Support modification for improving the performance of MnO$_x$–CeO$_y$/γ-Al$_2$O$_3$ in selective catalytic reduction of NO by NH$_3$

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**Highlights**
- Zr, Ti and Si were used to combine with Al as supports for Mn–Ce SCR catalysts.
- The SCR activity of MCA was enhanced by support modification.
- The deactivating effects of SO$_2$ on SCR could be reduced by addition of ZrO$_2$.
- The promotion brought by ZrO$_2$ addition was investigated comprehensively.

**Abstract**
The catalytic performances of catalysts with binary-oxides supports in selective catalytic reduction (SCR) of NO by NH$_3$ were studied. Binary metal oxides supports γ-Al$_2$O$_3$–SiO$_2$, γ-Al$_2$O$_3$–TiO$_2$, and γ-Al$_2$O$_3$–ZrO$_2$ were prepared by hydrolyzation and coprecipitation methods, after that MnO$_x$–CeO$_y$ was loaded using isovolumetric impregnation method. Characterizations for the samples involved N$_2$ adsorption–desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), H$_2$ temperature programmed reduction (H$_2$-TPR) and Fourier Transform infrared spectroscopy (FTIR). In the SCR tests, MnO$_x$–CeO$_y$/γ-Al$_2$O$_3$–ZrO$_2$ (MCAZ) showed outstanding NO removal efficiency and could abate the deactivation brought by SO$_2$ and H$_2$O. Moreover, the fluctuation of gas hourly space velocity (GHSV) appeared only a bit of influence on the activity at middle temperature. The characterization results exhibited that MnO$_x$–CeO$_y$/γ-Al$_2$O$_3$–ZrO$_2$ owned bigger specific surface area and appropriate pore diameter, highly dispersed amorphous Mn$_3$O$_4$ as well as rational ratio of Ce$^{4+}$/Ce$^{3+}$. The H$_2$-TPR results presented the promotion of the activity was partially due to the stronger oxidation ability at lower temperature. Through the FTIR analysis, and combining with the mechanism proposed by earlier research, it was supposed that the highly reactive nitrates on the surface favored the high NO conversion. Besides, FTIR revealed that the bidentate sulfates formed by adsorbed SO$_2$ produced new Lewis acid sites which promoted NH$_3$ adsorption and reduced the poisoning effect of SO$_2$ and H$_2$O.

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1. Introduction

Nitrogen oxides (NO, NO$_2$, and N$_2$O) emitted by stationary sources and mobile sources were the major sources of air pollution [1–3]. Due to the outstanding removal efficiency, highly N$_2$ selectivity and reasonable economic costs, selective catalytic reduction (SCR) is regarded as one of the most effective post-combustion technologies for the abatement of nitrogen oxides emission [1,4,5]. However, as the most widely engaged catalysts, V$_2$O$_5$/TiO$_2$ (with addition of WO$_3$ or MoO$_3$) catalysts are efficient only within a narrow temperature window of 300–400 °C, that means the SCR reactor has to be installed upstream the particulate collector and desulfurization, under which circumstance the catalyst will be attrited, sintered and poisoned by the dust and SO$_2$ in the flue gas soon [6–8]. Furthermore, the H$_2$O in the flue gas contributes to partially destroying the acid sites and then leads to the catalyst’s deactivation [9,10]. Considering these handicaps, placing the reactor downstream the particulate collector and desulfurization is a feasible solution. Therefore, the catalysts with excellent activity at low temperature and stable resistance to both SO$_2$ and H$_2$O receive quantities of attention in recent years.

To improve the catalyst’s performance, innovation of synthetic methods and component modification are considered as two crucial ways that work well. Thirupathi Boningari et al. optimized...
commercial SCR catalysts by adopting flame spray pyrolysis (FSP) synthesis technique [11] and investigated vanadia-based nanoparticles prepared by FSP with various supports [12]. In another way, component modification is more generally investigated due to its diversity as well as pertinence. Manganese oxides have attracted much interest for its high activity in NH3-SCR at low temperature. It has been corroborated that the activity of NO conversion is correlated with the valence of manganese and phase structure of MnOx [6,13]. Ceria has also been extensively studied as a SCR catalyst owing to its oxygen storage and redox properties [14,15]. Accordingly, scholars have tried a variety of Mn–Ce catalysts with different supports, such as MnOx–CeO2 binary-oxides catalyst [14,16–18], Mn–Ce/TiO2 [19–21], Mn–Ce/Al2O3 [20] and Mn–Ce/ ZSM5 [22]. However, due to the diverse properties of different support materials, each of them exhibits some bottlenecks which limit its application and further research [6,23,24]. Always, the carrier in the catalyst plays a role which affects the surface properties [25,26], mechanical properties, thermal stability [27,28], sulfur resistance [26,29,30] and SCR catalytic performance [23,31,32] of the catalyst. The doping of other metal oxides in the support aims at overcoming the weaknesses of the existing supports. Catalysts with binary-oxides carrier such as Ce/TiO2–SiO2 [26], Ce/TiO2– Al2O3 [29], Mn/γ-Al2O3(80%)–TiO2(20%) [33], ZrO2–V2O5/WO3– TiO2 [34] and MnOx/Co3O4-ZrO2 [29] are investigated recently. After the addition into the supports, indispensable properties including stronger sulfur resistance, higher specific surface areas and considerable redox abilities were confirmed, according to their SCR performances and characterization results.

