1. Introduction

Nitrogen oxides (NOx), which emitted from stationary and mobile sources, caused serious atmospheric pollution and destroyed the ecological environment [1–4]. Therefore, it is an urgent task to control the emission of NOx. In the past decades, many purification techniques have been developed to satisfy this purpose. In which, the selective catalytic reduction of NOx by NH3 (i.e., NH3-SCR) is considered as the most cost-effective method to remove NOx from the flue gas of thermal power plants [5–8]. It is well known that the commercial denitration catalysts are V2O5-WO3/TiO2 or V2O5-MoO3/TiO2, which exhibit excellent catalytic performance between 300 and 400 °C, but not suitable for low-load operating condition and low-temperature denitration (below 300 °C) [9–11].

However, in order to slow down the deactivation of denitration catalysts caused by dusts and SO2, the denitration unit is planned to be installed downstream of the precipitator and desulfurization device, where the concentration of dusts and SO2 has been decreased greatly [10]. Simultaneously, with regard to the transformation of the old thermal power plants, the denitration unit can only be added downstream of the precipitator and desulfurization device, because there is no enough space to install upstream of the precipitator and desulfurization device. However, the temperature of flue gas is remarkably lower than 300 °C after dusts removal and desulfurization. Therefore, the development of low-temperature denitration catalysts to satisfy this operating condition becomes a hot research topic.

Recently, MnOx/CeO2 catalysts have been widely investigated in low-temperature NH3-SCR reaction due to their excellent catalytic performance [12–16]. However, the operating temperature window and water resistance need to be further improved to satisfy the practical denitration application. Therefore, many methods have been adopted to broaden the operating temperature window and enhance the water resistance, such as the introduction of modifiers, change of preparation methods, modulation of synthesis...
parameters, and so on, which can remarkably affect the physicochemical properties of MnO$_2$/CeO$_2$ catalysts [10,17–20]. Liu et al. [21] prepared a series of MnO$_2$–CeO$_2$ catalysts with the acetic-acid-chelated titania support, and used for low-temperature NH$_3$–SCR reaction. They found that their catalytic performance is obviously better than that of commercial TiO$_2$–supported MnO$_2$–CeO$_2$ catalysts due to the high dispersion of active species. Furthermore, Ge et al. [22] reported that the dispersion of CeO$_2$ on the surface of γ-Al$_2$O$_3$ support is highly dependent on the solvents (water and acetic acid), which leads to the different physicochemical properties and catalytic performance of CuO–CeO$_2$/γ-Al$_2$O$_3$ catalysts for NO reduction by CO. However, as far as we know, the solvent effect on the dispersion of active species and the catalytic performance of MnO$_2$/CeO$_2$ catalysts for low-temperature NH$_3$–SCR reaction has not been reported.

Therefore, in the present work, we prepared a series of MnO$_2$/CeO$_2$ catalysts by modulating the solvents (deionized water (DW), anhydrous ethanol (AE), acetic acid (AA), and oxalic acid (OA) solution) with the purpose of improving the low-temperature NH$_3$–SCR performance, broadening the operating temperature window, and enhancing the H$_2$O + SO$_2$ resistance. The prepared catalysts were characterized by means of N$_2$–physisorption, XRD, EDS mapping, Raman, XPS, H$_2$–TPR, NH$_3$–TPD, in situ DRIFTS, and NH$_3$–SCR model reaction to explore the effect of solvents on the physicochemical properties, catalytic performance, and H$_2$O + SO$_2$ resistance of MnO$_2$/CeO$_2$ catalysts.

2. Experimental section

2.1. Catalysts preparation

CeO$_2$ was obtained by thermal decomposition of Ce(NO$_3$)$_3$·6H$_2$O at 500 °C for 5 h in the flowing air, and then, used as a support to prepare supported MnO$_2$/CeO$_2$ catalysts. In detail, CeO$_2$ was wet impregnated with required amount of Mn(NO$_3$)$_2$ solution in different solvents of deionized water (DW), anhydrous ethanol (AE), acetic acid (AA), and 0.1 M oxalic acid (OA) solution, respectively. The suspension was kept in magnetic stirring for 1 h and evaporated to remove the solvents at 110 °C during an oil bath. The obtained cakes were oven dried at 110 °C for 12 h, and finally calcined at 450 °C for 5 h in the flowing air. Furthermore, the loading amount of MnO$_x$ was fixed at 0.5 mmol MnO$_x$/g-CeO$_2$. The prepared catalysts were denoted as Mn/Ce–DW, Mn/Ce–AE, Mn/Ce–AA, and Mn/Ce–OA, respectively.

