CeO$_2$ Nanoparticle-Loaded MnO$_2$ Nanoflowers for Selective Catalytic Reduction of NO$_x$ with NH$_3$ at Low Temperatures

Shun Li $^1$, Zuquan Zheng $^2$, Zhicheng Zhao $^3$*, Youling Wang $^4$, Yao Yao $^3$, Yong Liu $^3$,*, Jianming Zhang $^1$,* and Zuotai Zhang $^2$,*

Abstract: CeO$_2$ nanoparticle-loaded MnO$_2$ nanoflowers, prepared by a hydrothermal method followed by an adsorption-calcination technique, were utilized for selective catalytic reduction (SCR) of NO$_x$ with NH$_3$ at low temperatures. The effects of Ce/Mn ratio and thermal calcination temperature on the NH$_3$–SCR activity of the CeO$_2$–MnO$_2$ nanocomposites were studied comprehensively. The as-prepared CeO$_2$–MnO$_2$ catalysts show high NO$_x$ reduction efficiency in the temperature range of 150–300 °C, with a complete NO$_x$ conversion at 200 °C for the optimal sample. The excellent NH$_3$–SCR performance could be ascribed to high surface area, intimate contact, and strong synergistic interaction between CeO$_2$ nanoparticles and MnO$_2$ nanoflowers of the well-designed composite catalyst. The in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization evidence that the SCR reaction on the surface of the CeO$_2$–MnO$_2$ nanocomposites mainly follows the Langmuir–Hinshelwood (L–H) mechanism. Our work provides useful guidance for the development of composite oxide-based low temperature NH$_3$–SCR catalysts.

Keywords: Mn–Ce mixed oxide; ion-adsorption; selective catalytic reduction; NO$_x$ conversion

1. Introduction

With the fast developing modern industrialization, nitrogen oxides (NO$_x$) emitted from industrial production and automobile exhaust have become one of the major environmental pollution issues, which may cause acid rain and greenhouse effects [1,2]. Long-term exposure to NO$_x$ can cause several side effects to human health, such as reduced lung function, increased risk of respiratory conditions, and increased response to allergens. As an eco-friendly and efficient approach, selective catalytic reduction of NO$_x$ with NH$_3$ (NH$_3$–SCR) is widely used for removing NO$_x$ [3–7]. The core of the NH$_3$–SCR technology is the catalyst. Although V$_2$O$_5$–WO$_3$ (MoO$_3$)/TiO$_2$ catalysts have been utilized commercially in the temperature range of 300–400 °C [8], the increasing demands for outstanding catalytic activity at low working temperature with high stability have stimulated the development of novel SCR catalysts.

During the past few decades, enormous research work has been carried out to exploit mixed metal oxides NH$_3$–SCR catalysts composed of TiO$_2$, VO$_x$, MnO$_y$, CeO$_2$, Fe$_2$O$_3$, ZrO$_3$ or WO$_3$, etc., owing to their high stability, strong synergistic interaction, excellent oxygen storage capacity, and redox ability [9–14]. Among all, CeO$_2$–MnO$_x$ composites with outstanding low-temperature activity, excellent oxygen storage, and release capacity,
and strong mechanical strength, have received considerable attention as a promising candidate NH\textsubscript{3}-SCR catalyst \cite{15–20}. Nevertheless, CeO\textsubscript{2}-MnO\textsubscript{x} composite catalysts still suffer from several deficiencies in practical applications due to their poor thermal stability, low reduction efficiency, and low sulfur resistance. Considering that the architecture of composite with close contact between each component is crucial for promoting the SCR catalytic activity, considerable work have been conducted to the design and fabrication of hierarchical CeO\textsubscript{2}-MnO\textsubscript{x} composites at nanoscale. For instance, it has been reported that CeO\textsubscript{2}-MnO\textsubscript{x} mixed oxides with hollow structures possess excellent low temperature NO\textsubscript{x} storage capacity and NH\textsubscript{3}–SCR activity owing to the large surface area, rich active sites, and confined micro-environment \cite{21–24}. Therefore, the development of well-designed CeO\textsubscript{2}-MnO\textsubscript{x} composite catalyst with desirable intimate contact at nanoscale is of importance for further enhancing their NH\textsubscript{3}–SCR catalytic performance.