In this study, aiming at promoting the SCR activities and resistance to SO2 and H2O, a second metal oxide (SiO2, TiO2, or ZrO2) was added into the support to modify MnOx–CeO2/γ-Al2O3. Besides, the superficial reaction stability and the effects of different gas hourly space velocities (GHSV) on the catalysts were also investigated respectively. To further investigate the changes of surface properties brought by the addition of the second metal, N2 adsorption-desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy analysis (XPS), H2 temperature programmed reduction (H2-TPR) and Fourier Transform infrared spectroscopy (FTIR) were carried out and analyzed in detail.

2. Experimental section

2.1. Preparation of catalysts

2.1.1. Preparation of MnOx/γ-Al2O3, MnOx–CeO2/γ-Al2O3, MnOx–CeO2/TiO2, MnOx–CeO2/SiO2 and MnOx–CeO2/ZrO2

In order to ascertain the best loading proportion of the active components (MnOx and CeOx), a series of MnOx/γ-Al2O3 and MnOx–CeO2/γ-Al2O3 were prepared by isovolumetric impregnation method. A requisite amount of manganese acetate (or both manganese acetate and cerium nitrate) was dissolved in ultrapure water, and then the γ-Al2O3 powder was added into the solution and uniformly mixed. The mixtures were impregnated for 24 h, dried at 100 °C for 6 h and calcined in a muffle furnace at 500 °C for 4 h. MnOx–CeO2/TiO2, MnOx–CeO2/SiO2 and MnOx–CeO2/ZrO2 were prepared by isovolumetric impregnation method using the best loading proportion of MnOx and CeOx.

2.1.2. Preparation of binary-oxides supports

In our work, γ-Al2O3–TiO2 and γ-Al2O3–SiO2 binary-oxides supports were prepared by hydrolyzation method while γ-Al2O3–ZrO2 was prepared by coprecipitation method. The proportions of γ-Al2O3/M are 3:1, 1:1, 1:3 (M represents TiO2, SiO2 or ZrO2, mole ratio) in the catalyst supports. A requisite amount of aluminum isopropoxide was dissolved in ultrapure water in the beakers.

The solutions were continuously stirred and heated in a water bath at 40 °C after that the oxalic acid (H2C2O4·2H2O) solution and tetraethyl orthosilicate (TEOS), or oxalic acid and tetrabutyl titanate (C8H18O4Ti) were slowly added into the above solution respectively under vigorously stirring in a water bath at 60 °C. The mixtures were filtered, washed several times, dried at 100 °C overnight, and then calcined in air at 500 °C for 4 h to produce γ-Al2O3–TiO2 and γ-Al2O3–SiO2. In the preparing process of γ-Al2O3–ZrO2, both aluminum nitrate and zirconium nitrate were dissolved into ultrapure water in a water bath at 40 °C, and then excess diluted ammonia was slowly dropped to the mixture solution until pH 9 with vigorously stirring in a water bath at 60 °C. The mixtures were filtered, washed several times, dried at 100 °C overnight, then calcined in air at 500 °C for 4 h to produce γ-Al2O3–ZrO2.

2.1.3. Preparation of loaded catalyst

Isovolumetric impregnation method was used to prepare loaded catalyst; the process was the same as Section 2.1.1. Finally, MnOx/γ-Al2O3, MnOx–CeO2/γ-Al2O3, MnOx–CeO2/SiO2, MnOx–CeO2/TiO2, MnOx–CeO2/ZrO2, MnOx–CeO2/γ-Al2O3–SiO2, MnOx–CeO2/γ-Al2O3–TiO2 and MnOx–CeO2/γ-Al2O3–ZrO2 catalysts were prepared and denoted as MA, MCA, MCS, MCT, MCZ, MCAS(a), MCAT(b) and MCZAC(c), respectively. The letters a, b and c represented the mole ratios of Al2O3 to SiO2, TiO2 and ZrO2.