2.2. Catalysts characterization

Textural characteristics of these catalysts were obtained by N$_2$–physisorption at 77 K on a Belsorp-max analyzer via the Brunauer–Emmet–Teller (BET) method. Before each analysis, the catalyst was degassed under vacuum at 300 °C for 4 h.

X-ray diffraction (XRD) patterns of these catalysts were collected on a Philips X’Pert 3 Powder diffractometer with Ni-filtered Cu K$_x$ radiation ($\lambda = 0.15418$ nm). X-ray tube was operated at 40 kV and 40 mA.

Energy dispersive spectrometer (EDS) mapping images of these catalysts were captured on a Philips XL30 scanning electron microscopy (SEM) equipped with an Oxford EDS analysis system operated at beam energy of 10 kV.

Raman spectra of these catalysts were recorded on a Renishaw inVia Reflex Laser Raman spectrometer with Ar$^+$ laser beam. The excitation wavelength and laser power are 532 nm and 5 mW, respectively. X-ray photoelectron spectra (XPS) of these catalysts were collected on a PHI 5000 VersaProbe system with monochromatic Al K$\alpha$ radiation (1486.6 eV), operating at an accelerating power of 15 kW. Prior to the measurement, the catalyst was outgassed in a UHV chamber (<5 × 10$^{-7}$ Pa) at ambient temperature. The charging effect of the sample was compensated by calibrating the binding energy with C 1 s peak at 284.6 eV.

H$_2$-temperature programmed reduction (H$_2$–TPR) experiments were carried out on a dynamic sorption analyzer (TP-5076) with a thermal conductivity detector (TCD). The reductant is H$_2$–Ar mixture (7% H$_2$ by volume, 30 ml min$^{-1}$). Before the reduction, 50 mg catalyst was pretreated in high purified N$_2$ (30 ml min$^{-1}$) at 300 °C for 1 h, and then cooled to ambient temperature. After that, the H$_2$–TPR started from room temperature to 600 °C at a rate of 10 °C min$^{-1}$.

NH$_3$–temperature programmed desorption (NH$_3$–TPD) experiments were also performed on a dynamic sorption analyzer (TP-5076). 200 mg catalyst was pretreated in high purified N$_2$ (30 ml min$^{-1}$) at 300 °C for 1 h. And then, the catalyst adsorbed NH$_3$–N$_2$ mixture (1% NH$_3$ by volume, 30 ml min$^{-1}$) at 100 °C for 1 h to be saturated, and subsequently flushed with high purified N$_2$ (30 ml min$^{-1}$) at the same temperature for 1 h to eliminate the gaseous NH$_3$, and further cooled to ambient temperature. Finally, the desorption process was carried out from room temperature to 700 °C at a rate of 10 °C min$^{-1}$.

In situ diffuse reflectance infrared Fourier transform spectra (in situ DRIFTS) of these catalysts by NH$_3$ adsorption were collected on a Nicolet 5700 FT-IR spectrometer with a high-sensitive MCT detector. Prior to the test, the catalyst was pretreated in high purified N$_2$ at 300 °C for 1 h to remove the surface adsorbed water. The sample background of each target temperature was collected during the cooling process. At room temperature, the catalyst was exposed to NH$_3$–N$_2$ mixture (1% NH$_3$ by volume, 50 ml min$^{-1}$) for 1 h to be saturated. And then, the gaseous NH$_3$ was purged by high purified N$_2$ (50 ml min$^{-1}$) for 1 h at room temperature. In situ DRIFTS were recorded at various target temperatures from room temperature to 300 °C at a rate of 10 °C min$^{-1}$ in high purified N$_2$ by subtraction of the corresponding background reference.