In this work, a rational designed CeO\textsubscript{2} nanoparticle-loaded MnO\textsubscript{2} nanoflowers (NFs) with adjustable Ce/Mn ratios were prepared through combining a simple hydrothermal and subsequent ion-adsorption-calcination method, as illustrated in Scheme 1. A variety of physical and chemical characterization methods were used to investigate the phase composition, microstructure, and surface characteristics. The unique architecture of the CeO\textsubscript{2}-MnO\textsubscript{x} nanocomposites consisting of MnO\textsubscript{2} nanoflowers loaded with ultrasmall CeO\textsubscript{2} nanoparticles allows the composite with high surface area, intimate contact, and strong synergistic interaction between CeO\textsubscript{2} and MnO\textsubscript{2}. The catalysts displayed excellent low-temperature NH\textsubscript{3}–SCR activity for NO\textsubscript{x} reduction, obtaining a nearly 100% conversion efficiency at 200 °C. Moreover, the NH\textsubscript{3}–SCR reaction mechanism was revealed by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs).

Scheme 1. Schematic of the synthesis process for CeO\textsubscript{2}-MnO\textsubscript{2} nanocomposites.

2. Experimental

2.1. Materials

The chemicals of CeCl\textsubscript{3}·7H\textsubscript{2}O (AR, ≥99.9%), MnCl\textsubscript{2}·4H\textsubscript{2}O (AR, ≥99.99%), and KMnO\textsubscript{4} (AR, ≥99.5%) were purchased from Aladdin Reagents and used as received without any further purification. Water was deionized (D.I. water) to reach the Nanopure grade (18.2 MΩ·cm at 25 °C).

2.2. Synthesis of MnO\textsubscript{2} NFs

MnO\textsubscript{2} NFs were synthesized using a hydrothermal method. Typically, 0.5 g KMnO\textsubscript{4} was dissolved in 50 mL of D.I. water and stirred for 15 min. After that, 1 mol/L MnCl\textsubscript{2}·4H\textsubscript{2}O solution was added into the above solution and stirred for 1 h. Then the mixed solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated in a conventional oven at 100 °C for 12 h. After cooling down to room temperature, the as-obtained powder was washed with D.I. water for three times and dried at 60 °C.

2.3. Synthesis of CeO\textsubscript{2}-MnO\textsubscript{x} Nanocomposites

Typically, 0.1 g of the as-synthesized MnO\textsubscript{2} NFs powder was ultrasonically dispersed in 100 mL of aqueous solution containing certain amount of CeCl\textsubscript{3}·7H\textsubscript{2}O (0.02, 0.04, 0.06, and 0.08 g), denoted as Ce/Mn-1, Ce/Mn-2, Ce/Mn-3, and Ce/Mn-4, respectively. Subsequently, the suspension was magnetically stirred for 24 h to ensure the complete adsorption...
of the Ce ions onto the MnO$_2$ NFs. Then the samples were collected after washing with D.I.
water and dried at 60 °C for 12 h. Finally, the as-obtained sample was calcined at different
temperatures (300 to 600 °C) for 2 h.

2.4. Materials Characterizations

2.4.1. Crystal Structure

The crystal structure was investigated by powder X-ray diffraction (XRD) with a
Bruker D8 Advance diffractometer (Bruker, Karlsruhe, Germany) with CuKα radiation. The
morphology and microstructure were studied by field emission scanning electron
microscopy (SEM, Zeiss Merlin, Carl Zeiss NTS GmbH, Oberkochen, Germany) and trans-
mission electron microscopy (TEM, FEI Talos F200X, Thermo Fisher Scientific, Hillsboro,
OR, USA), equipped with an energy-dispersive X-ray spectroscopy (EDS). X-ray photoelec-
tron spectroscopy (XPS) characterizations were performed using a PHI 5600 XPS system
(Perkin-Elmer, Waltham, MA, USA). The obtained spectra were calibrated with the C1s
peak at 284.6 eV. The specific surface areas and pore size distributions were estimated by
the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods with N$_2$
adsorption and desorption isotherms obtained on a Micrometrics ASAP 2020 system.