2.2. Apparatus and catalytic experiments

The SCR activity was tested in a fixed bed quartz reactor system. It consisted of a vertical quartz tube (20 mm nominal ID × 406.4 mm long) and a 3-zone temperature controlled furnace (Fig. 1). Fine catalyst powder was pressed into thin wafers, then crushed and sieved within a size range of 40–80 mesh. In each test, 500 mg catalyst was used while the temperature ranged from 60 °C to 380 °C. The reaction conditions were as follows: total flow rate was 350 ml/min, which corresponded to a GHSV of approximately 20,000 h–1. Small variations (about 10%) existed due to the different densities of catalysts. Effects of the environmental conditions could be ignored because the tests were operated under the similar testing conditions (approximately 27.5 °C and 1007 hPa). The simulated flue gas was composed of 1000 ppm NO, 1000 ppm NH3, 5% O2, 500 ppm SO2 (when used), 5% H2O vapor (when used) and N2 as the balance gas. A peristaltic pump transferred water into the stainless steel tube, wrapped with a temperature-controlled heating tape and then H2O (g) was generated. The heated N2 took the H2O (g) along and mixed with the flue gas. A set of mass flow controllers was used to control every kind of gas accurately. The gas compositions in the inlet and outlet were analyzed by a flue gas analyzer (Testo 350 XL, Germany).

The total conversion of NO was calculated from the equation below:

\[
\text{NO Removal Efficiency} \% = \left( \frac{\text{NO}}{\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}}} \times 100 \right)
\]

where \([\text{NO}]_{\text{inlet}}\) is the inlet NO concentration (ppm) and \([\text{NO}]_{\text{outlet}}\) is outlet NO concentration (ppm).

2.3. Catalyst characterization

2.3.1. Specific surface area and pore diameter analysis

The specific surface areas of the catalysts were measured using a Micromeritics ASAP 2020 M+C volumetric sorption analyzer (Micromeritics Instrument Corp., USA) at 77 K. Each sample was degassed for 16 h at 250 °C before the isotherms were measured by standard nitrogen adsorption. The specific surface areas were
calculated by the BET (Brunauer–Emmett–Teller) method, while the pore size distributions were obtained from the desorption branches of N$_2$ adsorption isotherm and calculated by the BJH (Barrett–Joyner–Halenda) formula.

2.3.2. X-ray diffraction (XRD)

To examine the crystallinity and dispersity of the species in the catalysts, X-ray powder diffraction patterns were carried out on a Bruker D8-Advance X-ray diffraction equipment, under the following conditions: Cu target K$_\alpha$ ray ($\lambda = 0.1543$ nm); scanning voltage 40 kV, scanning current 40 mA; scanning speed 0.2 s, scanning step 0.02°.

2.3.3. X-ray photoelectron spectroscopy (XPS)

The oxidation states of the metals on the surface of catalysts were analyzed by X-ray photoelectron spectroscopy performed on a K-Alpha 1063 X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA) using 72 W Al K$_\alpha$ radiation from micro aggregation monochromator. The binding energies were referenced to the C 1s line at 284.6 eV from adventitious carbon.

2.3.4. H$_2$ temperature programmed reduction (H$_2$-TPR)

The H$_2$-TPR experiments were performed on a custom made thermal conductivity detector (TCD) setup using 50 mg catalysts. Prior to H$_2$-TPR experiments, catalysts were pretreated at 300 °C for 1 h in nitrogen (50 mL/min) and then the sample temperature was lowered to 100 °C. A feed containing 6 vol% H$_2$ in Ar was fed to the catalyst at a flow rate of 50 mL/min and the temperature of the catalyst was raised from 100 to 800 °C at a heating rate of 10 °C min$^{-1}$. The hydrogen consumption was measured quantitatively by a TCD.

2.3.5. Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy studies were carried out with a SHIMADZU FTIR-8400S IRprestige-21 apparatus. Its resolution factor was 2 cm$^{-1}$ from 400 cm$^{-1}$ to 4000 cm$^{-1}$ and scans were collected at a scan speed of 5 kHz. Circular self-supporting wafers of different samples were used. Powders of the samples (2 mg) were grinded and mixed with KBr (200 mg, spectroscopically pure) before tableting on a hydraulic press. The pretreatment process was as follows: samples were purged with high purity nitrogen for 2 h at 300 °C, after that several combinations of different gases were introduced to the reaction tube for 60 min at 50 °C. The gases combinations included NH$_3$ + N$_2$, NO + O$_2$ + N$_2$, SO$_2$ + O$_2$ + N$_2$, and SO$_2$ + O$_2$ + H$_2$. O + N$_2$. The last step was N$_2$ purging at 200 °C for 30 min. The FTIR experiments were conducted immediately after the pretreatment.

3. Results and discussion

3.1. SCR catalytic activity

Initially, the potential catalytic performance of Mn/γ-Al$_2$O$_3$ and Mn–Ce/γ-Al$_2$O$_3$ were evaluated (using the feed: 1000 ppm NO, 1000 ppm NH$_3$, 5% O$_2$ and N$_2$ as the balance gas) to optimize the loading amount of Mn and Ce and to investigate the influence of Mn + Ce co-cations on NO removal efficiency. Afterward the optimal proportions of the metal oxides in the supports were investigated. All these results were supplied in the Supplementary data.

