Clean gas flow

N_2

H_2O

N_2

N_2

H_2O

Mn/Ce–ZrO$_2$

$(NH_4)_2SO_4$ s

NO_x

NH_3

NH_3

NO_x

NH$_3$ inject

NO_x

SO_2

NO_x

NO_x

Gas flow

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CONTENTS

Environmental health and toxicology

Environmental catalysis and materials

A comparative study of Mn/CeO$_2$, Mn/ZrO$_2$ and Mn/Ce-ZrO$_2$ for low temperature selective catalytic reduction of NO with NH$_3$ in the presence of SO$_2$ and H$_2$O

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Abstract

Ce-ZrO$_2$ is a widely used three-way catalyst support. Because of the large surface area and excellent redox quality, Ce-ZrO$_2$ may have potential application in selective catalytic reduction (SCR) systems. In the present work, Ce-ZrO$_2$ was introduced into a low-temperature SCR system and CeO$_2$ and ZrO$_2$ supports were also introduced to make a contrastive study. Mn/CeO$_2$, Mn/ZrO$_2$ and Mn/Ce-ZrO$_2$ were prepared by impregnating these supports with Mn(NO$_3$)$_2$ solution, and have been characterized by N$_2$-BET, XRD, TPR, TPD, XPS, FT-IR and TG. The activity and resistance to SO$_2$ and H$_2$O of the catalysts were investigated. Mn/Ce-ZrO$_2$ and Mn/CeO$_2$ were proved to have better low-temperature activities than Mn/ZrO$_2$, and yielded 98.6% and 96.8% NO conversion at 180°C, respectively. This is mainly because Mn/Ce-ZrO$_2$ and Mn/CeO$_2$ had higher dispersion of manganese oxides, better redox properties and more weakly adsorbed oxygen species than Mn/ZrO$_2$. In addition, Mn/Ce-ZrO$_2$ showed a good resistance to SO$_2$ and H$_2$O and presented 87.1% NO conversion, even under SO$_2$ and H$_2$O treatment for 6 hours, and the activity of Mn/Ce-ZrO$_2$ was almost restored to its original level after cutting off the injection of SO$_2$ and H$_2$O. This was due to the weak water absorption and weak sulfation process on the surface of the catalyst.

Key words: low temperature; selective catalytic reduction; manganese; Ce-ZrO$_2$; SO$_2$ poisoning

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Introduction

Selective catalytic reduction (SCR) of NO with NH$_3$ in the presence of oxygen is widely used to reduce NO production in combustion processes due to its low cost and high efficiency (Kašpar et al., 2003). The commonly adopted commercial catalyst is V$_2$O$_5$-WO$_3$(MoO$_3$)/TiO$_2$, and its working temperature must be in the 300–400°C range (Broer and Hammer, 2000; Choo et al., 2003) in order to attain good catalytic activity and avoid pore plugging from the deposition of ammonium sulfate on the catalyst surface. Consequently, in order to avoid reheating the flue gas, the SCR catalyst unit must be located upstream of the desulfurizer and electrostatic precipitator. However, the high concentration of dust reduces the performance and longevity of catalysts. Therefore, it is necessary to develop low-temperature SCR catalysts which can be located downstream of the desulfurizer and electrostatic precipitator. Most flue gas contains small amounts of SO$_2$ even after the desulfurizer. Catalysts for low-temperature SCR

are generally very sensitive to SO$_2$ and can be deactivated by direct reaction between SO$_2$ and a component of the catalyst or by deposition of ammonia sulfate on the catalyst surface (Casapu et al., 2009; Zhu et al., 2000; Kijlstra et al., 1998). Furthermore, the deactivation activity of SO$_2$ will be more intense when H$_2$O is present (Huang et al., 2002). Catalyst deactivation by SO$_2$ and H$_2$O needs to be considered.

Many transition metal oxides have been used to improve the low-temperature activity. Among these metal oxides, manganese oxides have attracted special attention, due to their various types of labile oxygen which can complete the catalytic cycle, resulting in a significant enhancement of catalytic activity at low temperature (Wallin et al., 2004; Smirniotis et al., 2001; Chen et al., 2012). Various Mn-base catalysts such as MnOx/TiO$_2$ (Qi and Yang, 2003; Pena et al., 2004), MnOx/Al$_2$O$_3$ (Kijlstra et al., 1997) and MnOx/AC (Marban and Fuertes, 2001; Tang et al., 2007) have been prepared and tested, and they showed various levels of catalytic activity under different conditions. In some reports, CeO$_2$ has been used to improve the SCR

activity and the resistance to SO_2 of catalysts (Reddy et al., 2003; Baidya et al., 2009; Shen et al., 2011). However, the surface area of CeO_2 is not large enough and its redox quality needs to be improved (Zhang et al., 2011). $Ce-ZrO_2$ is a widely used three-way catalyst support (Fornasiero et al., 1995). It has been reported that Zr can modify the catalyst surface area (Chary et al., 2006) and the insertion of Zr into the ceria lattice can improve the lattice oxygen mobility, resulting in a better redox quality (Liu et al., 2009). Therefore, there is reason to believe that $Ce-ZrO_2$ supports may have good performance in SCR catalytic systems.

In this article, a $Ce-ZrO_2$ support is introduced into the low-temperature SCR catalytic system to support manganese oxides. CeO_2 and ZrO_2 supports are also used to make a contrastive study. $Mn/Ce-ZrO_2$ and Mn/CeO_2 showed better activities than Mn/ZrO_2; and $Mn/Ce-ZrO_2$ showed better resistance to SO_2 and H_2O than Mn/CeO_2 and Mn/ZrO_2 in a 6-hr sulfur tolerance test. The reason for the better resistance of $Mn/Ce-ZrO_2$ toward SO_2 and H_2O was also studied.