2.5. NH$_3$–SCR Activity Measurement

The SCR activity of the catalysts was evaluated using a conventional fixed-bed quartz
microreactor operating in a steady state flow mode under atmospheric pressure. In a
typical test, the as-obtained catalysts (50 mg) and quartz sand (200 mg) were mixed and
packed between two quartz glass wool plugs. The simulated flue gas composition was
NO (500 ppm), NH$_3$ (500 ppm), O$_2$ (2%), and balance gas N$_2$. The total flow rate was
100 mL min$^{-1}$, which corresponds to a gas hourly space velocity (GHSV) of 16,000 h$^{-1}$.
The concentrations of NO were measured by a chemiluminescence NO$_x$ analyzer (42i-HL,
Thermo Scientific). The NO conversion rate was calculated by the following equation:

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

(1)

3. Results and Discussion

3.1. Effect of CeO$_2$ and MnO$_2$ Ratio

The CeO$_2$-MnO$_2$ nanocomposites with different Ce/Mn ratios were synthesized first.
The morphology of the catalysts (taking Ce/Mn-3 as a representative) was characterized
by SEM and TEM. As shown in the SEM images (Figure 1a,b), the as-prepared CeO$_2$-MnO$_2$
catalyst possesses flower-like morphology with sizes of about 200–300 nm. The TEM images
(Figure 1c,d,g) clearly display that the nanoflowers are composed of numerous sheets with
thickness of several nanometers. From the HRTEM image (Figure 1e), the interplanar
spacings were measured to be 0.32 and 0.70 nm, which can be assigned to the (111) plane
of CeO$_2$ and (001) plane of δ-MnO$_2$, respectively. The EDS spectrum (Figure 1f) confirms
that the composites contain three elements of Ce, Mn, and O, with atomic content of
7.2%, 31.2%, and 61.6%, respectively. Meanwhile, the EDS mapping diagrams (Figure 1h–j)
clearly display the homogenous distribution of Mn, Ce, and O elements throughout the
NFs, demonstrating the uniform growth of CeO$_2$ nanoparticles on the MnO$_2$ NFs. Such a
uniform distribution is highly expected to promote their interaction and synergistic effect
of Ce and Mn mixed oxides during the catalytic reactions [24,25].
The crystal structure of the CeO$_2$-MnO$_2$ catalysts with different Ce and Mn ratios after thermal treatment at 300 °C was analyzed by XRD. As shown in Figure 2, all diffraction peaks of the pristine MnO$_2$ sample could be well indexed to δ-MnO$_2$ crystal structure (JCPDS No. 80-1098) with predominant crystal planes of (001), (002), and (111). After the adsorption of Ce$^{3+}$ and the following calcination treatment, the diffraction peaks corresponding to CeO$_2$ (JCPDS No. 81-0792) appeared with predominant crystal planes of (111), (200), and (220), demonstrating the formation of CeO$_2$-MnO$_2$ composites. The peak intensity of CeO$_2$ gradually increases with the increasing CeCl$_3$·7H$_2$O content. The broad diffraction peaks suggest the small crystal size of the loaded CeO$_2$, which is consistent with the TEM observations.
The NH$_3$–SCR activity of the as-prepared catalysts calcinated at 300 °C was evaluated. As shown in Figure 3, all the CeO$_2$-MnO$_2$ composite catalysts with different Ce and Mn ratios exhibit much higher activity in a relatively wide range of temperature from 50 to 300 °C, compared to pristine MnO$_2$. As the Ce content increases, the NO conversion rate increases significantly, while decreases at higher Ce contents. Among all samples, Ce/Mn-3 (300) shows the optimal NH$_3$–SCR catalytic performance, reaching the highest NO conversion rate of about 87.6% at 250 °C.