3.1.1. The activity of catalysts with single and binary-oxides supports

The SCR performances over catalysts with various supports operating under specified experimental condition were displayed in Fig. 2.

It could be seen from Fig. 2(a), with the same loading amount of Mn and Ce, MCA, MCT and MCZ displayed high SCR activities with a similar tendency. However, MCS was much inactive with its best removal efficiency of 75% at 340 °C. MCA performed the best removal efficiency almost in the whole temperature range and approximately 95% conversion was obtained at its highest efficiency temperature (250 °C). Different with MCT, MCZ was a little more active at middle temperature and less active at higher temperature. Fig. 2(b) illustrated that the NO removal efficiency increased rapidly over low temperature range after the addition.
Compared with other catalysts, MCAS gave a rather unpromising efficiency at low temperature. It is likely that the low activity of MCAS was rendered by the addition of SiO₂ and the decrease of Al₂O₃ content, which meant that the increase of activity was largely due to temperature rise rather than the synergism of the two oxides in the support. The curve of MCAT performance was much similar with that of MCA except that the latter showed a bit more active at middle-high temperature (180–320 °C). It could be conjectured that Ti did not play a mutual promotion role in the course of the SCR using MCAT (at least when the preparation method above was used). Additionally, it could be observed that MCAZ took the lead in all the temperature range compared with MCA. A broad high-efficiency temperature range was observed in low-middle-high temperature, that meant MCAZ could withstand the frequently variation of the temperature in the SCR.

3.1.2. The stability of the catalysts and the effect of GHSV

The results of reacting stability of MCA and MCAZ at 150 °C, 200 °C and 250 °C were shown in Fig. 3(a). With time went by, the efficiency of MCAZ and MCA showed almost no decline after 24 h. Actually, all the efficiencies decayed a little except for those of MCAZ at 200 °C and 250 °C. A contiguous tendency of decrease could be predicted because of the deposition of the ammonium nitrate or other by-products on the active sites at lower temperature. Nevertheless, MCAZ showed not only higher efficiency but also slighter decline in this set of tests. The capacity of MCAZ to process different flue gas load was measured by the GHSV tests (Fig. 3(b)). When the GHSV was 15,000 h⁻¹, higher NO removal efficiency was yielded across all the temperature range. On the whole, higher GHSV corresponded to lower activity, and GHSV showed a more apparent effect at low temperature (100–180 °C) than that at middle-high temperature (180–300 °C). It meant the reaction could sustain stable efficiency when the load of flue gas changed, namely, the fluctuation of processing load could hardly affect the performance of MCAZ at middle-high temperature. The fine stability of MCAZ was attributed to the porosity characteristics: as the entry and the exit of flue gas were more convenient due to the suitable pore size, the NO removal efficiency could stay at a high level for a long time.

3.1.3. The activity with H₂O and SO₂ in the system

Water vapor and SO₂ always play significant roles in NH₃-SCR because of their deactivation effects. Therefore a comparative study was conducted to measure the performance of MCA and
MCAZ in this regard. In Fig. 4 the solid and dot lines represented the SCR performance of MCAZ and MCA respectively.

Fig. 4(a) illustrated the comparison study on the SCR activity in the simulated flue gas with SO2. When the temperature was 250 °C, both the MCA and MCAZ could obtain a normal efficiency at the beginning time. Afterward both efficiencies began to decline, but MCAZ was less influenced with a drop of 11% (94.7–83.4%). Meanwhile, the efficiency of MCA descended 22% (90.3–68.3%) and a continuous declining trend was observed as time went by. It indicated the declining participation of zirconium had certain effects on reducing the deactivation brought by SO2. As shown in Fig. 4(b), the NO removal efficiency remained approximately 95% with 5% water vapor in system at 250 °C. However, when the reaction temperature was 150 °C, the results changed. The activity curve showed an obvious decay and a downward trend. Yet the deactivation was reversible after the H2O (g) was purge out of the system at 150 °C. The curve remained almost horizontal in the reminding time (2.5 h) at 200 °C. It implied that H2O vapor could hardly stay and deposit in the pores of MCAZ at 200 °C or higher temperature. Fig. 4(c) illustrated the activity performance of MCAZ and MCA in the system with SO2 and water vapor simultaneously. The synergistic deactivating effect of the H2O and SO2 handicapped the performance of both catalysts greatly because they both faced a large decline after the addition of SO2 and H2O. Surprisingly, as a function of the zirconium loading, MCAZ owned much better performance than MCA at every temperature though the curve trends of them were similar. In addition, the results were in accord with other articles at the point that the deactivation of SO2 is irremovable [24,35]. When the SO2 stream was cut off, the efficiency could not return to the level before.