1 Materials and methods

1.1 Preparation of supports and catalysts

Ce-Zr hydroxide was prepared by a co-precipitation method. $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot 2H_2O$ were used as precursors and were dissolved in distilled water with the molar ratio of 1:1. An aqueous solution of ammonia was used as the precipitator and was added dropwise in the metal salt solution until the pH rose to 10. The resulting precipitates were stirred for 3 hr and then aged for 1 hr, and finally filtered, washed, and dried at 80°C overnight. Ce and Zr hydroxides were prepared with the same process, and used $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot 2H_2O$ as precursors, respectively.

Mn-base catalysts were prepared by impregnating the support powders of Ce, Zr and Ce-Zr hydroxides with $Mn(NO_3)_2$ solution for 12 hr, and the molar ratio of Mn/(Ce+Zr) was 0.6:1. Then the samples were dried at 80°C overnight and at 110°C for 6 hr, and finally were calcined at 500°C for 6 hr. The catalysts included Mn/CeO_2, Mn/ZrO_2 and $Mn/Ce-ZrO_2$.

In order to obtain CeO_2, ZrO_2, and $Ce-ZrO_2$, some of the hydroxides of Ce, Zr and Ce-Zr were calcined at 500°C for 6 hr. All the chemicals used in the study were of analytic grade.

1.2 Characterization of supports and catalysts

BET surface areas of the catalysts were measured by nitrogen adsorption at –196°C using a NOVA 2000 automated gas sorption system (Quantachrome Instruments, USA). The pore size distribution was calculated from the desorption branch of the N_2 adsorption isotherm using the Barrett-Joyner- Halenda (BJH) formula.

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/Max 2500 system using Cu $K\alpha$ radiation (40 kV, 100 mA) (Rigaku Corporation, Japan).

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD spectrometer equipped with monochromated Al $K\alpha$ radiation (1486.6 eV) (Shimadzu, Japan). Sample charging effects were eliminated by correcting the observed spectra with the C 1s binding energy value of 284.6 eV. The normal operating pressure in the analysis chamber was controlled to 10^{-9} Pa during the measurement.

The temperature-programmed desorption of ammonia (NH_3-TPD) was performed on a tp-5080 automated chemisorption analyzer using 0.1 g catalyst. The powder catalyst was first pretreated in a flow of N_2 (30 mL/min) at 500°C for 1 hr. Subsequently, the sample was cooled down to room temperature and saturated with a stream of pure NH_3 for 30 min (total flow rate = 1 mL/min (STP)). After saturation, the sample was flushed in a pure N_2 flow for 30 min at 100°C. Finally, the sample was heated up to 500°C with a heating rate of 10°C/min. The amount of NH_3 desorption from the catalysts was quantified by a thermal conductivity detector (TCD).

Hydrogen temperature-programmed reduction (H_2-TPR) was performed in the same instrument as the NH_3-TPD using 0.1 g catalyst. The sample was first pretreated in N_2 (30 mL/min) at 500°C for 1 hr and then cooled to room temperature. Subsequently, the sample was heated up to 900°C at a rate of 10°C/min under 5 vol.% H_2/N_2. The consumption of H_2 was measured by a TCD.

FT-IR spectra were acquired with a Nicolet Magna-560 FT-IR spectrometer using a thin self-supporting sample wafer accumulation of 100 scans running at 4 cm^{-1} resolution.

Thermo gravimetric analyses (TGA) were performed on 0.01 g of sample with a NETZSCH Thermal Analysis System under a nitrogen flow of 20 mL/min, using a heating rate of 10°C/min from room temperature to 900°C (NETZSCH Corporation, Germany).

1.3 Catalytic activity test

The SCR activity measurement was performed in a fixed-bed flow reactor. The concentrations of simulated gases were as follows: 600 ppm NO, 660 ppm NH_3, 6 vol.% O_2, 3 vol.% H_2O (when used), 100 ppm SO_2 (when used) and N_2 as balance gas. In all the runs, the total gas flow rate was maintained at 300 mL/min over 0.5 g catalyst and GHSV was about 45,000 hr^{-1}. The feed gases were mixed and preheated in a chamber before entering the reactor. The water vapor was generated by passing N_2 through a gas-washing bottle containing deionized water at different heating temperatures. During the measurements, the concentrations of NO at the inlet and outlet of the reactor were monitored by a flue gas analyzer (KM900/KM9106, Kane International Ltd., United Kingdom). The NO conversion

was calculated using the following equation:

$$\text{NO conversion} = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \times 100\% \qquad (1)$$

where, NO$_{\text{in}}$ (ppm) is the inlet NOx concentration; NO$_{\text{out}}$ (ppm) is the outlet NOx concentration.

2 Results and discussion

2.1 Catalyst characterization

The BET surface area, pore volume, and pore size of different samples are summarized in **Table 1**. The BET surface areas of CeO$_2$, ZrO$_2$ and Ce-ZrO$_2$ were 49.85, 45.93 and 69.77 m^2/g, respectively, which indicated that the mixture of Ce and Zr could increase the surface area. This was mainly because Zr^{4+} could improve the thermal stability of CeO$_2$ and inhibit the sintering of CeO$_2$ during the combustion process (Wu et al., 2008). The surface areas of Mn/ZrO$_2$ and Mn/Ce-ZrO$_2$ were larger than those of ZrO$_2$ and Ce-ZrO$_2$. In some reports, surface areas of catalysts were smaller than those of the supports (Zhang et al., 2011; Ko et al., 2012) because the free pores of the support were partially occupied during the impregnation process. In the present work, hydroxides were used as catalyst supports, and some interaction between hydroxides and Mn might occur during the impregnation process. The BET surface area of Mn/CeO$_2$ was smaller than that of CeO$_2$, which indicated that the interaction between Mn and Ce could be ignored.