2.3. Catalytic performance measurement

The catalytic performance of these catalysts for NH$_3$–SCR model reaction was measured under steady state, involving a feed stream with a fixed composition of 500 ppm NO, 500 ppm NH$_3$, 5% O$_2$, 5% H$_2$O (when used), 100 ppm SO$_2$ (when used), and N$_2$ in balance. 400 mg catalyst was fitted in a quartz tube and pretreated in high purified N$_2$ at 300 °C for 1 h, and then cooled to room temperature. After that, the mixed reaction gases were switched on. The reaction was conducted at different temperatures with a space velocity of 60,000 ml g$^{-1}$ h$^{-1}$. NO concentration of inlet ([NO]$_{in}$) and outlet ([NO]$_{out}$) was detected by a chemiluminescence NO analyzer. The concentration of by-product N$_2$O was measured by a N$_2$O analyzer. All of the data were collected after waiting for 30 min until the gaseous composition reached steady state at each reaction temperature. The same experiment was repeated three times, and taken the average value to ensure the reproducibility of the data and reduce the corresponding experimental error. Finally, NO conversion was calculated from the following equation:

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

In addition, steady state kinetic measurements were carried out on these catalysts. Prior to each test, the catalyst was diluted 5 times by quartz sand to decrease the influence of diffusion on NO.
conversion. The apparent activation energy ($E_a$) for NH$_3$-SCR model reaction over these catalysts was obtained from Arrhenius formula:

$$Lnk = LnA - \frac{E_a}{RT}$$

(2)

In which, $k$ is the reaction rate constant, $A$ is the pre-exponential factor, $R$ is the standard gas constant, and $T$ is the reaction temperature.

3. Results and discussion

3.1. Catalytic performance and H$_2$O + SO$_2$ resistance (NH$_3$-SCR model reaction)

Catalytic performance of these MnO$_x$/CeO$_2$ catalysts for low-temperature NH$_3$-SCR reaction is exhibited in Fig. 1. It can be seen from Fig. 1(a) that all of these catalysts present the same change trend during the heating process: firstly, NO conversion increases rapidly with the elevation of reaction temperature; secondly, the growth of NO conversion begins to slow with further elevation of reaction temperature; finally, NO conversion declines gradually when the temperature is above 200 °C due to the oxidation of NH$_3$ [9]. In addition, for Mn/ Ce-DW catalyst, NO conversion is below 80% during the whole test temperature range of 50–300 °C. However, Mn/ Ce-OA catalyst exhibits above 80% NO conversion during a wide operating temperature range of 100–250 °C. NO conversion of Mn/ Ce-AE and Mn/ Ce-AA catalysts is located between Mn/ Ce-DW and Mn/ Ce-OA catalysts. In other words, the catalytic activity of these MnO$_x$/CeO$_2$ catalysts for low-temperature NH$_3$-SCR reaction can be ranked by Mn/ Ce-DW < Mn/ Ce-AE < Mn/ Ce-AA < Mn/ Ce-OA.

It is well known that the target products for NH$_3$-SCR of NO are N$_2$ and H$_2$O. However, by-product N$_2$O usually generates during the reaction process due to the non-selective oxidation of NH$_3$ and partial reduction of NO, which is also an important air pollutant. Therefore, the generated N$_2$O concentration was also detected in the whole reaction temperature range of 50–300 °C to further evaluate the catalytic performance of these MnO$_x$/CeO$_2$ catalysts, and the results are presented in Fig. 1(b). When the temperature is below 250 °C, N$_2$O concentration of Mn/ Ce-DW, Mn/ Ce-AE, and Mn/ Ce-OA catalysts is very similar, which is obviously lower than that of Mn/ Ce-AA catalyst. Moreover, when the temperature is above 250 °C, Mn/ Ce-OA catalyst exhibits the lowest N$_2$O concentration. Combining with the results of NO conversion in Fig. 1(a), we can conclude that Mn/ Ce-OA catalyst displays the best catalytic performance for NH$_3$-SCR of NO to N$_2$ among these MnO$_x$/CeO$_2$ catalysts. Furthermore, Fig. 1(c) shows that the measured apparent activation energy ($E_a$) of NO conversion over these MnO$_x$/CeO$_2$ catalysts is 56.24, 32.73, 21.23, and 13.79 kJ mol$^{-1}$ for Mn/ Ce-DW, Mn/ Ce-AE, Mn/ Ce-AA, and Mn/ Ce-OA, respectively. The obtained results suggest that the removal of NO is the easiest on the surface of Mn/ Ce-OA catalyst, while the most difficult over Mn/ Ce-DW catalyst, which is consistent with the results of catalytic activity.