3.2. Characterization of catalysts

3.2.1. Specific surface area and pore diameter analysis

The BET specific surface area, BJH pore volume and pore diameter are summarized in Table 1.

The specific surface area of the samples decreased in the following order: MCAS > MCAZ > MCAT > MCA. MCAS owned the highest specific surface area since the particle of SiO2 is finer than that of others. However, there have been articles reporting that catalysts containing SiO2 as support or active component always give unsatisfactory performance due to its less active sites and inactive surface properties [36]. As can be seen in Table 1, catalysts with binary-oxides support possessed higher specific surface area than MCA, which revealed that the addition of TiO2 and ZrO2 into γ-Al2O3 could expand the specific surface area to a certain extent. Researchers who probed into the relationship between specific surface area and SCR activity elucidated that the material owning higher specific surface area always provided more reactive sites for the reactants [8], by which the reaction of NO conversion could be partially promoted. After the addition of ZrO2, the specific surface area of MCAZ raised about 26%, so the higher specific surface area might be a reason for the superiority to MCA. Interestingly, compared with many other SCR catalysts [37–39], the pore diameters of the catalysts (40–86 nm) were rather big. It was inferred that the bigger size of the pore facilitated the entry, stay and collision for the reactants. Moreover, the catalysts with broader pore diameter could cope with high GHSV since it promoted the entrance and storage of the gas. Similarly, benefited from the broader pore, the catalysts would be difficult to get clogged and passivated, hence it was capable in the simulated flue gas with SO2 and H2O. However, it was unexpected that the pore volume diminished as the pore size got smaller. To explain this, the pore size distribution should be taken into consideration, as pore volume characteristic is determined by macropore and mesopore primarily, with ascopore and micropore as auxiliary.

3.2.2. XRD analysis of catalysts

The powder X-ray diffraction patterns of MCA, MCAS, MCAT and MCAZ are shown in Fig. 5.

Different oxides component in the supports were labeled: γ-Al2O3 (Tetragonal, PDF-#46-1131), ZrO2 (Tetragonal, PDF-#79-1770), TiO2 (Anatase, tetragonal, PDF-#75-1537) and MnO2 (Tetragonal, PDF-#44-0141). For MCA, the crystal phases appeared at 2θ = 32.5°, 36.76°, 45.64° and 66.98° were diffraction peaks of γ-Al2O3. The intensity of the peaks belonging to γ-Al2O3 decreased dramatically when a secondary metal oxide was added. Except for the major peak at 66.98°, other diffraction peaks of γ-Al2O3 were barely detected, while MCAT and MCAZ showed sharp characteristic peaks of themselves. The peaks of SiO2 were hard to confirm due to the variety of possibilities of Si–Al–O. The characteristic peaks of MnO2, Mn3O4, CeO2 and Ce2O3 could be hardly detected in all four patterns, which was due to the widely dispersion and poorer crystalline on the surface. Be consistent with other literatures, MnO2 and CeO2 existed as highly dispersed amorphous states [26,37,40], which were beneficial for the reduction–oxidation in the SCR.

3.2.3. XPS study

The XPS spectra for Mn2p, Ce3d, O1s, levels of compounds from various catalysts are shown in Figs. 6–8. After a nonlinear background was subtracted, the peaks were deconvoluted into several sub-bands using the Gaussian function.

3.2.3.1. Mn. From Fig. 6, it can be seen that Mn 2p region contained a spin–orbit doublet with Mn 2P1/2 ranging a binding energies (BE) of 649.2–568.6 eV and Mn 2P3/2 ranging a BE of 637–649.2 eV. In consideration of the nitrate in the precursor, three types of photo-electron with different binding energies could be observed in all samples, which indicated that there were three species of Mn compounds. The peaks at 641.3 eV, 642.2 eV and 644.2–644.5 eV should be assigned to Mn2O3, MnO3 and manganese nitrate respectively. This was in good agreement with several other literatures [41–44]. The manganese nitrate existed for the reason that the nitrate in the preparing system was not decomposed completely. Based on a series of thermodynamic calculations, the decomposition of...
MnO$_2$ to Mn$_3$O$_4$ happened at 880 K and the decomposition of Mn$_2$O$_3$ to Mn$_3$O$_4$ happens at 1000–1200 K. During the process of preparation, the samples were calcined at the temperature of 500 °C (773.15 K) for 4 h, so the manganese oxides existed at the states of MnO$_2$ and Mn$_2$O$_3$ in the samples. After the addition of ZrO$_2$, the ratio of Mn$^{3+}$ and Mn$^{4+}$ changed from 1.18 to 2.66, which is beneficial for the NO removal efficiency because the Mn$_2$O$_3$ was more activity in the reduction due to the high dispersion and the low degrees of crystallinity in the catalyst. In addition, Lee et al. [4], Smirniotis et al. [41] and Thirupathi and Smirniotis [39] have pointed out that amorphous MnO$_2$ also bring a promotion of NO conversion because of its oxidation capacity. A small amount of amorphous MnO$_2$ existing on the surface of the samples was a subordinate reason for excellent SCR performance.