The XRD patterns of the catalysts are shown in **Fig. 1**. The diffraction peaks of Mn/ZrO$_2$ were attributed to Mn$_2$O$_3$ and ZrO$_2$ and the diffraction peaks of Mn/CeO$_2$ and Mn/Ce-ZrO$_2$ were attributed to Mn$_2$O$_3$ and CeO$_2$. CeO$_2$ diffraction peaks in Mn/Ce-ZrO$_2$ were broader than in Mn/CeO$_2$ due to the poorer crystallinity of CeO$_2$ in Mn/Ce-ZrO$_2$. Furthermore, ZrO$_2$ diffraction peaks could not be detected in Mn/Ce-ZrO$_2$, which might be due to the amorphous state of ZrO$_2$, the strong background of CeO$_2$ or the incorporation of Zr in the ceria lattice (Fornasiero et al., 1995). In all of the three catalysts, Mn$_2$O$_3$ was the only crystal phase of manganese oxides that could be detected. The Scherrer Formula was used to calculate the grain size of Mn$_2$O$_3$ in Mn/ZrO$_2$, Mn/CeO$_2$ and Mn/Ce-ZrO$_2$, and the results were 305, 212 and 180 Å, respectively. These results suggested that Mn/Ce-ZrO$_2$ had the best manganese
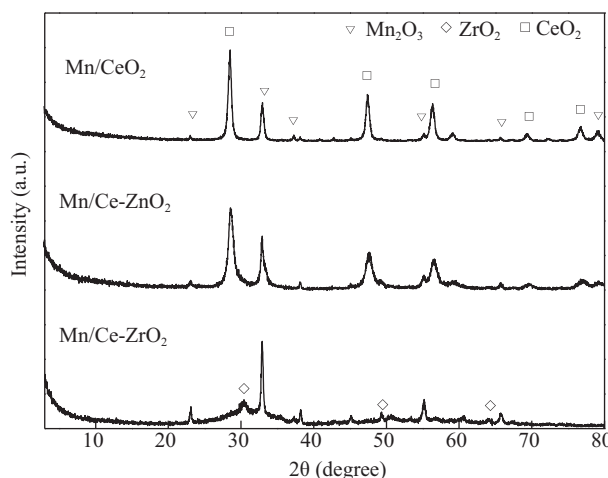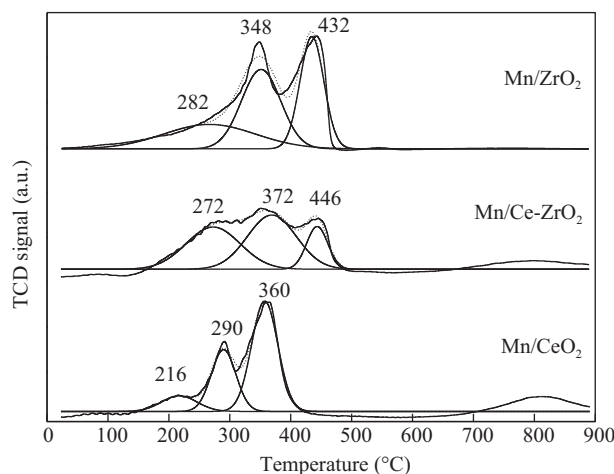

Fig. 1   XRD patterns of different catalysts.

oxide dispersion. This was consistent with a report (Lee et al., 2012) which pointed out that the introduction of Ce into the catalyst improved the manganese dispersion.

H$_2$-TPR analysis was conducted in the present study to investigate the redox behavior of the three catalysts. As shown in **Fig. 2**, three reduction peaks were detected in every sample, and the number in the figure represents the temperature at the peak center. The reduction temperatures of Mn/CeO$_2$ shifted towards lower temperature compared to those of Mn/ZrO$_2$ and Mn/Ce-ZrO$_2$, indicating that Mn/CeO$_2$ was more easily reduced. The low temperature peak area of Mn/Ce-ZrO$_2$ was much larger than that of Mn/ZrO$_2$ and Mn/CeO$_2$, suggesting that Mn/Ce-ZrO$_2$ had more reductive species at low temperature. Therefore, Mn/CeO$_2$ and Mn/Ce-ZrO$_2$ have better redox properties.

According to the previous reports (Ko et al., 2012; Azalim et al., 2011; Wei et al., 2012), the reduction peak positions of CeO$_2$, ZrO$_2$ and Ce-ZrO$_2$ were different from those of Mn/CeO$_2$, Mn/ZrO$_2$ and Mn/Ce-ZrO$_2$. Furthermore, it was reported that the reduction peaks of MnOx in Mn/TiO$_2$ were centered at 303, 392 and 463°C (Thirupathi and Smirniotis, 2011; 2011) and they

Table 1   BET analysis results of various catalysts

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
CeO$_2$	49.85	0.0642	4.07
ZrO$_2$	45.93	0.1127	7.43
Ce-ZrO$_2$	69.77	0.0816	3.62
Mn/CeO$_2$	38.20	0.0940	7.78
Mn/ZrO$_2$	129.76	0.1976	4.66
Mn/Ce-ZrO$_2$	96.50	0.1524	4.78

Fig. 2   Temperature-programmed reduction profiles of different catalysts.
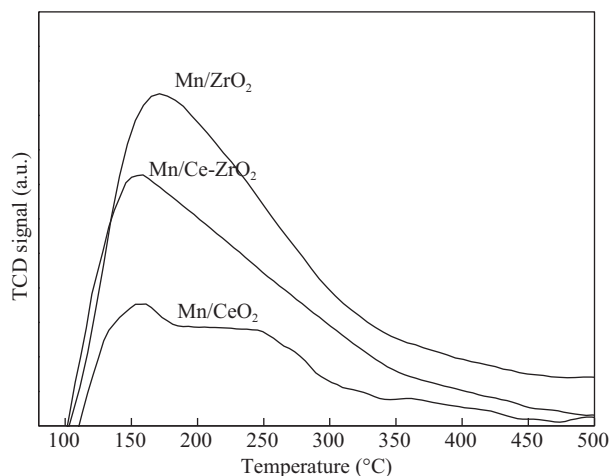
Fig. 3 Temperature-programmed desorption profiles of different catalysts.

were also different from those of Mn/CeO_2, Mn/ZrO_2 and $Mn/Ce-ZrO_2$. These results indicated that there might be interaction between the catalyst support and the active component. Due to the interaction of different components in the catalysts, the reduction peaks could not be attributed to the reduction of a single component but the combined reduction of different components.