The specific surface areas (SSAs) and pore features are crucial factors determining the catalytic activity. As shown in Figure 4a, the N$_2$ adsorption–desorption isotherms of the as-prepared catalysts exhibit type IV isotherm with H3 hysteresis loops, demonstrating their mesoporous structure. The CeO$_2$-MnO$_2$ composite catalysts possess significantly higher...
SSAs in comparison to the pristine MnO$_2$, estimated by the BET method. The measured SSAs follow the order of Ce/Mn-3 (342 m$^2$ g$^{-1}$) > Ce/Mn-4 (206 m$^2$ g$^{-1}$) > Ce/Mn-2 (154 m$^2$ g$^{-1}$) > Ce/Mn-1 (145 m$^2$ g$^{-1}$) > MnO$_2$ (67 m$^2$ g$^{-1}$). Figure 4b displays the pore size distribution curves estimated by the BJH method. For all samples, the pore size is mostly distributed in the range of 4 to 10 nm, which belongs to the mesoporous structure. The SSAs for the as-prepared CeO$_2$ loaded MnO$_2$ NFs are significantly higher than most of the reported CeO$_2$-MnO$_x$ nanocomposite catalysts [26–28]. The large SSAs and porous features of the as-synthesized CeO$_2$-MnO$_2$ catalysts (e.g., Ce/Mn-3 (300)) with more catalytic active sites show great advantages for the adsorption and diffusion of gaseous reactants toward high NH$_3$-SCR activity [29].

Figure 4. (a) N$_2$ adsorption–desorption isotherm and (b) pore size distribution of MnO$_2$ NFs and CeO$_2$-MnO$_2$ catalysts with different Ce/Mn ratios.
3.2. Effect of Thermal Treatment Temperature

To further optimize the NH$_3$–SCR catalytic activity of the CeO$_2$-MnO$_2$ composite catalysts, the effect of thermal treatment temperature was investigated, selecting the Ce/Mn-3 sample with the highest activity. Figure 5 displays the XRD patterns of Ce/Mn-3 catalysts after calcinating at four different temperatures of 300 °C, 400 °C, 500 °C, and 600 °C. The samples of Ce/Mn-3 (300), Ce/Mn-3 (400), and Ce/Mn-3 (500) exhibit consistent diffraction peaks, which can be indexed to δ-MnO$_2$ (JCPDS No. 80-1098) with predominant crystal planes of (001), (002) and (111) and CeO$_2$ (JCPDS No. 81-0792) with predominant crystal planes of (111), (200), and (220). For the sample treated under 600 °C, secondary phases of Mn$_2$O$_3$ (JCPDS No. 89-2809) and Mn$_3$O$_4$ (JCPDS No. 75-1560) appeared.

![Figure 5. XRD patterns of the Ce/Mn-3 catalysts calcinated at different temperatures.](image)

The SEM images of Ce/Mn-3 catalysts after thermal treatment at different temperatures are displayed in Figure 6. It is clearly shown that spherical flower-like morphology structure was well maintained when the calcination temperature was under 500 °C (Figure 6a–d), compared with that of Ce/Mn-3 (300). Nevertheless, the flower-like hierarchical microstructure of the catalyst for Ce/Mn-3 (600) sample disappeared, forming irregular shaped particles (Figure 6e,f).

Subsequently, the NH$_3$–SCR activity of different as-prepared Ce/Mn-3 catalysts were tested. As shown in Figure 7, in the range of 50~200 °C, the NO conversion rate of the catalysts (except for Ce/Mn-3 (300)) increases with the increasement of thermal treatment temperature. Among all the catalysts, Ce/Mn-3 (400) exhibited the highest SCR performance in the low-temperature window from 150 to 300 °C, reaching a 100% removal rate of NO at 200 °C. The activity declined for the catalysts treated at higher temperatures (above 500 °C), which could be ascribed to the changes of structural and surface characteristics of the catalyst, discussed as follows.
Figure 6. SEM images of the Ce/Mn-3 catalysts calcinated at different temperatures: (a) and (b) 400 °C, (c) and (d) 500 °C, and (e) and (f) 600 °C.