### Table 1

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Average pore diameter (nm)</th>
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<tr>
<td>MCA</td>
<td>129.09</td>
<td>0.3584</td>
<td>86.226</td>
</tr>
<tr>
<td>MCAS</td>
<td>180.94</td>
<td>0.1984</td>
<td>40.257</td>
</tr>
<tr>
<td>MCAT</td>
<td>141.72</td>
<td>0.299</td>
<td>60.063</td>
</tr>
<tr>
<td>MCAZ</td>
<td>163.51</td>
<td>0.2728</td>
<td>50.347</td>
</tr>
</tbody>
</table>

### Figs.

- **Fig. 5.** XRD patterns of MCA, MCAZ, MCAT and MCAS.
- **Fig. 6.** Mn$_{2p}$ XPS spectra for MCA, MCAT and MCAZ.
- **Fig. 7.** Ce$_{3d}$ XPS spectra for MCA, MCAT and MCAZ.
- **Fig. 8.** O$_{1s}$ XPS spectra for MCA, MCAT and MCAZ.

### 3.2.3.2. Ce

In Fig. 7, the peaks labeled $\nu$ were assigned to the Ce 3d$_{5/2}$ and those labeled $\mu$ correspond to Ce 3d$_{3/2}$. The spectra exhibited six features of Ce$^{4+}$ (doublets $v_2/\mu_1$, $v_3/\mu_3$ and $v_4/\mu_4$) and two features of Ce$^{3+}$ (doublets $v_2/\mu_2$) [8,28]. It is apparent that the Ce$^{4+}$ and Ce$^{3+}$ were coexisting but the ratio of them changed. The Ce$^{4+}$/Ce$^{3+}$ improved from 0.97 to 1.63 and 2.69 after the addition of a secondary metal. Accordingly, on the surface of MCAT and MCAZ, Ce$^{4+}$ was more dominate while Ce$^{4+}$ and Ce$^{3+}$ functioned...
together to achieve high efficiency. The special redox couple Ce⁴⁺/Ce³⁺, in the form of CeO₂/ Ce₂O₃, could easily generate labile oxygen vacancies and highly mobile oxygen during the process of the redox shift [8,46]. The reduced state species Ce³⁺, together with Mn³⁺, played a role in creating charge imbalance, vacancies and unsaturated chemical bonds [26]. The function of oxidation state specie Ce⁴⁺ and Mn⁴⁺ was inferred to be assisting both the H-abstraction of NH₃ (to provide NH₂) and the formation of reactive nitrite intermediates at low temperature, together with O₂ adsorbed on the surface [47].

3.2.3.3. O. In Fig. 8, potential existence of each kind of O species was presented. The peaks appearing at binging energies value 533.5 eV, 529.2 eV, 530.7 eV and 530 eV could be attributed to the oxygen from MnOₓ, CeO₂, γ-Al₂O₃ and ZrO₂, respectively [41,48–50]. In Fig. 8 (b), the peak at binding energy value 530.8 eV represented the oxygen in γ-Al₂O₃ and TiO₂ [51]. The ratio of the oxygen in active component and supports in each sample was calculated. The lowest value (0.24) appeared in MCAT, while the highest value (0.35) belonged to MCAZ, which meant that there was a slightly bigger amount of MnO₃ and CeO₂ on the surface of γ-Al₂O₃–ZrO₂ than on other supports.

From another point of view, the oxygen in the catalysts could be divided into two kinds of species: the lattice oxygen (529.78 eV, denoted as Oₓ) and the chemisorbed oxygen on/and weakly bonded oxygen species (531.58 eV, denoted as Oₓ) [52]. In the MCAZ, the Oₓ/Oₓ value came to 1.4 (Fig. 8(d)), that meant the chemisorbed species in MCAZ appeared [29]; it could be seen [57,59]), and ZrO₂ [63]) and 1502 cm⁻¹ in the following order: MnO₂ and NO + O₂ sites [41] and/or the group decomposed from —NH and CeO₂ in the support, the MnO₂ was more favorable for NO catalytic oxidation than MnO₂. The XPS results together, it might be reasonable to speculate that highly dispersed amorphous Mn₂O₃ was more favorable for NO catalytic oxidation than MnO₂. Literature also reported that the weaker Mn²⁺–O bond favored the catalytic oxidation of NO due to its lower strength, and this promoted the generation and release of NO₂ produced as well [55,56].