NH_3-TPD analysis was carried out to measure the surface acidity of the three catalysts. As shown in **Fig. 3**, the shapes of the NH_3-TPD patterns of the three samples were similar. Only one broad desorption peak was detected in the experiment, which spanned the temperature range from 100 to 450°C. The peak could be assigned to the successive desorption of ammonia physically adsorbed to weak acid sites (100–220°C) and strong acid sites (220–440°C, which was similar to a previous report (Mhamdi et al., 2009). The NH_3 desorption peak of Mn/CeO_2 was very weak, because cerium oxides could hardly give any contribution to NH_3 adsorption (Shen et al., 2009). With the introduction of Zr into the support, the bound NH_3 uptake increased significantly, suggesting that Zr gave rise to more acid sites for the catalysts.

XPS analyses were carried out to investigate the chemical states and atom concentration on the surface of catalysts. **Figure 4** shows the Mn 2p, O 1s, Zr 3d and Ce 3d photoelectron peaks of the catalysts measured by XPS. The Mn 2p photoelectron peaks of Mn/CeO_2 were very broad. A significant increase in the intensity and sharpening of Mn 2p peaks could be noted when Zr was introduced in $Mn/Ce-ZrO_2$, and Mn/ZrO_2 had the most intense Mn 2p

peaks. This suggested that the surface atom concentration of Mn for Mn/ZrO_2 was higher than that for the other two catalysts. Mn $2p_{3/2}$ spectra of the catalysts were composed of two overlapping peaks around the BE of 643.5 and 641.2 eV due to Mn^{4+} and Mn^{3+}, respectively (Qi and Yang, 2004; Thirupathi and Smirniotis, 2012). All peaks of the catalysts around 641.2 eV were sharper than those around 643.5 eV, indicating that Mn_2O_3 was a major phase and MnO_2 was a minor phase in the catalysts. Only the crystal pattern of Mn_2O_3 could be detected in the catalysts from the XRD analysis, but the XPS analysis showed the co-existence of Mn_2O_3 and MnO_2 on the surface of the catalysts. Thus the MnO_2 in the three catalysts might be amorphous.

O 1s spectra of the samples were composed of two overlapping peaks. The first peak in the range of 529.5–530.5 eV (O_β) was due to the lattice oxygen (Larachi et al., 2002; Carja et al., 2007; Yu et al., 2010) and the second peak in the range of 531.3–531.7 eV (O_α) corresponded to the weakly surface-adsorbed oxygen (Tejuca and Fierro, 1989; Qin et al., 2007). O_β shifted towards higher BE when Zr was introduced. This might due to the higher BE of lattice oxygen in ZrO_2 than that in CeO_2. Meanwhile, the O_α area of Mn/CeO_2 and $Mn/Ce-ZrO_2$ was larger than that of Mn/ZrO_2 due to more weakly adsorbed species on the surface of Mn/CeO_2 and $Mn/Ce-ZrO_2$. As reported previously, gas phase oxygen participated in the SCR reaction by filling the oxygen vacancies over the catalyst surface (Ettireddy et al., 2012), and the surface-adsorbed oxygen favored SCR activity (Wu et al., 2008). The BE of Zr 3d was similar in $Mn/Ce-ZrO_2$ and Mn/ZrO_2 and the BE of Ce 3d was similar in $Mn/Ce-ZrO_2$ and Mn/CeO_2. Therefore, it could be concluded that the mixture of Zr and Ce in $Mn/Ce-ZrO_2$ did not change the BE of Zr and Ce very much.

The surface atom percentage of catalysts and atomic ratio of $Mn/(Ce+Zr)$ are shown in **Table 2**. The overall ratio of Ce/Zr for $Mn/Ce-ZrO_2$ was 1, but it was 7.5 on the surface of $Mn/Ce-ZrO_2$, which indicated that Ce was more easily accumulated on the surface of $Mn/Ce-ZrO_2$ than Zr. The Mn concentration on the surface of Mn/ZrO_2 was much higher than that on the surface of Mn/CeO_2 and $Mn/Ce-ZrO_2$, suggesting that Zr caused Mn to accumulate on the surface of the catalysts. This might be the reason for the sharp diffraction peaks of Mn_2O_3 in Mn/ZrO_2 (**Fig. 1**). The enrichment of Mn and Ce on the surface of the catalysts resulted in the higher ratio of $Mn/(Ce+Zr)$ for Mn/ZrO_2 than that for Mn/CeO_2 and $Mn/Ce-ZrO_2$. This

Table 2 Surface atom percentage and the ratio of $Mn/(Ce+Zr)$ of different catalysts determined from XPS