Figure 8 exhibits the N$_2$ adsorption–desorption isotherms and the pore size distributions of various Ce/Mn-3 catalysts calcinated at different temperatures. From Figure 8a, all the catalysts display IV type N$_2$ isotherm with H3 type loops, which correspond to the mesoporous structure. Among all samples, the Ce/Mn-3 catalyst prepared at 300 °C has the largest SSA. The SSAs follow the order of Ce/Mn-3 (300) (342 m$^2$ g$^{-1}$) > Ce/Mn-3 (400) (147 m$^2$ g$^{-1}$) > Ce/Mn-3 (500) (97 m$^2$ g$^{-1}$) > Ce/Mn-3 (600) (23 m$^2$ g$^{-1}$). Figure 8b displays the pore size distribution curves estimated by the BJH method, demonstrating that the mesopores are mainly distributed from 4 to 20 nm.
Figure 7. (a) NO conversion curves of the Ce/Mn-3 catalysts calcinated at different temperatures, (b) recycling catalytic activity tests of Ce/Mn-3 (400), and (c) SEM image of Ce/Mn-3 (400) after catalytic reactions.

XPS spectra were measured to analyze the element oxidation states of the composite catalysts calcinated at different temperatures. Figure 9 shows the high-resolution Ce 3d, Mn 2p, and O 1s XPS spectra. As displayed in Figure 9a, the peaks of Ce$^{3+}$ are located at ~885.7 eV and ~903.1 eV, while the remaining peaks are attributed to Ce$^{4+}$ [30–32]. As listed in Table 1, the calculated Ce$^{3+}$ content (24.84%) in Ce/Mn-3 (400) is the highest among all CeO$_2$-MnO$_2$ samples, which is beneficial for the adsorption of NH$_4^+$ [33]. In addition, the Mn 2p 3/2 peaks in Figure 9a can be fitted into three peaks, which belong to Mn$^{2+}$ (640.7–641.5 eV), Mn$^{3+}$ (642.2–643.5 eV), and Mn$^{4+}$ (644.8 eV), respectively [34,35]. Generally, Mn with high oxidation states (Mn$^{4+}$) can promote the oxidation performance of NO over CeO$_2$-MnO$_2$ catalysts at low temperatures. The Ce/Mn-3 (400) catalyst contains more Mn$^{4+}$ (38.55%) than other samples (Table 1), indicating that the catalyst may exhibit outstanding NH$_3$-SCR activity at low-temperature owing to the excellent oxidation ability. Figure 9c shows the XPS spectra of O 1s, which could be deconvoluted into lattice oxygen O$_{latt}$ (~529.6 eV), surface oxygen O$_{surf}$ (~531.3 eV), and chemically adsorbed oxygen O$_{ads}$ (~532.1 eV) [36]. As listed in Table 1, the Ce/Mn-3 sample contains the largest ratio of O$_{ads}$ (23.83%), which has great advantage for the SCR reaction [27,37]. These results are well consistent with the NH$_3$-SCR activity of different catalysts as discussed above.
Figure 8. (a) N₂ adsorption–desorption isotherm and (b) pore size distribution of Ce/Mn-3 catalysts calcinated at different temperatures.