3.2.4. H₂-TPR analysis

The reduction/oxidation (redox) properties of the catalysts were demonstrated by H₂-TPR (Fig. 9). The overlapping peaks in all profiles were deconvoluted using Gaussian function to separate peaks corresponding to different species of MnO₂ and CeO₂. As shown in Fig. 9, it was apparent that the redox abilities differed though same active component were used, namely, these differences were brought by the discrepancy of supports. Ettireddy et al. [53], Shen et al. [29] and Trawczynski et al. [54] demonstrated that MnO₂ was reduced by H₂ in the following order: MnO₂ → Mn₂O₃ → Mn₂O₄ → MnO. Therefore, the first low temperature peaks were correlated to reduction of MnO₂ while the peaks near 350 °C were attributed to reduction of Mn₂O₃, this favored well with the papers aforementioned. After doping TiO₂ and ZrO₂ in the support, the reduction temperature of MnO₂ shifted to lower position, which reflected the increase of oxygen mobility within the low temperature range. Among these profiles, the peak of MnO₂ in MCAZ shifted about 44 °C to lower temperature and this could contribute to the better low temperature activity of MCAZ in comparison with that of the other two catalysts. Besides, the peaks at 595 °C, 581 °C and 566 °C were attributed to the reduction of CeO₂ [29]; it could be seen that the interaction of the two metal oxides in the supports shifted the reduction peak of CeO₂ to lower temperature as well. Furthermore, the area ratios of the first reduction peaks to the second ones for MCA, MCAT and MCAZ were 0.87, 0.42 and 0.37, respectively. These indicated that the dominant MnO₂ species in MCAZ appeared to be Mn₂O₃, which was in fine consistence with the XPS results though the specific ratio figures were not the same. Considering the higher catalytic activity of MCAZ at low temperature and the XRD results together, it might be reasonable to speculate that highly dispersed amorphous Mn₂O₃ was more favorable for NO catalytic oxidation than MnO₂. Literature also reported that the weaker Mn²⁺–O bond favored the catalytic oxidation of NO due to its lower strength, and this promoted the generation and release of NO₂ produced as well [55,56].

3.2.5. FTIR study

The FTIR spectra of pre-prepared samples of MCAZ were analyzed with peak deconvolution.

3.2.5.1. NH₃ and NO + O₂ FTIR. The NH₃ and (NO + O₂) FTIR spectra of MCAZ was shown in Fig. 10(a). The strongest band at 1611 cm⁻¹ should be associated with the asymmetric deformation vibration of NH₃ (δ(NH₃)) which was adsorbed on Lewis acid sites [57]. There were no remarkable bands at the regions belonging to Brønsted acid sites [57,58]. Other N–H vibrations were weaker but dispersed widely, the wavenumbers were as follows: 1530 cm⁻¹ (δ(NH₃)), 1489 cm⁻¹ (δ(NH₄⁰⁺)) on Mn sites and Al₂O₃ sites [41] and/or (δ(N–H)) from the amines or amides [18]. 1402 cm⁻¹ and 1262 cm⁻¹ (coordinate NH₃ species [41]). The weak band at 1356 cm⁻¹ was conjectured as the oxidized species such as nitrate or nitrite because MnO₇–CeO₃ is highly active for oxidation of ammonia at low temperatures [18]. The spectra clearly demonstrated the interaction of NH₃ with MCAZ in these different ways: coordination on Lewis acid sites, protonation and deprotonation of ammonia, formation of amid species, being oxidized by active oxygen. It also could be seen that most NH₃ was adsorbed and coordinated on the Lewis acid sites because of the acidic property of the material. In (NO + O₂) FTIR curve, the adsorbed N species existed mainly as nitrate because the strongest band was assigned to bridging bidentate nitrate species (ν(N=O), 1624 cm⁻¹ [60,61]. Zhang et al. [62] demonstrated that among monodentate, isolated, bidentate and bridging nitrates adsorbed on the Al₂O₃, the last two owned the weakest thermal stability, which meant that the adsorbed nitrates could participate in the redox reaction sufficiently. Two overlapping bands, located at 1548 cm⁻¹ (bridging nitrate species and/or N₂O₅ [63]) and 1502 cm⁻¹ (monodentate nitrate), were much smaller. The formation of the band in the 1280–1480 cm⁻¹ could be attributed in part to the reaction of produced NO₂ with surface oxygen. The band could be deconvoluted to three bands at 1354 cm⁻¹ (nitrito), 1380 cm⁻¹ (NO₂ stretch in NO₃⁻) and 1410 cm⁻¹ (monodentate nitrate) [61,64]. Besides, two weak bands at 1768 cm⁻¹ and 1267 cm⁻¹ could be assigned to adsorbed
N$_2$O$_4$ derived from NO$_2$ at low temperature [60,63] and chelating nitro [60,61], respectively.