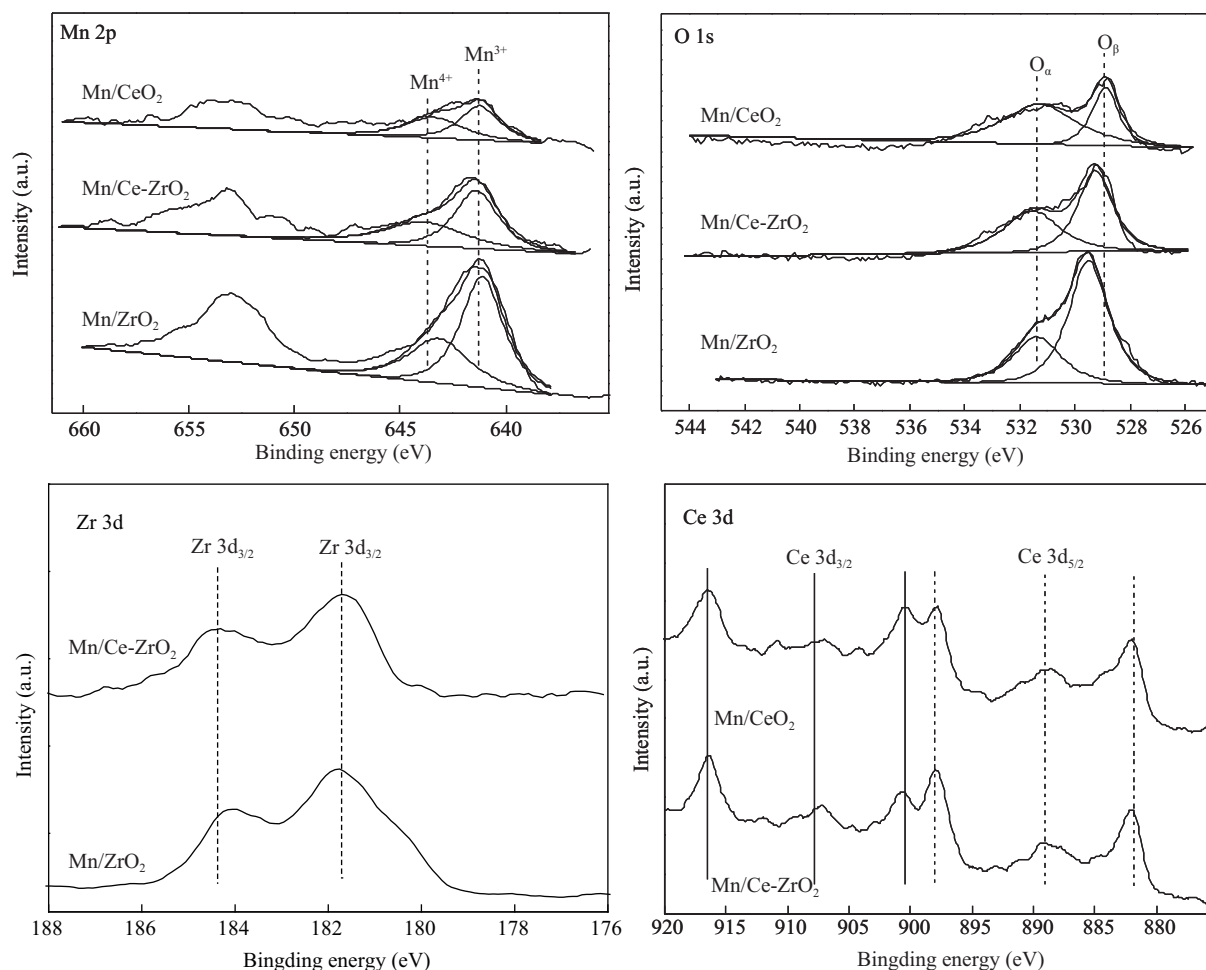| Sample	Surface atom percentage (%)						$Mn/(Ce+Zr)$
	Ce	Zr	Mn^{3+}	Mn^{4+}	O_α	O_β	
Mn/CeO_2	24.14	0	3.39	2.98	56.61	12.88	0.26
$Mn/Ce-ZrO_2$	21.41	2.84	4.69	3.52	43.57	23.97	0.34
Mn/ZrO_2	0	9.47	14.48	8.18	14.65	53.22	2.39

Fig. 4 XPS spectra of Mn 2p, O 1s, Zr 3d and Ce 3d for different catalysts.

was in agreement with the literature of Ettireddy et al. (2007) which studied Mn-based TiO₂-supported catalysts and found that the surface atom ratio of Mn/Ti increased significantly at higher Mn loading, due to the formation of microcrystalline Mn oxide species on the catalyst surface. O_α was much higher and O_β was much lower in Mn/CeO₂ and Mn/Ce-ZrO₂ than that in Mn/ZrO₂, suggesting that the introduction of Ce increased the amount of O_α in Mn/Ce-ZrO₂.

2.2 SCR catalytic activity

The effect of manganese loading on SCR activity is shown in **Fig. 5a**. The activity of the Ce-ZrO₂ support was very low (less than 25%, data not shown). After the addition of Mn, the activities of the catalysts increased sharply, which suggested that Mn species played a significant role in this reaction. This was consistent with the report of Qi and Yang (2003) concerning the MnOx/TiO₂ catalyst. With the increase of the loading amount of Mn, the SCR activity increased first and then decreased, and the maximum activity value occurred when the temperature reached 180°C. At all of the reaction temperatures, the optimal value for Mn/(Ce+Zr) was 0.6. Therefore, 0.6 was

chosen as the ratio of Mn/(Ce+Zr) in later experiments.