Figure 9 shows the high-resolution Ce 3d, Mn 2p, and O 1s XPS spectra. As displayed in Figure 9a, the peaks of Ce³⁺ are located at ~885.7 eV and ~903.1 eV, while the remaining peaks are attributed to Ce⁴⁺[30–32]. As listed in Table 1, the calculated Ce³⁺ content (24.84%) in Ce/Mn-3 (400) is the highest among all CeO₂-MnO₂ samples, which is beneficial for the adsorption of NH₄⁺[33]. In addition, the Mn 2p 3/2 peaks in Figure 9a can be fitted into three peaks, which belong to Mn²⁺ (640.7 ~ 641.5 eV), Mn³⁺ (642.2 ~ 643.5 eV), and Mn⁴⁺ (644.8 eV), respectively[34,35]. Generally, Mn with high oxidation states (Mn⁴⁺) can promote the oxidation performance of NO over CeO₂-MnO₂ catalysts at low temperatures. The Ce/Mn-3 (400) catalyst contains more Mn⁴⁺ (38.55%) than other samples (Table 1), indicating that the catalyst may exhibit outstanding NH₃-SCR activity at low-temperature owing to the excellent oxidation ability. Figure 9c shows the XPS spectra of O 1s, which could be deconvoluted into lattice oxygen O_latt (~529.6 eV), surface oxygen O_surf (~531.3 eV), and chemically adsorbed oxygen O_ads (~532.1 eV)[36]. As listed in Table 1, the Ce/Mn-3 sample contains the largest ratio of O_ads (23.83%), which has great advantage for the SCR reaction[27,37]. These results are well consistent with the NH₃–SCR activity of different catalysts as discussed above.
Figure 9. High-resolution XPS spectra of Ce/Mn-3 catalysts calcinated at different temperatures: (a) Ce 3d, (b) Mn 2p, and (c) O 1s.
Table 1. The calculated ratios of Ce$^{3+}$, Mn$^{4+}$, and O$_{ads}$ in different catalysts based on XPS analysis.

|          | Ce$^{3+}$/Ce (%) | Mn$^{4+}$/Mn (%) | O$_{ads}$/O (%) |
|----------|-----------------|-----------------|---------------|
| Ce/Mn-3 (300) | 23.79           | 34.4            | 19.8          |
| Ce/Mn-3 (400) | 24.84           | 38.55           | 23.83         |
| Ce/Mn-3 (500) | 11.8            | 17.32           | 6.47          |
| Ce/Mn-3 (600) | 18.94           | 10.1            | 2.89          |

3.3. In Situ DRIFTs Studies

To disclose the NH$_3$–SCR reaction mechanism over the CeO$_2$-MnO$_2$ composite catalysts, in situ DRIFTs analysis was conducted by tracking the changes in the adsorbed species on the catalyst (taking Ce/Mn-3 (300) as a representative) surface during the reaction process. Figure 10a shows the NH$_3$ adsorption DRIFT spectra at 200 °C over the CeO$_2$-MnO$_2$ composite catalyst. The bands at 1692, 1642, and 1458 cm$^{-1}$ belong to the NH$^{+4}$ adsorbed on the Brønsted acid site, while the peaks at 3334, 1626, and 1040~1200 cm$^{-1}$ belong to the NH$_3$ adsorbed on the Lewis acid site [17,38,39]. In addition, the peaks at 992, 965, and 930 cm$^{-1}$ represent weakly adsorbed gaseous NH$_3$ on the catalyst’s surface. As increasing the adsorption time, the peak at 1458 cm$^{-1}$ belonging to the Brønsted acid site gradually disappeared, indicating that the surface NH$_3$ adsorption is dominated by the Lewis acid site. The DRIFT spectra of NO + O$_2$ adsorption on the CeO$_2$-MnO$_2$ composite catalyst along with the time at 200 °C are presented in Figure 10b. The peaks at 1574, 1530, and 1514 cm$^{-1}$ belonging to nitrates weakened after NO and O$_2$ were introduced for 30 min, indicating the generation of intermediate products released from the active site to produce N$_2$ and H$_2$O [40].

![Figure 10](image-url)

Figure 10. In situ DRIFTs of Ce/Mn-3 (300) at 200 °C over different time: (a) NH$_3$ adsorption, (b) NO + O$_2$ adsorption, (c) reaction of pre-adsorbed NH$_3$ with NO + O$_2$, and (d) reaction of pre-adsorbed NO with NH$_3$. 