It is well known that H$_2$O + SO$_2$ resistance of low-temperature denitration catalysts is another important indicator in the practical application. Therefore, we evaluated the H$_2$O + SO$_2$ resistance of these MnO$_x$/CeO$_2$ catalysts, and the corresponding results are shown in Fig. 2. It can be seen from this figure that NO conversion of these MnO$_x$/CeO$_2$ catalysts decreases to some extent when H$_2$O and SO$_2$ are introduced; once the H$_2$O and SO$_2$ are cut off, NO conversion recovers gradually, but not recovers completely due to the generation of surface hydroxyl groups and the deposition of sulfates [6,23]. Interestingly, we can find that Mn/ Ce-OA catalyst exhibits the highest NO conversion among these MnO$_x$/CeO$_2$ catalysts during the whole test process, which indicates that Mn/ Ce-OA catalyst is the most promising for practical application. The obtained results indicate that the solvents can remarkably influence the catalytic performance of these MnO$_x$/CeO$_2$ catalysts in the absence and presence of H$_2$O and SO$_2$ for NH$_3$-SCR reaction. In order to further clarify the reason, the physicochemical properties of these catalysts are characterized and discussed in the following sections.

3.2. Textural and structural characteristics (N$_2$-physisorption, XRD, EDS mapping, and Raman)

The textural properties (such as BET specific surface area and pore structure) of denitration catalysts can remarkably affect their catalytic performance, but we find that BET specific surface area, total pore volume, and mean pore diameter of these MnO$_x$/CeO$_2$ catalysts with different solvents have no obvious difference in Table 1. It suggests that textural property is not the most important parameter.
Table 1  
BET specific surface area, total pore volume, and mean pore diameter of these MnO$_x$/CeO$_2$ catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET specific surface area (m$^2$ g$^{-1}$)</th>
<th>Total pore volume (cm$^3$ g$^{-1}$)</th>
<th>Mean pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn/Ce-DW</td>
<td>61.2</td>
<td>0.2048</td>
<td>13.4</td>
</tr>
<tr>
<td>Mn/Ce-AE</td>
<td>57.3</td>
<td>0.2022</td>
<td>14.1</td>
</tr>
<tr>
<td>Mn/Ce-AA</td>
<td>60.2</td>
<td>0.2100</td>
<td>14.0</td>
</tr>
<tr>
<td>Mn/Ce-OA</td>
<td>60.7</td>
<td>0.2014</td>
<td>13.3</td>
</tr>
</tbody>
</table>

Fig. 2. H$_2$O + SO$_2$ resistance of these MnO$_x$/CeO$_2$ catalysts at 200 °C.

influence factor in our present work. Therefore, we also carried out structural characterization over these MnO$_x$/CeO$_2$ catalysts. Fig. 3 shows that only the diffraction peaks of cubic fluorite-type structure CeO$_2$ can be detected in the XRD patterns of these MnO$_x$/CeO$_2$ catalysts, while the signals of MnO$_x$ are absent, which indicate that MnO$_x$ species are highly dispersed on the surface of CeO$_2$. However, there is no more information about the solvent effect on the dispersion of MnO$_x$ species can be given from XRD results. Moreover, in order to figure out the solvent effect on the dispersion of MnO$_x$ species, EDS mapping experiment was carried out, and the corresponding results are displayed in Fig. 4. We can find that the dispersion of MnO$_x$ species over Mn/Ce-AE, Mn/Ce-AA, and Mn/Ce-OA catalysts is remarkably better than that of Mn/Ce-DW catalyst.

Fig. 3. XRD patterns of these MnO$_x$/CeO$_2$ catalysts.