The catalytic activities of Mn/CeO₂, Mn/Ce-ZrO₂ and Mn/ZrO₂ for low-temperature SCR were measured in the temperature range from 100 to 220°C and the results are shown in **Fig. 5b**. The activity of Mn/CeO₂ and Mn/Ce-ZrO₂ was higher than that of Mn/ZrO₂. Characterization results showed that Mn/ZrO₂ had the largest BET surface area and the strongest surface acidity, while Mn/ZrO₂ had the worst dispersion of manganese oxides, the weakest reductive capability and the least adsorbed oxygen species on its surface. Therefore, combined with the characterization results and the results of the catalytic activities, the dispersion of manganese oxides, the reductive capability and the adsorbed oxygen species on the surface of the catalysts were the determinants of catalytic activity. This was consistent with previous reports. The reports pointed out that the dispersion of the manganese oxide played an important role in the formation of amorphous-phase manganese oxide, which had good performance in the SCR reaction (Kijlstra et al., 1997; Kapteijn et al., 1994; Huang and Yang, 2001). In the meantime, a strong reductive capability of catalysts and oxygen ions on the surface of catalysts promoted the catalytic activity (Wu et al.,
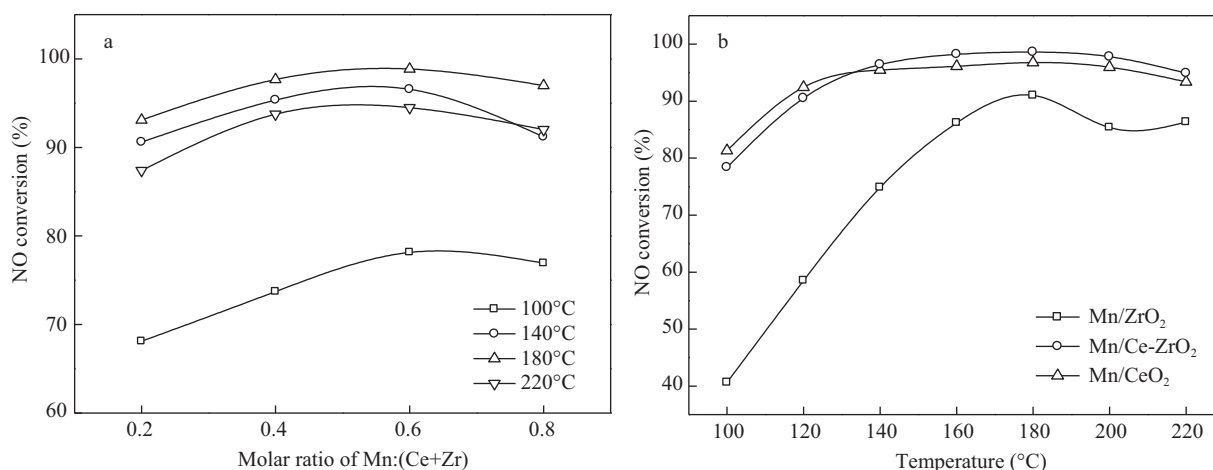
Fig. 5   NO conversion over different catalysts with different MnOx loading (a) and over different catalysts (b).
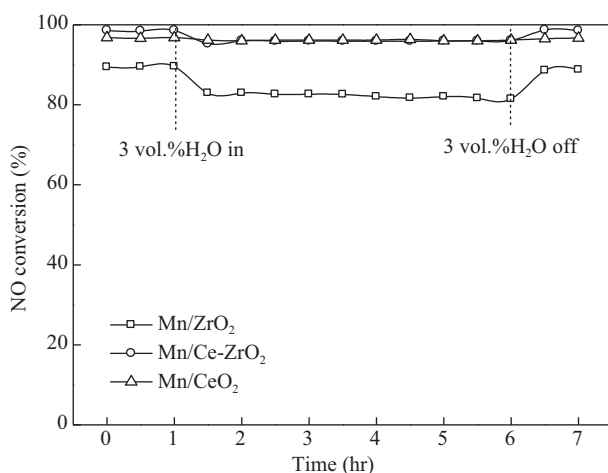

Fig. 6   Effect of H$_2$O on NO conversion over different catalysts at 180°C.

2008; Liu et al., 2007). For all of the three catalysts, the maximum activity value appeared at 180°C, being 98.6%, 96.8% and 91.0% for Mn/Ce-ZrO$_2$, Mn/CeO$_2$ and Mn/ZrO$_2$, respectively.

2.3 Effect of H$_2$O on SCR catalytic activity

In order to evaluate the resistance to H$_2$O of all the catalysts, the catalysts were subjected to a stream of 3 vol.% H$_2$O at 180°C. As shown in **Fig. 6**, the activity of Mn/CeO$_2$ was almost unchanged when H$_2$O was added. Meanwhile, the activities of Mn/ZrO$_2$ and Mn/Ce-ZrO$_2$ slightly decreased from 89.5% and 98.6% to 82.9% and 95.3% with the addition of H$_2$O, respectively. After the removal of H$_2$O, the activities of Mn/ZrO$_2$ and Mn/Ce-ZrO$_2$ were restored to their original levels. These results showed that these catalysts had good resistance to H$_2$O and the inhibitory effect of H$_2$O was reversible for these catalysts. The slight inhibitory effect on catalytic activity could be contributed to the competitive adsorption of H$_2$O, which blocked active sites available for the adsorption of NH$_3$ and NO (Amiridis et al., 1996; Tufano and Turco, 1993).

2.4 Effect of H$_2$O and SO$_2$ on SCR catalytic activity

There are small amounts of SO$_2$ remaining in flue gas even after the desulfurizer. Thus it is necessary to investigate the effect of SO$_2$ + H$_2$O on SCR activity. Before 3 vol.% H$_2$O and 100 ppm SO$_2$ were added, the SCR reaction was stabilized for 1 hr at 180°C. As shown in **Fig. 7a**, when 3 vol.% H$_2$O and 100 ppm SO$_2$ were added into the flue gas, a sharp decline of the NO conversion for Mn/Ce-ZrO$_2$ from 98.5% to 91.2% was observed in the first hour, and then it nearly stabilized. On the contrary, sustained declines of NO conversions for Mn/CeO$_2$ and Mn/ZrO$_2$ were detected over 6 hr, from 96.8% to 61.5% and from 89.5% to 67.1%, respectively. After the removal of SO$_2$ and H$_2$O, the activity of Mn/Ce-ZrO$_2$ almost returned to the original level, from 87.1%, and the activity of Mn/ZrO$_2$ returned to 79.7%, which was 10% lower than its original level. But the activity of Mn/CeO$_2$ was almost unchanged. These results revealed that the mixed support of Ce-ZrO$_2$ used in Mn/Ce-ZrO$_2$ evidently improved the resistance of the catalyst to SO$_2$ and H$_2$O.