The in situ DRIFT spectra of the CeO$_2$-MnO$_2$ catalyst with NO + 5% O$_2$ reacted with the pre-adsorbed NH$_3$ at 200 °C are displayed in Figure 10c. Notably, all vibration bands belonging to the adsorbed ammonia species (NH$_3$ and NH$_4^+$) vanished rapidly after 3 min after introducing NO and O$_2$, demonstrating the reaction with different ammonia species. The peak at 1455 cm$^{-1}$ vanished in 30 min, and a new adsorption peak located at 1557 cm$^{-1}$ assigned to the bidental nitrate was observed. The peak at 1397 cm$^{-1}$ could be ascribed to the intermediate species from the surface adsorbed NH$_3$ and NO$_x$ species. As shown in Figure 10d, the in situ DRIFT spectra were further measured to reveal the reaction of NH$_3$ with pre-adsorbed NO on the surface of the CeO$_2$-MnO$_2$ catalyst at 200 °C. After introducing NH$_3$, the vibration peaks of weakly adsorbed NO$_2$ at 1598 and 1574 cm$^{-1}$ on the surface of Ce/Mn-3 disappeared rapidly. In addition, new vibration peaks at 1685 and 1469 cm$^{-1}$ owing to the adsorption of NH$_4^+$ at the Brønsted acid site were observed. Additionally, a new adsorption peak at 1513 cm$^{-1}$ was also detected, which can be ascribed to the bidentate nitrate species resulting from the oxidation of NH$_3$ by O$_2$ [9]. Based on the above analysis, we can conclude that the Langmuir–Hinshelwood (L-H) may play an important role in the NH$_3$–SCR reactions over the CeO$_2$-MnO$_2$ composite catalysts because of the formation of a larger amount of absorbed NH$_3$ (NH$_4^+$), NO$_2$, and NH$_2$ intermediate [9,41].

Moreover, further studies were carried out to reveal the effect of SO$_2$ and H$_2$O on the NH$_3$–SCR catalytic activity of the CeO$_2$-MnO$_2$ composite catalyst. The results indicated that the deactivation of the catalyst with the presence of H$_2$O can be ascribed to the competitive adsorption between NH$_3$ and H$_2$O on the Lewis acid sites, which is a reversible process. In the case of SO$_2$, it will lead to permanent catalyst poisoning through the sulfation of surface active sites. In addition, the competitive adsorption of NO and SO$_2$ as well as the formation of (NH$_4$)$_2$SO$_4$ on the catalysts’ surface may also contribute to the partial deactivation of the CeO$_2$-MnO$_2$ catalyst. These conclusions are consistent with previous reports [42]. To regenerate the deactivated CeO$_2$-MnO$_2$ catalyst, water washing and thermal or reductive regeneration methods can be used. Further works are still needed to clarify the mechanism of poisoning effect of SO$_2$ and H$_2$O and corresponding regeneration methods.

4. Conclusions

In summary, we have synthesized a novel CeO$_2$-MnO$_2$ composite catalyst composed of CeO$_2$ nanoparticles grown on MnO$_2$ nanoflowers by combining hydrothermal method and ion-adsorption-calcination technique. The unique flower-like hierarchical microstructure and high specific surface area endow the catalysts with desirable intimate contact and synergistic effect, which leads to excellent NH$_3$–SCR NO$_x$ reduction activity in a wide temperature window from 150 to 300 °C, obtaining a maximal NO conversion of nearly 100% at 200 °C. Moreover, the high contents of Ce$^{3+}$, Mn$^{4+}$, and surface O$_{ads}$ in the CeO$_2$-MnO$_2$ catalyst could be also responsible for their excellent catalytic performance. Furthermore, in situ DRIFT experiments reveal that the NH$_3$–SCR reaction route on the surface of the CeO$_2$-MnO$_2$ hybrid catalysts is dominated by the L-H mechanism. The obtained CeO$_2$-MnO$_2$ composites in this work have great prospects for NH$_3$-SCR reaction of NO$_x$ at low temperatures.

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