Fig. 4. EDS mapping images of these MnO$_x$/CeO$_2$ catalysts.
which suggests that the solvents of anhydrous ethanol (AE), acetic acid (AA), and oxalic acid (OA) solution can efficiently promote the dispersion of MnOx species on the surface of CeO2 compared with deionized water (DW) as a solvent. Furthermore, Raman spectra of these MnOx/CeO2 catalysts exhibit a main vibration band at 462 cm⁻¹ and a wide shoulder around 608 cm⁻¹, which can be attributed to F2g vibration mode of cubic fluorite-type structure CeO2 and defect-induced mode (denoted as D) related to oxygen vacancy, respectively (Fig. 5) [24–26]. It is widely reported that oxygen vacancy can promote the dissociation of NOx species, which is beneficial to the enhancement of catalytic performance for denitrification reaction [27]. Quantitative analysis of Raman spectra shows that the oxygen vacancy concentration (i.e., I_D/I_F2g) of these MnOx/CeO2 catalysts is in the order of Mn/Ce-DW < Mn/Ce-AA < Mn/Ce-OA, which is consistent with the results of catalytic performance. These phenomena indicate that the solvents can obviously influence the dispersion of MnOx species, and consequently lead to different electron interaction between MnOx and CeO2, and finally affect the generation of oxygen vacancy and the catalytic performance for NH3-SCR reaction.

3.3. Surface analysis (XPS)

In order to further investigate the solvent effect on the surface properties of these MnOx/CeO2 catalysts, XPS measurements were carried out, and the corresponding results are presented in Fig. 6. Ce 3d spectra (Fig. 6(a)) of these MnOx/CeO2 catalysts can be fitted with eight binding energy peaks, labeled as u, v, u′, v′, u″, v″, u‴, and v‴, respectively. In which, u″ and v‴ are attributed to Ce³⁺, while the other six peaks are ascribed to Ce⁴⁺ [28–30]. The results of Mn 2p spectra (Fig. 6(b)) exhibit that Mn⁴⁺, Mn³⁺, and Mn²⁺ co-exist on the surface of these MnOx/CeO2 catalysts due to the interaction between MnOx and CeO2 through electron transfer [31]. It is widely reported that the appearance of Ce³⁺ is accompanied with the generation of oxygen vacancy, and further promotes the dissociation of NOx species; Mn⁴⁺ is beneficial to the oxidation of NO to NO₂, and enhances the catalytic performance for NH3-SCR reaction through a “fast SCR” route [20,31]. Therefore, the contents of Ce³⁺ and Mn⁴⁺ on the surface of these MnOx/CeO2 catalysts are calculated from XPS, and listed in Table 2. We can find that both of Ce³⁺ and Mn⁴⁺ contents are in the order of Mn/Ce-DW < Mn/Ce-AA < Mn/Ce-OA, which is in agreement with the results of catalytic performance. In addition, it is well known that surface oxygen species of the denitrification catalysts also benefit for the oxidation of NO to NO₂, and enhances the catalytic performance for NH₃-SCR reaction through a “fast SCR” route. So, O 1s spectra of these MnOx/CeO2 catalysts are analyzed carefully. Fig. 6(c) shows that O 1s spectra of these catalysts can be fitted with two components, the strong binding energy peak at 529.0 eV (O′) is assigned to the lattice oxygen, and the shoulder around 531.2 eV (O″) is attributed to the surface adsorbed oxygen species [32]. Interestingly, the content of O″ (i.e., O″/(O′ + O″)) is also in the order of Mn/Ce-DW < Mn/Ce-AA < Mn/Ce-OA (Table 2), which is consistent with the results of catalytic performance. Moreover, the atomic ratio of Mn/Oe over these MnOx/CeO2 catalysts is also ranked by Mn/Ce-DW < Mn/Ce-AA < Mn/Ce-OA, which further indicates that the solvents can significantly influence the dispersion of MnOx species. Especially, XPS analysis suggests that the solvent of oxalic acid (OA) is more beneficial to the dispersion of MnOx species on the surface of CeO2 (i.e., Mn/Ce-OA catalyst), and consequently leads to largest amounts of Ce³⁺, Mn⁴⁺, and surface adsorbed oxygen species, and finally exhibits the most excellent catalytic performance for NH3-SCR reaction.

