing the $\text{Mn}/(\text{Mn}+\text{Ce})$ mass ratio promoted the NO activity of MnO_x - CeO_2 / WO_3 - ZrO_2

up to $\text{Mn}/(\text{Mn}+\text{Ce}) = 0.5$. On further increasing the $\text{Mn}/(\text{Mn}+\text{Ce})$ value, the drop in low temperature SCR activity was caused by a poorer dispersion of MnO_x on the carrier surface. The superior SCR activity of MnO_x - CeO_2 / WO_3 - ZrO_2 with the mass ratio of $\text{Mn}/(\text{Mn}+\text{Ce})$ of 0.5 was because it has a higher oxidation activity and the lowest oxidation temperature of NO to NO_2 , better textural properties that promoted the dispersion of the active components, and a higher surface atomic concentration of Ce and Mn with a larger value of Ce^{3+}/Ce that promoted the synergism between Mn and Ce. In addition, the more active oxygen adsorbed on the surface of catalysts was more easily moved, and the catalyst had lower NH_3 and NO desorption temperatures and more acid sites and nitrate species on the surface that participated in the NH_3 -SCR reaction. An excellent redox ability also contributed the better NH_3 -SCR performance of the MnO_x - CeO_2 / WO_3 - ZrO_2 monolithic catalyst with the mass ratio of $\text{Mn}/(\text{Mn}+\text{Ce})$ of 0.5.

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