The effect of SO$_2$ and H$_2$O on NO conversion over Mn/Ce-ZrO$_2$ at different temperatures (160, 180 and 200°C are shown in **Fig. 7b**). Similar NO conversion and resistance to SO$_2$ and H$_2$O were observed at 180 and 200°C. The activity measured at 160°C had a faster decline compared with that at 180 and 200°C. However, it still showed a high level of activity for NO conversion (79.4%) even at 160°C. These results showed that the resistance to SO$_2$ and H$_2$O for Mn/Ce-ZrO$_2$ increased with increasing temperature.

2.5 FT-IR spectra and TGA for the catalysts

FT-IR analyses were performed in order to investigate formation of sulfate on the catalysts, and the results are shown in **Fig. 8**. Compared to the fresh catalysts, a new peak appeared at 1104 or 1106 cm^{-1}, which was attributed to free SO$_4^{2-}$ for all the used catalysts of Mn/Ce-ZrO$_2$, Mn/ZrO$_2$ and Mn/CeO$_2$ (Huang et al., 2008). Meanwhile,
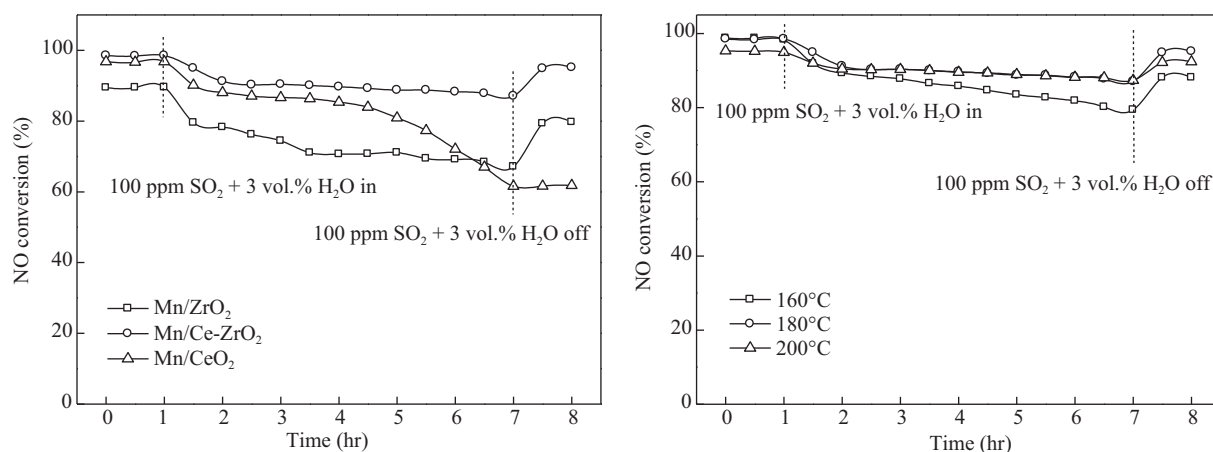
Fig. 7 Effect of H$_2$O and SO$_2$ on NO conversion over different catalysts at 180°C (a) and over Mn/Ce-ZrO$_2$ catalyst at different temperatures (b).
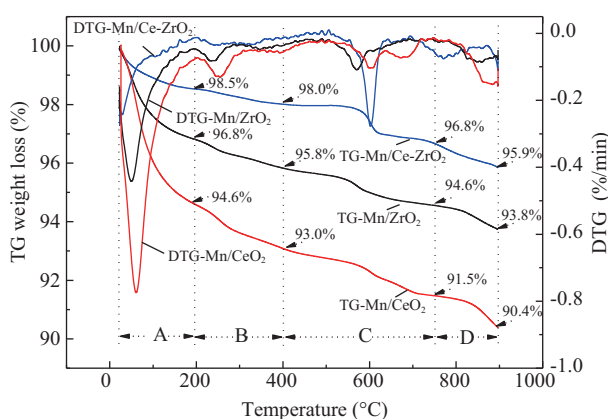

Fig. 9 TGA of the catalysts after 6 hr treatment with H$_2$O and SO$_2$.

the peaks at 1373, 1379 or 1382 cm^{-1} arising from the nitrate species spectrum (Huang and Yang, 2001) were clearly larger in the used catalysts than those in the fresh ones. The peaks in the fresh catalysts could be attributed to incompletely decomposed Mn(NO$_3$)$_2$. Previous reports (Madia et al., 2002; Liu and He, 2010) have pointed out that NH$_4$NO$_3$ can form on the surface of the catalysts during the reaction process and it could exist stably, because its decomposition temperature is about 200°C. Therefore, the larger peaks in the used catalysts could be attributed to NH$_4$NO$_3$ formation during the reaction process. After reaction, Mn/CeO$_2$ had the sharpest band around 1104 cm^{-1} but Mn/Ce-ZrO$_2$ had the weakest band around 1106 cm^{-1}. The result showed that Mn/Ce-ZrO$_2$ had the weakest sulfation during the reaction process. The poisoning effect of SO$_2$ on catalysts mainly took place via two approaches: the deposition of ammonium sulfate on the catalyst surface covering available active sites (Huang et al., 2002; Yu et al., 2010; Zhu et al., 2001) and the sulfation of active components resulting in their inactivation (Kijlstra et al., 1997, 1998). Therefore, the weak sulfation of Mn/Ce-ZrO$_2$ corresponded to its good resistance to SO$_2$ poisoning.