3.4. Reduction behavior and surface acidity (H₂-TPR, NH₃-TPD, and NH₃ adsorption in situ DRIFTS)

It is well known that the redox properties and surface acidities of denitrification catalysts are the most important influence factors for NH3-SCR reaction. Therefore, we adopted H₂-TPR and NH₃-TPD techniques to investigate the redox properties and surface acidities of these MnOx/CeO2 catalysts, respectively, as shown in Fig. 7. H₂-TPR profiles of these MnOx/CeO2 catalysts (Fig. 7(a)) exhibit three reduction peaks α, β, and γ, which can be ascribed to the step-wise reduction of MnOx. i.e., MnO₂/Mn₂O₃ → Mn₃O₄ → MnO → Mn. The reduction of surface CeO₂, respectively [32,33]. Interestingly, we can find that H₂ consumption of these MnOx/CeO2 catalysts is in the order of Mn/Ce-DW < Mn/Ce-AA < Mn/Ce-OA, which is consistent with the results of catalytic performance. Moreover, the atomic ratio of Mn/Oe over these MnOx/CeO2 catalysts is also ranked by Mn/Ce-DW < Mn/Ce-AA < Mn/Ce-OA, which further indicates that the solvents can significantly influence the dispersion of MnOx species. Especially, XPS analysis suggests that the solvent of oxalic acid (OA) is more beneficial to the dispersion of MnOx species on the surface of CeO2 (i.e., Mn/Ce-OA catalyst), and consequently leads to largest amounts of Ce³⁺, Mn⁴⁺, and surface adsorbed oxygen species, and finally exhibits the most excellent catalytic performance for NH3-SCR reaction.

It can be seen from NH₃-TPD results (Fig. 7(b)) that all of these MnOx/CeO2 catalysts present four desorption peaks labeled as I, II, III, and IV, which are attributed to the desorption of physisorbed NH₃, and the desorption of NH₃ from weak, medium-strong, and strong acid sites, respectively [34]. Some interesting results are obtained from the quantitative analysis of NH₃-TPD (Table 4). Physisorption (peak I) is too weak to activate NH₃ molecules, while the adsorbed NH₃ species on strong acid sites (peak IV) are hardly to desorb, which are not much contribution to low-temperature NH₃-SCR reaction. Therefore, we focus on the adsorption of NH₃ molecules on weak and medium-strong acid sites (peaks II and III). Table 4 shows that the acid amounts of peak II and peak III (i.e., S₉ + S₁₀) over these MnOx/CeO2 catalysts are ranked by Mn/Ce-DW < Mn/Ce-AA < Mn/Ce-OA. In other word, Mn/Ce-AA catalyst possesses the largest amount of acid sites, which is beneficial to the adsorption and activation of NH₃ molecules, and further promotes the enhancement of catalytic performance for NH₃-SCR reaction.

In situ DRIFTS of NH₃ adsorption was carried out over the representative samples (Mn/Ce-DW and Mn/Ce-OA catalysts) to clarify the type of surface acid sites and the evolution of adsorbed NH₃
species during the heating process, as exhibited in Fig. 8. For Mn/Ce-DW catalyst (Fig. 8(a)), when it is exposed to NH3-N2 mixed gas at room temperature, NH3 molecules are adsorbed on the surface of Mn/Ce-DW catalyst to generate several IR vibration bands between 1000 and 1700 cm\(^{-1}\). According to the literatures, the bands at 1070, 1114, 1168, 1305, and 1580 cm\(^{-1}\) are attributed to NH3 molecules coordinated on Lewis (L) acid sites; while the bands at 1391 and 1440 cm\(^{-1}\) are ascribed to NH4\(^+\) ions bonded on Brønsted (B) acid sites [10,31,35]. Some interesting results can be obtained during the heating process: firstly, the bands of L acid at 1114 and 1580 cm\(^{-1}\) disappear when the temperature increases to

![Fig. 6. XPS spectra of these MnO\(_x\)/CeO\(_2\) catalysts: (a) Ce 3d, (b) Mn 2p, and (c) O 1s.](image)

**Table 2**
The surface composition and atomic ratio of these MnO\(_x\)/CeO\(_2\) catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Atomic concentration (at%)</th>
<th>Atomic ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce</td>
<td>Mn</td>
</tr>
<tr>
<td>Mn/Ce-DW</td>
<td>17.71</td>
<td>1.95</td>
</tr>
<tr>
<td>Mn/Ce-AE</td>
<td>17.84</td>
<td>3.83</td>
</tr>
<tr>
<td>Mn/Ce-AA</td>
<td>15.79</td>
<td>3.91</td>
</tr>
<tr>
<td>Mn/Ce-OA</td>
<td>16.34</td>
<td>4.96</td>
</tr>
</tbody>
</table>