In fact, the mechanism of NH$_3$-SCR on MnO$_x$ has been investigated using in situ FTIR coupled with transient isotopic labeled studies [65]. The literature reported that the lattice oxygen on the surface of catalyst acted as a “transfer station” in the NH$_3$-SCR, especially in the oxidation of NH$_3$, while the main job of the gaseous oxygen in the flue gas was filling the vacancies over the catalyst surface. The reaction between adsorbed (or coordinated) ammonia and lattice oxygen was practically instantaneous, and the NO participated in the process by forming nitrates and exchanging oxygen with the lattice oxygen on the surface. The N from the NH$_3$ and the N from the NO stayed on the catalyst for a long time and underwent some transitions between several active intermediates. After a series rearrangement of chemical bonds H$_2$O and N$_2$ were generated as products. Afterward the gaseous oxygen filled the vacancies again before the beginning of next reduction–oxidation cycle. The discussion of FTIR above showed a brief description of NH$_3$ and NO adsorption. In connection with the results of H$_2$-TPR and XPS analysis of O (Section 3.2.3.3), it might be reasonable to speculate that the oxygen on the surface of the material not only supplied abundant chemisorbed and lattice oxygen, but also enhanced the oxidation of NH$_3$ and the formation of highly reactive surface nitrates. The nitrates possessed higher activity in the redox reaction with adsorbed NH$_3$ species comparing with NO$_x$, which promoted the NO removal efficiency as well.

3.2.5.2. SO$_2$ + O$_2$ FTIR. The SO$_2$ + O$_2$ and SO$_2$ + H$_2$O + O$_2$ FTIR spectra of MCAZ were shown in Fig. 10(b). The curve of SO$_2$ + O$_2$ FTIR showed a band at 1404 cm$^{-1}$, that evidenced the adsorbed gaseous SO$_2$ deposited on the surface of the catalysts [66]. The other curve did not have this band since the SO$_2$ reacted with H$_2$O and O$_2$ to form sulfite and/or sulfate. Goodman et al. [67] and Mitchel et al. [68] investigated SO$_2$ adsorption on $\gamma$-Al$_2$O$_3$ particles and found that the band centered at 1065 cm$^{-1}$ was assigned to adsorbed SO$_2$ identified as sulfite, more specially, the band could be assigned to $\nu_3(S=O)$ of HSO$_3$ (1100–1000 cm$^{-1}$), referenced from the Sadtler handbook of infrared spectra [69]. In addition, the band at 1234 cm$^{-1}$ and 1233 cm$^{-1}$ could be attributed to $\nu_3(S=O)$ of HSO$_3$ in sulfonic acids [69]. Peak et al. [70] reported that the band between 1250 and 1050 cm$^{-1}$ was the mainly infrared sulfate vibrations that were accessible to FTIR investigation. Two possible bidentate sulfates might exist: bidentate binuclear sulfate and bidentate mononuclear sulfate. The existence of the later would shift the band to higher wavenumbers (much higher than was observed); thus the bands at 1123 cm$^{-1}$ were assigned to asymmetric stretching bands of bidentate binuclear sulfate. The bands around 1170 cm$^{-1}$ were uncertain since the bidentate SO$_2^-$ could bridge with metallic cations, proton and/or hydrogen bond. Chang et al. [58,71] held the opinion that the bidentate sulfate could provide new acid sites for NH$_3$ adsorption and the emerging sites were mainly Lewis acid sites, as characterized by pyridine IR. The poison mechanism of SO$_2$ is widely discussed and a common opinion is that the existence of SO$_2$ in the system promotes the formation of M(SO$_4$)$_2$, which in which M represents NH$_4$, Mn, Ce, Al, or some cations taking part in the SCR [40]. However, the sulfates and sulfites play a role in proliferating acidity, especially the Lewis acid sites on the surface, benefit from which NH$_3$ adsorption is enhanced and the formation of the intermediate –NH$_2$ is promoted [57], thus the SCR activity of MCAZ was better than MCA in the flue gas with SO$_2$ (shown in Fig. 4). It is noteworthy that the adsorbed SO$_2$ could inhibit neither the depositions of (NH$_4$)$_2$SO$_4$/NH$_3$HSO$_4$ nor the competitive adsorption between SO$_2$ with NO on the Mn and Ce sites, namely, the promotion for NH$_3$ adsorption and the deactivation of SO$_2$ happened simultaneously. Therefore, the application of the catalyst in a flue gas with high concentration of SO$_2$ is probably challenging.

![Fig. 10. Deconvoluted FTIR spectra for MCAZ purged by (a) NH$_3$ and (NO + O$_2$), (b) (SO$_2$ + O$_2$) and (SO$_2$ + O$_2$ + H$_2$O).](image-url)
and adsorbed bidentate sulfates were inferred to be propitious to excellent performance by FTIR.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2013.12.076.

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