TGA were performed to distinguish the species of sulfate salts on the surfaces of the used catalysts, and the results are shown in **Fig. 9**. It can be seen that the

weight losses of the used catalysts can be divided into four phases according to the peaks from DTG: A (< 200°C), B (200°C–400°C), C (400–750°C), and D (> 750°C). These four phases can be attributed to the departure of water molecules and hydration, the decomposition of ammonia sulfate and ammonium bisulfate (Mao et al., 2011), the decomposition of cerous sulfate and zirconium sulfate (Strydom and Pretorius, 1993; Poston et al., 2003) and the decomposition of manganese sulfate (Mao et al., 2011), respectively. The weight losses in different phases are shown in **Table 3**. It can be seen that the weight losses corresponding to the dehydration process and the decomposition of sulfates in Mn/Ce-ZrO$_2$ were much lower than those in Mn/CeO$_2$. This indicated that there were fewer water molecules and less hydration and sulfate forming on Mn/Ce-ZrO$_2$ than on Mn/CeO$_2$. These results agreed well with the outcomes of the resistance to SO$_2$ and H$_2$O of Mn/Ce-ZrO$_2$, Mn/ZrO$_2$ and Mn/CeO$_2$.

Table 3 Different weight losses for the used catalysts

Sample	Weight loss resulting from the dehydration process (%)	Weight loss resulting from the decomposition of sulfates (%)		
		Ammonia sulfate	Cerous and zirconium sulfate	Manganese sulfate
Mn/Ce-ZrO$_2$	1.5	0.5	1.2	0.9
Mn/ZrO$_2$	3.2	1.0	1.2	0.8
Mn/CeO$_2$	5.4	1.6	1.5	1.1

3 Conclusions

In this work, CeO$_2$, ZrO$_2$ and a mixture of Ce-ZrO$_2$ were used to support manganese oxides. It was found that Mn/Ce-ZrO$_2$ and Mn/CeO$_2$ have better low-temperature activities than Mn/ZrO$_2$. This was mainly due to the higher dispersion of manganese oxides, better redox character and more surface adsorbed oxygen of Mn/Ce-ZrO$_2$ and Mn/CeO$_2$ compared to Mn/ZrO$_2$. Furthermore, Mn/Ce-ZrO$_2$ had better resistance to SO$_2$ and H$_2$O due to the weak
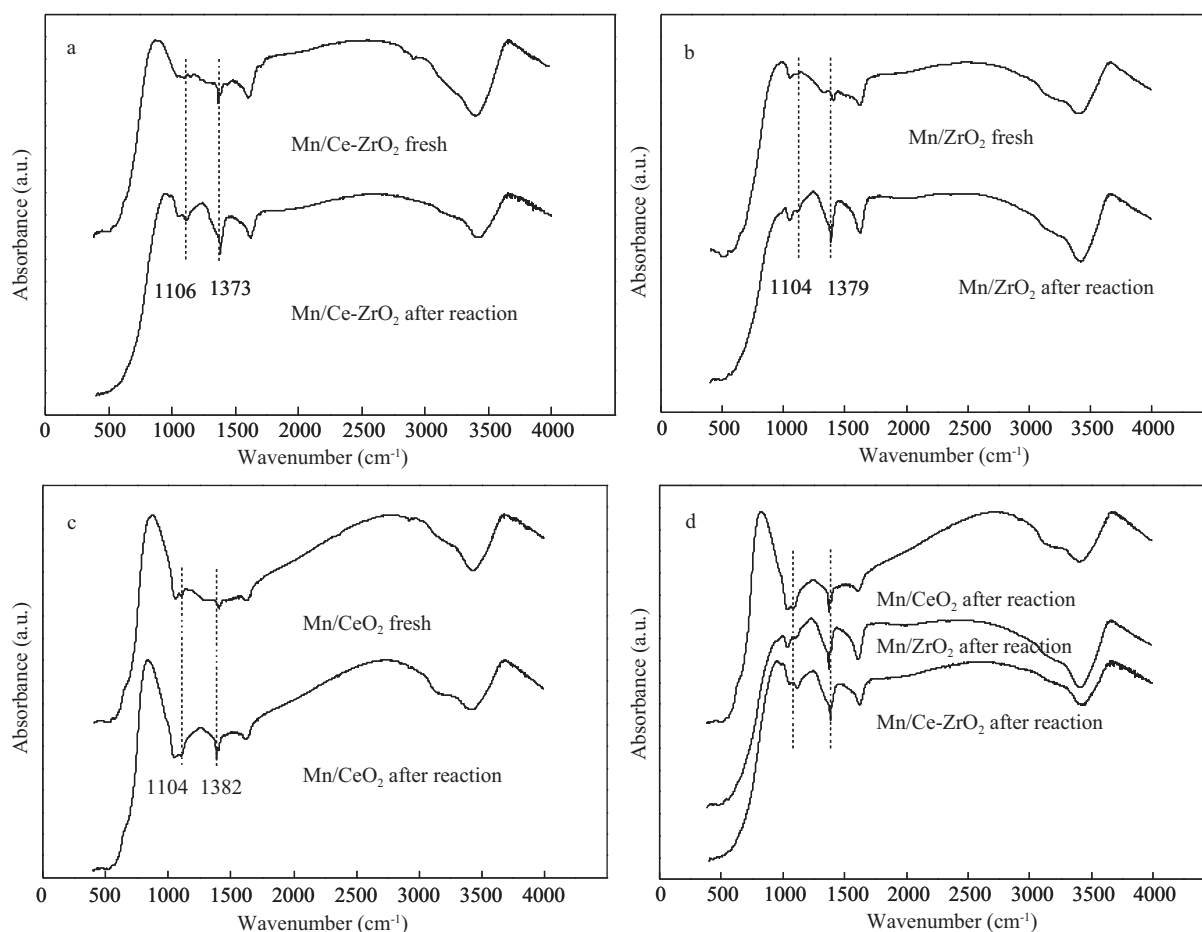
Fig. 8　FT-IR spectrum of the catalysts before and after 6 hr treatment with H_2O and SO_2.

water absorption and weak sulfation process on the surface of the catalyst.

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