**Table 3**
The information of peak temperature and H\(_2\) consumption of these MnO\(_x\)/CeO\(_2\) catalysts obtained from H\(_2\)-TPR.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Peak temperature (°C)</th>
<th>H(_2) consumption (μmol g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T_{10})</td>
<td>(T_{30})</td>
</tr>
<tr>
<td>Mn/Ce-DW</td>
<td>235</td>
<td>314</td>
</tr>
<tr>
<td>Mn/Ce-AE</td>
<td>228</td>
<td>309</td>
</tr>
<tr>
<td>Mn/Ce-AA</td>
<td>217</td>
<td>309</td>
</tr>
<tr>
<td>Mn/Ce-OA</td>
<td>209</td>
<td>283</td>
</tr>
</tbody>
</table>

**Table 4**
Quantitative analysis of NH\(_3\)-TPD over these MnO\(_x\)/CeO\(_2\) catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Acid amount (a.u.)</th>
<th>Total acid amount (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(S_1)</td>
<td>(S_3)</td>
</tr>
<tr>
<td>Mn/Ce-DW</td>
<td>1296</td>
<td>1232</td>
</tr>
<tr>
<td>Mn/Ce-AE</td>
<td>908</td>
<td>1486</td>
</tr>
<tr>
<td>Mn/Ce-AA</td>
<td>961</td>
<td>1424</td>
</tr>
<tr>
<td>Mn/Ce-OA</td>
<td>1014</td>
<td>1460</td>
</tr>
</tbody>
</table>

**Fig. 6.** XPS spectra of these MnO\(_x\)/CeO\(_2\) catalysts: (a) Ce 3d, (b) Mn 2p, and (c) O 1s.
150 °C; secondly, two new bands appear at 1263 and 1594 cm⁻¹ at the same temperature of 150 °C, which are assigned to the deformation species of coordinated NH₃ [10]; finally, all of these IR bands related to NH₃ adsorption decrease gradually with the elevation of temperature to 300 °C. In situ DRIFTS of NH₃ adsorption over Mn/Ce-OA catalyst shows that IR bands of L species, deformation species of coordinated NH₃, and B species can also be detected at the corresponding positions (Fig. 8(b)). Interestingly, compared with Mn/Ce-DW catalyst, the bands related to deformation species of coordinated NH₃ over Mn/Ce-OA catalyst appear at a lower temperature of 75 °C, which indicates that Mn/Ce-OA catalyst is more efficient to activate the adsorbed NH₃ species. Furthermore, it is widely reported that the strength of L acid is obviously stronger than that of B acid [34,36]. Therefore, B acid may be more important than L acid for low-temperature NH₃-SCR reaction, while the situation of high-temperature NH₃-SCR reaction is just the opposite. Consequently, we further investigate the revolution of integral peak area of B acid with the increase of temperature over Mn/Ce-DW and Mn/Ce-OA catalysts (Fig. 9). We can find that both of them exhibit a similar volcanic curve, while the peak area of B acid over Mn/Ce-OA catalyst is remarkably larger than that on Mn/Ce-DW catalyst during the heating process, which indicates that Mn/Ce-OA catalyst is more beneficial to the adsorption and activation of NH₃ molecules.

3.5. Interaction with reactants (NO + NH₃ + O2 co-adsorption in situ DRIFTS)

In order to investigate the interaction between MnOₓ/CeO₂ catalysts and reactants to further understand the reaction mechanism of NH₃-SCR, in situ DRIFTS of NO + NH₃ + O₂ co-adsorption were performed. Firstly, the catalyst was placed in an in situ DRIFTS cell and pretreated with high purified N₂ at 300 °C for 1 h to eliminate the physisorbed water. Secondly, the sample background of each target temperature was collected in the cooling process. At
room temperature, the catalyst was exposed to a NO-NH3-O2-N2 mixture (3000 ppm NO, 3000 ppm NH3, and 5% O2 by volume) at a rate of 50 ml min\(^{-1}\) for 1 h to be saturated. Finally, in situ DRIFTS data were recorded at various target temperatures from room temperature to 300 °C at a rate of 10 °C min\(^{-1}\) by subtraction of the corresponding sample background. In situ DRIFTS of NO + NH3 + O2 co-adsorption for the representative MnOx/CeO2 catalysts are displayed in Fig. 10. For Mn/Ce-DW catalyst (Fig. 10(a)), when it is exposed to the NO-NH3-O2-N2 mixed gases at room temperature, several IR vibration bands related to the adsorbed NOx and NH3 species are observed between 1000 and 1600 cm\(^{-1}\). According to some literatures \cite{10, 11, 37–39}, the bands at 1017 and 1579 cm\(^{-1}\) are attributed to bidentate nitrates; the band at 1239 cm\(^{-1}\) can be ascribed to bridging nitrates; while the bands at 1278 and 1540 cm\(^{-1}\) are assigned to monodentate nitrates. Furthermore, combining with the results of NH3 adsorption in situ DRIFTS, the bands at 1314 and 1432 cm\(^{-1}\) are related to NH3 molecules coordinated on L acid sites and NH4\(^{+}\) ions bonded on B acid sites, respectively. Some interesting phenomena can be observed in the heating process: firstly, the bands of L acid and B acid disappear at 175 °C due to the desorption of NH3 as well as the reaction between the adsorbed NH3 species and NOx species; secondly, the band intensity of bidentate nitrates, bridging nitrates, and monodentate nitrates increases with the elevation of temperature, and tends to steady state from 175 to 225 °C, while decreases with further increase of temperature to 300 °C. However, IR signals of the main by-product N2O and reactants (NO and NH3) are not detected during the heating process, which is because that the signals of these gas-phase molecules are obviously weaker than those of the adsorbed species.

With regard to Mn/Ce-OA catalyst (Fig. 10(b)), all the bands of bidentate nitrates, monodentate nitrates, L acid, and B acid can be detected at the corresponding positions. Moreover, a new band for L acid appears at 1178 cm\(^{-1}\) \cite{10, 31}, which may be related to its larger amount of acid sites than Mn/Ce-DW catalyst. Interestingly, we can find that all of the L acid and B acid disappear at a lower temperature of 150 °C, while two new bands of bridging nitrates (1211 cm\(^{-1}\)) and monodentate nitrates (1493 cm\(^{-1}\)) appear at 100 °C \cite{10, 38}, which suggest that Mn/Ce-OA catalyst is more beneficial to the activation and transformation of the adsorbed NH3 species and NOx species than Mn/Ce-DW catalyst. These phenomena can be explained from the following aspects: firstly, the results of NH3-TPD and NH3 adsorption in situ DRIFTS present that Mn/Ce-OA catalyst displays the largest amount of acid sites, which is beneficial to the adsorption and activation of NH3 molecules; secondly, the results of H2-TPR and XPS show that Mn/Ce-OA catalyst exhibits the most excellent redox property as well as the largest amounts of Mn4\(^{+}\) and surface adsorbed oxygen species, which can promote the oxidation of NO to NO2 and the further adsorption to form nitrates; finally, the results of Raman and XPS exhibit that Mn/Ce-OA catalyst possesses abundant of oxygen vacancy and Ce3\(^{+}\), which benefit for the dissociation and transformation of NOx species. All of these improved physicochemical properties result in the excellent catalytic performance and good H2O + SO2 resistance of Mn/Ce-OA catalyst for low-temperature NH3-SCR reaction.

4. Conclusions

In summary, we have carefully investigated the solvent effect on the physicochemical properties and catalytic performance of MnOx/CeO2 catalysts for low-temperature NH3-SCR reaction. The obtained results indicate that MnOx/CeO2 catalyst with oxalic acid as a solvent (i.e., Mn/Ce-OA catalyst) exhibits the best catalytic performance and good H2O + SO2 resistance. The reason may be that oxalic acid is beneficial to the dispersion of MnOx and enhances the electron interaction between MnOx and CeO2, which lead to the most excellent redox property and the largest amounts of oxygen vacancy, Ce3\(^{+}\), Mn4\(^{+}\), surface adsorbed oxygen species, and acid sites. Large amounts of Mn4\(^{+}\) and surface adsorbed oxygen species, as well as excellent redox property can promote the oxidation of NO to NO2; abundant of oxygen vacancy and Ce3\(^{+}\) benefit for the dissociation and transformation of NOx species; large amount of acid sites is conducive to the adsorption and activation of NH3 molecules. All of these result in the best catalytic performance and good H2O + SO2 resistance. In the present work, we have successfully enhanced the low-temperature NH3-SCR performance of MnOx/CeO2 catalysts by the optimal solvent effect, which can provide a scientific reference for the development of practical denitrification catalysts.

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References